DOE-ER-0031/43 Distribution Categories UC-423, -424

FUSION MATERIALS SEMIANNUAL PROGRESS REPORT FOR THE PERIOD ENDING

December 31, 2007

Prepared for DOE Office of Fusion Energy Sciences (AT 60 20 10 0)

DATE PUBLISHED: March 2008

Prepared for OAK RIDGE NATIONAL LABORATORY Oak Ridge, Tennessee 37831 Managed by UT-Battelle, LLC For the U.S. DEPARTMENT OF ENERGY

FOREWORD

This is the forty-third in a series of semiannual technical progress reports on fusion materials science activities supported by the Fusion Energy Sciences Program of the U.S. Department of Energy. This report focuses on research addressing the effects of materials properties and performance from exposure to the neutronic, thermal and chemical environments anticipated in the chambers of fusion experiments and energy systems. This research is a major element of the national effort to establish the materials knowledge base of an economically and environmentally attractive fusion energy source. Research actives on issues related to the interaction of materials with plasmas are reported separately.

The results reported are the product of a national effort involving a number of national laboratories and universities. A large fraction of this work, particularly in relation to fission reactor irradiations, is carried out collaboratively with partners in Japan, Russia, and the European Union. The purpose of this series of reports is to provide a working technical record for the use of program participants, and to provide a means of communicating the efforts of fusion materials scientists to the broader fusion community, both nationally and worldwide.

This report has been compiled and edited under the guidance of R. L. Klueh and Renetta Godfrey, Oak Ridge National Laboratory. Their efforts, and the efforts of the many persons who made technical contributions, are gratefully acknowledged.

G. R. Nardella Research Division Office of Fusion Energy Sciences

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Amono-metallic V-4Cr-4Ti thermal convection loop was operated in vacuum (~10-5Pa) at a maximum Li temperature of 700°C for 2,355h and Li flow rate Two-layer, physical vapor deposited Y2O3-vanadium, of 2-3cm/s. electrically-insulating coatings on V-4Cr-4Ti substrates as well as uncoated tensile and sheet specimens were located in the flow path in the hot and cold legs. After exposure, specimens at the top of the hot leg showed a maximum mass loss equivalent to ~1.3µm of uniform metal loss. Elsewhere, small mass gains were observed on the majority of specimens that also showed an increase in hardness and room temperature yield stress and a decrease in ductility consistent with interstitial uptake. Specimens that lost mass showed a decrease in yield stress and hardness. Profilometry showed no significant thickness loss from the coatings.

2.0 **CERAMIC COMPOSITE MATERIALS**

2.1 DIMENSIONAL AND MICROSTRUCTURAL STABILITY OF 3C-SIC IN HIGH TEMPERATURE IRRADIATION CONDITIONS- S. Kondo, Y. Katoh, L. L. Snead (Oak Ridge National Laboratory)

Microstructural analysis of 3C-SiC following neutron-irradiation at high temperatures provided quantitatively reliable data of temperature and fluence dependence of cavity swelling and dislocation evolution. Post-irradiation annealing effects on microstructural defects were also studied. Cavities were observed for all irradiation conditions (1050-1460°C, up to 9.6 dpa) except for 1050°C, 1.4 dpa. However, the magnitude of cavity swelling was very small below ~1300°C: the largest cavity swelling observed below that temperature was only ~0.01% at 1300°C. 9.3dpa. The temperature dependent increase in the cavity swelling was observed clearly above ~1400°C. Fluence dependent swelling became plainly visible above ~1400°C, and the maximum value observed in this work was 0.25% at 1460°C, 9.6 dpa. The dominating dislocation structure in the high temperature regime is Frank faulted loop. Minor black spots and small loop populations, which dominated the defect microstructure in lower temperature regime, were still coexisted with the Frank loops up to ~1150°C. Defect number density decreased and the size increased with increasing temperature. Significant decrease in the number density and increase in the size was observed at 1300-1460°C.

2.2 EFFECT OF NEUTRON IRRADIATION ON DC ELECTRICAL CONDUCTIVITY OF SILICON CARBIDE CERAMICS AND COMPOSITES FOR FUSION FLOW CHANNEL INSERT APPLICATIONS-Y. Katoh, S. Kondo, L. L. Snead (Oak Ridge National Laboratory)

The objective of this work is to help addressing the electrical conductivity issue for the silicon carbide-based flow channel insert in lead-lithium blanket of fusion breeding reactors; specifically to establish control schemes for electrical conductivity of SiC composites by identifying the conduction mechanism in composite structures and to address neutron irradiation effect

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on electrical conductivity in SiC composites and constituents. SUMMARY High purity chemically vapor-deposited silicon carbide (SiC) and 2D continuous SiC fiber, chemically vapor-infiltrated SiC matrix composites with pyrocarbon interphases were examined for temperature dependent (RT to 800°C) electrical conductivity and the influence of neutron irradiation on it. In the 2D composites, trans-thickness electrical conductivity was dominated by bypass conduction via interphase network at relatively low temperatures, whereas conduction through SiC constituents dominated at higher temperatures. The Influence of neutron irradiation on electrical properties appeared very strong for SiC, resulting typically in by orders lower ambient conductivity and steeper temperature dependency. Through-thickness electrical conductivity of neutron-irradiated 2D SiC composites with thin PyC interphase will likely in the order of 10 S/m in the typical operating temperature range for flow channel inserts. Mechanisms of electrical conduction in the composites and irradiation-induced modification of electrical conductivity of the composites and their constituents are discussed.

2.3 MICROSTRUCTURES OF CHEMICALLY VAPOR-DEPOSITED SILICON CARBIDE AFTER IRRADIATION CREEP DEFORMATION—Y. Katoh, S. Kondo, L. L. Snead (Oak Ridge National Laboratory)

Microstructures of silicon carbide were examined by transmission electron microscopy (TEM) after creep deformation under neutron irradiation. Thin strip specimens of polycrystalline and monocrystalline, chemically vapordeposited, beta-phase silicon carbide were irradiated in High Flux Isotope Reactor to 0.7 - 4.2 dpa at nominal temperatures 640 - 1080°C in an elastically pre-strained bend stress relaxation configuration with the initial stress of ~100 MPa. Irradiation creep caused permanent strains of 0.6 to 2.3 x 10-4. Tensile-loaded near-surface portions of the crept specimens were examined by TEM. The main microstructural features observed were dislocation loops in all samples, and appeared similar to those observed in samples irradiated in non-stressed conditions. Slight but statistically significant anisotropy in dislocation loop microstructure was observed in one irradiation condition, and accounted for at least a fraction of the creep strain derived from the stress relaxation. The estimated total volume of loops accounted for 10 - 45% of the estimated total swelling. The results imply that the early irradiation creep deformation of SiC observed in this work was driven by anisotropic evolutions of extrinsic dislocation loops and matrix defects with undetectable sizes.

2.4 MODELING SiC/SiC COMPOSITES WITH OFF-AXIS FIBERS – C. H. Henager, Jr. (Pacific Northwest National Laboratory)

A time-dependent fiber-bridging model that accounts for fiber orientation has been developed and its predictions are compared to strength and crack growth data for a braided weave composite. The level of agreement suggests that existing models of off-axis bridging fibers are not adequate for fusion reactor designs using SiC/SiC composites in off-axis orientations.

2.5 JOINING SIC/SIC COMPOSITES FOR FUSION APPLICATIONS – C. H. Henager, Jr. (Pacific Northwest National Laboratory)

The use of SiC composites in fusion environments may require joining of plates using non-mechanical joints, such as reactive joining or brazing. One promising joining method is the use of solid-state displacement reactions between Si and TiC to produce Ti3SiC2 + SiC. Such joints, while stronger

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than the SiC-composite interlaminar shear strength, which is a critical metric for joint performance, requires pressure and bonding at elevated temperatures. We are exploring the processing envelope for this joint in advance of the US-Japan TITAN collaboration so that we can produce viable joints to undergo irradiation studies in HFIR. Joining pressure appears to require almost 30 MPa at 1673K in order to produce strong and dense joints.

2.6 COMPATIBILITY OF INTERFACES AND FIBERS FOR SIC-COMPOSITES IN FUSION ENVIRONMENTS – C. H. Henager, Jr. and R. J. Kurtz (Pacific Northwest National Laboratory)

The use of SiC composites in fusion environments is predicated on stability under neutron irradiation, on outstanding high-temperature mechanical properties, and on chemical inertness and corrosion resistance. However, SiC is susceptible to many forms of corrosion in water and in water vapor where silica formation is required as a protective layer because silica forms stable hydroxides that are volatile, even at low temperatures. SiC composites have an additional concern that fine-grained fibers and weak interfaces provide the required fracture toughness, but these components may also exhibit susceptibility to corrosion that can compromise material properties. In this work we examine and review the compatibility of fibers and interfaces, as well as the SiC matrix, in proposed fusion environments including first wall, tritium breeding, and blanket modules and module coolants.

3.0 FERRITIC/MARTENSITIC STEELS AND ODS STEELS

3.1 ON THE ROLE OF ALLOY COMPOSITION AND PROCESSING PARAMETERS IN NANOCLUSTER FORMATION AND DISPERSION STRENGTHENING IN NANOSTRUCTURED FERRITIC ALLOYS -M. J. Alinger and G. R. Odette (University of California Santa Barbara) and D. T. Hoelzer (Oak Ridge National Laboratory)

An extensive experimental study to characterize the sequence-of-events that lead to the formation of a very high density of Y-Ti-O solute nanoclusters (NFs) in mechanically alloyed (MA), hot isostatically pressed (HIPed) ferritic stainless steels is reported. Yttria and O dissolve in the Fe-14Cr3W(0.4Ti) powders during MA. The dissolved Y and O, and when present Ti, subsequently precipitate during hot consolidation. The number densities and volume fractions of the NF decrease, and their radii increase, with increasing consolidation temperature. The NF form at 850 and 1000°C in both attritor and higher energy SPEX milled alloys containing Y, both with and without Ti additions. SPEX milling produces higher volume fractions of NFs and higher hardness in these cases. The presence of Ti refines the NFs, and both Ti and high milling energy (SPEX versus attritor) are necessary for the formation NFs at the highest consolidation temperatures of 1150°C. Microhardness trends closely mirror the effects of the compositional and processing variables on the NFs. However, the precise structure and composition of the NFs are not well understood. Indeed, their character varies, depending on the alloy composition and processing variables. The NFs appear to range from coherent solute enriched zones, or sub-oxides, to complex oxide phases.

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3.2 EMBRITTLEMENT OF IRRADIATED F82H IN THE ABSENCE OF IRRADIATION HARDENING—R. L. Klueh (Oak Ridge National Laboratory), K. Shiba (Japan Atomic Energy Agency), and M. A. Sokolov (Oak Ridge National Laboratory)

Neutron irradiation of 7-12% Cr ferritic/martensitic steels below 425–450°C produces microstructural defects and precipitation that cause an increase in yield stress. This irradiation hardening causes embrittlement, which is observed in a Charpy impact or fracture toughness test as an increase in the ductile-brittle transition temperature. Based on observations that show little change in strength in steels irradiated above 425–450°C, the general conclusion has been that no embrittlement occurs above these temperatures. In a recent study of F82H steel, significant embrittlement was observed after irradiation at 500°C. This embrittlement is apparently due to irradiation-accelerated Laves-phase precipitation. Observations of the embrittlement in the absence of hardening has been examined and analyzed with thermal-aging studies and computational thermodynamics calculations to illuminate and understand the effect.

4.0 COPPER ALLOYS

No contributions.

5.0 REFRACTORY METALS AND ALLOYS

5.1 THE INFLUENCE OF NEUTRON IRRADIATION AND TRANSMUTATION IN FFTF ON THE MICROSTRUCTURAL AND MICROCHEMICAL DEVELOPMENT OF Mo-41Re AT 470-730°C – D. J. Edwards and F. A. Garner (Pacific Northwest National Laboratory)

Specimens of Mo-41 wt% Re irradiated in the Fast Flux Test Facility (FFTF) experience significant and non-monotonic changes in density that arise first from radiation-induced segregation, leading to non-equilibrium phase separation, and second by progressive transmutation of Re to Os. As a consequence the density of Mo-41Re initially decreases and then increases thereafter. Beginning as a single-phase solid solution of Re and Mo, irradiation of Mo-41 wt% Re over a range of temperatures (470-730°C) to 28-96 dpa produces a high density of thin platelets of a hexagonal close-packed phase identified as a solid solution of Re, Os and possibly a small amount of Mo. These hcp precipitates are thought to form in the alloy matrix as a consequence of strong radiation-induced segregation to Frank loops. Grain boundaries also segregate Re to form the hcp phase, but the precipitates are much bigger and more equiaxed in shape. Although not formed at lower dose, continued irradiation at 730° C leads to the co-formation of late-forming Chi-phase, an equilibrium phase that then competes with the preexisting hcp phase for rhenium.

6.0 AUSTENITIC STAINLESS STEELS

6.1 THE CONFLICTING ROLES OF BORON ON THE RADIATION RESPONSE OF PRECIPITATE-FORMING AUSTENITIC ALLOYS -T. Okita, N. Sekimura (Department of Quantum Engineering and Systems Science, University of Tokyo) and F. A. Garner (Pacific Northwest National Laboratory)

The behavior of void swelling at 400°C of model f.c.c. alloy Fe-15Cr-16Ti-0.25Ti-0.05C doped with boron was examined in the FFTF-MOTA. Boron additions modify the neutron-induced swelling of Fe-15Cr-16Ni-0.25Ti-0.05C somewhat, but the changes appear to arise primarily from the influence of boron as a chemical species rather than as a source of helium. Boron additions initially depress swelling strongly, but the effect saturates by 100 appm. The reduction in swelling is thought to arise from boron's influence on distribution and precipitation of carbon. As the boron level is raised to significantly larger levels swelling then swelling begins to increase, but at a slower rate per boron atom. This subsequent increase is thought to reflect the higher He/dpa ratio generated by the boron, overwhelming the helium produced by (n,) reactions with nickel.

6.2 VERY HIGH SWELLING AND EMBRITTLEMENT OBSERVED IN A Fe-18Cr-10Ni-Ti HEXAGONAL FUEL WRAPPER IRRADIATED IN THE BOR-60 FAST REACTOR - V. S. Neustroev (Research Institute of Atomic Reactors, Dimitrovgrad, Russia) and F. A. Garner (Pacific Northwest National Laboratory)

The highest void swelling level ever observed in an operating fast reactor component has been found after irradiation in BOR-60 with swelling in Kh18H10T (Fe-18Cr-10Ni-Ti) austenitic steel exceeding 50%. At such high swelling levels the steel has reached a terminal swelling rate of ~1%/dpa after a transient that depends on both dpa rate and irradiation temperature. The transient duration at the higher irradiation temperatures is as small as 10-13 dpa depending on which face was examined. When irradiated in a fast reactor such as BOR-60 with a rather low inlet temperature, most of the swelling occurs above the core center-plane and produces a highly asymmetric swelling loop when plotted vs. dpa. Voids initially harden the alloy but as the swelling level becomes significant the elastic moduli of the alloy decreases strongly with swelling, leading to the consequence that the steel actually softens with increasing swelling. This softening occurs even as the elongation decreases as a result of void linkage during deformation. Finally, the elongation decreases to zero with further increases of swelling. This very brittle failure is known to arise from segregation of nickel to void surfaces which induces a martensitic instability leading to a zero tearing modulus and zero deformation.

6.3 ANOMALOUSLY LARGE DEFORMATION OF 12Cr18Ni10Ti AUSTENITIC STEEL IRRADIATED TO 55 DPA AT 310°C IN THE BN-350 REACTOR -M. N. Gusev, O. P. Maksimkin, I. S. Osipov (Institute of Nuclear Physics, Kazakhstan) and F. A Garner (Pacific Northwest National Laboratory)

Whereas most previous irradiation studies conducted at lower neutron exposures in the range 100-400°C have consistently produced strengthening and strongly reduced ductility in stainless steels it now appears possible that higher exposures may lead to a reversal in ductility loss for some steels. A new radiation-induced phenomenon has been observed in 12Cr18Ni10Ti

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stainless steel irradiated to 55 dpa. It involves "a moving wave of plastic deformation" at 20°C that produces "anomalously" high values of engineering ductility, especially when compared to deformation occurring at lower neutron exposures. Using the technique of digital optical extensometry the "true stress σ –true strain ϵ " curves were obtained. It was shown that a moving wave of plastic deformation occurs as a result of an increase in the intensity of strain hardening, d\sigma/d\epsilon(ϵ). The increase in strain hardening is thought to arise from an irradiation-induced increase in the propensity of the $\gamma \rightarrow \alpha$ martensitic transformation.

6.4 ANISOTROPIC SWELLING OBSERVED DURING STRESS-FREE REIRRADIATION OF AISI 304 TUBES PREVIOUSLY IRRADIATED UNDER STRESS - F. A. Garner (Pacific Northwest National Laboratory), J. E. Flinn, (Argonne National Laboratory, EBR-II Project, [Retired]) and M. M. Hall, (Bechtel Bettis Company)

A "history effects" experiment was conducted in EBR-II that involved the reirradiation of AISI 304 cladding and capsule tubes. It is shown that when irradiated tubes had not previously experienced stress, subsequent irradiation led to additional swelling strains that were isotropically distributed. However, when tubes previously irradiated under a 2:1 biaxial stress were reirradiated without stress the additional swelling strains were not isotropically distributed. The tubes retained a memory of the previous stress state that appears to be attempting to distribute strains in the directions dictated by the previous stress state. It is clear, however, that the memory of that stress state is fading as the anisotropic dislocation microstructure developed during irradiation under stress is replaced by an isotropic dislocation microstructure during subsequent exposure in the absence of stress. It is also shown that once the transient regime of swelling nears completion, further changes in stress state or irradiation temperature have no influence on the swelling rate thereafter.

7.0 MHD INSULATORS, COATINGS, INSULATING CERAMICS AND OPTICAL MATERIALS

7.1 FURTHER CHARACTERIZATION OF THE TRANS-FORMATION OF Al₂O₃ TO LiAIO₂ IN Pb-17 Li AT 800°C– B. A. Pint and K. L. More (Oak Ridge National Laboratory, USA)

In order to study the compatibility of -Al2O3with Pb-17Li, a FeCrAl substrate was pre-oxidized at 1000°Cto thermally grow an external alumina scale. The specimen was then isothermally exposed to Pb-Li for1000h at 800°C in a Mo capsule. The alumina layer prevented dissolution of the metallic substrate but was found to transform to LiAlO2. The current report includes additional XRD and TEM characterization of the external oxide layer before and after exposure to Pb-Li.

8.0 BREEDING MATERIALS

No contributions.

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9.0 RADIATION EFFECTS, MECHANISTIC STUDIES, AND EXPERIMENTAL METHODS

9.1 MULTISCALE MODELING OF POINT DEFECT INTER-ACTIONS IN BCC FE-CR ALLOYS –K. L. Wong, H.-J. Lee, B. D. Wirth (University of California, Berkeley), J.-H. Shim (Korea Institute of Science and Technology), and B. Sadigh (Lawrence Livermore National Laboratory)

Predictive performance models of ferritic/martensitic alloys in fusion neutron irradiation environments require knowledge of point defect interactions with Cr, which can be investigated by a multiscale modeling approach. Molecular dynamics simulations, using Finnis-Sinclair-type potentials, have been used to investigate interstitial diffusion, and the resulting atomic transport of Cr and Fe using interatomic potentials that predict Cr as either an under- or oversized solute with otherwise constant materials properties. Ab-initio calculations on vacancy–Cr interactions reveal complex electronic and magnetic interactions between Cr and Fe. These values have been used to calculate the ratio of Cr-to-Fe diffusion by a vacancy mechanism using the LeClaire multi-frequency model and a kinetic lattice Monte Carlo model, both of which indicate that Cr diffuses faster than Fe by a vacancy mechanism. The results are discussed in the context of the radiation-induced segregation of Cr at grain boundaries in BCC Fe-Cr alloys.

9.2 MOLECULAR DYNAMICS SIMULATION OF MIXED DISLOCATION INTERACTION WITH STACKING FAULT TETRAHEDRON - H.-J. Lee and B. D. Wirth (University of California, Berkeley)

The interaction between a 60 degree mixed dislocation and a stacking fault tetrahedron (SFT) is investigated using molecular dynamics (MD) simulation. The interaction strongly depends on the sense of the dislocation Burgers vector, with un-faulting and stable shear ledge formation occurring in one case, while simple bypass and immediate reconstruction of the SFT is observed for the opposite Burgers vector direction. SFT un-faulting by a mixed dislocation occurs following the constriction of a mixed dislocation on the SFT, which produces a Shockley partial that can glide on the SFT face(s). In particular, when the dislocation core as a super-jog pair. After dislocation bypass, a smaller SFT and vacancy clusters remain behind. When the dislocation glides on the base plane of the SFT, the strong repulsion between the mixed dislocation and the SFT induced SFT collapse.

9.3 MOLECULAR DYNAMICS SIMULATION OF DISLOC-ATION-VOID INTERACTIONS IN BCC MO - H.-J. Lee and B. D. Wirth (University of California, Berkeley)

Molecular dynamics (MD) and molecular statics (MS) simulations have been performed to simulate the plastic deformation processes in irradiated body centered cubic (BCC) Mo. Considering the unique non-planar core structures of the screw dislocation in BCC metals, the behavior of screw dislocation motion as a function of temperature and applied shear stress is first discussed. A transition from smooth to rough motion of the screw dislocation is observed with increasing shear stress, as well as a change of dislocation glide plane from {110} to {112} with increasing temperature. The interaction of a screw dislocation with nanometer-sized voids observed in both dynamic and static conditions is then reported. The obstacle strength calculated from MS calculations shows a large increase in critical resolved shear stress for

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void diameter larger than about 3 nm. However, the MD results indicate that the screw dislocation interaction with void occurs via a simple shear mechanism.

9.4 POST-IMPLANTATION THERMAL DESORPTION OF HELIUM FROM POLY- AND SINGLE-CRYSTALLINE IRON – Donghua Xu and Brian D. Wirth (Department of Nuclear Engineering, University of California, Berkeley)

The results of He desorption measurements are presented for both poly-(PC) and single-crystalline (SC) iron (>99.99%) using constant rate (1 K/s) heating following room temperature 4He implantations at energies of 5 and 10 keV, and fluences of 1014 and 1015 He/cm2. A sharp desorption peak due to BCC-FCC phase transformation is observed for both PC and SC specimens, which provides precise temperature calibration. Within the BCC structural range, three groups (I: below 300 °C; II: 300-600 °C; III: 600-900 °C) of desorption signal are identified for PC specimens while only two groups (I: below 300 °C; II: 550-900 °C) are identified for SC specimens. The low T group appears broader for PC specimens than for SC specimens. PC and SC desorption spectra show similar dependence on implantation energy and fluence, namely that the relative intensity at low and intermediate temperatures decreases with increasing implantation energy or fluence, while the fluence effect is much more pronounced than the energy effect. Simple first order dissociation kinetics are used to estimate the average activation energies associated with all the desorption groups, and these energies range from about 1.1 to 3.4 eV. However, precise identification of the mechanisms controlling each desorption event requires further study by complementary characerization and modeling techniques. The present SC iron data are expected to provide an appropriate experimental reference for future ratetheory or kinetic Monte-Carlo modeling of helium defect evolution in BCC iron.

9.5 INTERACTION OF HenVm CLUSTERS WITH COHERENT AND SEMI-COHERENT Fe/Cu INTERFACES – R. J. Kurtz, H. L. Heinisch, and F. Gao (Pacific Northwest National Laboratory)

Previous computational modeling has shown that interstitial and substitutional He as well as He-divacancy clusters are strongly bound to extended defects in Fe such as dislocations, grain boundaries and particlematrix interfaces. One aspect of the earlier work was the interaction of He with nanometer-scale, coherent particles embedded in an Fe matrix. Our earlier research also established that the core of an edge dislocation strongly traps He. Thus we hypothesized that a semi-coherent interface might be a stronger trap for He than a coherent interface due to the array of misfit dislocations needed to accommodate the lattice parameter mismatch between the particle and the matrix in the semi-coherent case. In the present study we employ atomisitic simulations to compare the binding of HenVm complexes to coherent and semi-coherent bcc Fe/ bcc Cu interfaces. The simulations show that the binding energy of HenVm complexes to a coherent Fe/Cu interface range from 0.35 eV for a single vacancy up to 0.70 eV for a He1V2 complex. A semi-coherent interface was found to be a much stronger trap for He near the core of a misfit dislocation. Binding energies varied from 0.86 eV for a substitutional He atom up to 2.38 eV for a He1V2 complex. These binding energies were found to be significantly larger than the values obtained for simple edge dislocations in Fe. The trend in binding

energies can be rationalized in terms of the spatial dependence of excess atomic volume for each interface.

9.6 INTERACTION OF VACANCIES AND HELIUM ATOMS WITH a/2 <111> SCREW DISLOCATIONS IN α-Fe - H. L. Heinisch, F. Gao, R. J. Kurtz (Pacific Northwest National Laboratory)

Migration energies of vacancies and He atoms in and near the core of an a/2<111> screw dislocation in α -Fe were determined in atomistic simulations using conjugate gradient relaxation and the Dimer method for determining saddle point energies. Results for defects in initial positions in and near the screw dislocation core were obtained for migration toward and away from the dislocation line, as well as along the dislocation line direction. For both vacancies and individual interstitial helium atoms migration is favored toward and along the screw dislocation. Vacancies trapped in the dislocation core migrate along the dislocation with a migration energy of about 0.4 eV, which is about half the migration energy of vacancies in the perfect crystal.

9.7 MIGRATION OF VACANCIES, HE INTERSTITIALS AND HE-VACANCY CLUSTERS AT GRAIN BOUNDARIES IN ALPHA-FE – F. Gao, H. L. Heinisch and R. J. Kurtz (Pacific Northwest National Laboratory)

The dimer method for searching transition states has been used to systematically study possible migration paths of vacancies, He interstitials and He-vacancy (He/V) clusters at $\Sigma 11 < 110 > \{323\}$ and $\Sigma 3 < 110 > \{111\}$ grain boundaries (GBs) in α -Fe. Vacancies trapped at the GBs diffuse along the GBs with migration energies much less than that within the perfect crystal. Long-time dynamics simulations of diffusion pathways reveal that vacancies migrate one-dimensionally along the close-packed rows in the $\Sigma 3$ GB, and one-dimensionally in zigzag paths within the $\Sigma 11$ GB. Also, dimer saddle point searches show that He interstitials can diffuse along the GBs with migration energies of 0.4-0.5 eV, similar to those of individual vacancies at the GBs, and the corresponding mechanisms are determined. The rate-controlling activation energy for migration of a He-divacancy cluster in the GBs determined using the dimer method is about 0.9 eV, which is comparable to the migration energy for a He-divacancy cluster in bulk α -Fe.

9.8 MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION - A. Caro, P. Erhart, M. Serrano de Caro, B. Sadigh (Lawrence Livermore National Laboratory), E. Lopasso (Centro Atomico Bariloche, Argentine), D. Farkas (Virginia Polytechnical Institute), S.G. Srinivasan, and C. Jiang (LANL)

Computer simulations of processes related to radiation damage have provided deep insight into atomistic processes at the origin of all changes that irradiation produces on mechanical properties of materials. However, as progress continues and more and more complex materials are developed, like the nanostructured Oxide Disperse Strengthened (ODS) ferritic steels, the simulations are confronted with the necessity to capture intricate thermodynamic and kinetic effects. The work reported here is an attempt to bring simulation capabilities to new domains where such effects are accurately described. In this report we present our recent results on the nature of the phase diagram of FeCr in the low Cr region, where finite solubility together with the existence of new intermetallic phases may be at the origin of the explanation of embrittlement and swelling under irradiation, with their intricate dependence on Cr composition. Our work in the last few 192

years has followed a systematic approach to model this alloy that started with a methodology to generalize many-body classic potentials to incorporate complex formation energy curves. Application to Fe-Cr allowed us to predict the implications of the ab initio results of formation energy on the phase diagram of this alloy and to get a detailed insight into the processes leading to precipitation of α' phase under irradiation. In this period we report on the consequences of the negative heat of formation at low Cr composition on the formation of new phases at low T, in particular ordered intermetallic phases, whose existence have been the subject of speculation in recent years.

9.9 APPLICATION OF DIGITAL MARKER EXTENSOMETRY TO DETERMINE THE TRUE STRESS-STRAIN BEHAVIOR OF IRRADIATED METALS AND ALLOYS - M. N. Gusev, O. P. Maksimkin, I. S. Osipov (Institute of Nuclear Physics, Almaty, Kazakhstan) and F. A. Garner (Pacific Northwest National Laboratory)

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To study the mechanisms of deformation hardening and flow localization of radioactive materials, a non-contact "digital marker extensometry" technique has been employed. It allows researchers to easily define plasticity parameters and true stresses in experiments where highly radioactive miniature specimens are used. The engineering and "true stress – true local strain" relationships of irradiated metal polycrystals during plastic flow and hardening have been investigated experimentally after irradiation in two reactors in Kazakhstan. The true curves were obtained for copper, nickel, iron, molybdenum, as well as for the Russian stainless steels 08Cr16Ni11Mo3 and 12Cr18Ni10Ti. Describing these curves using the equation $\sigma_i = \sigma_0 + k\sqrt{\varepsilon_i}$ demonstrates that the concept of ultimate stress in highly irradiated materials is an artifact arising from flow localization and is not fully informative of the operating hardening mechanisms.

10.0	DOSIMETRY, DAMAGE PARAMETERS, AND ACTIVATION CALCULATIONS	210
	No contributions.	
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	No contributions.	

1.0 VANADIUM ALLOYS

INITIAL CHARACTERIZATION OF V-4Cr-4Ti AND MHD COATINGS EXPOSED TO FLOWING Li – ORNL Loop Team: B. A. Pint, S. J. Pawel, M. Howell, J. L. Moser, G. W. Garner, M. L. Santella, P. F. Tortorelli, F. W. Wiffen and J. R. Distefano (Oak Ridge National Laboratory)

OBJECTIVE

Conduct an experiment with flowing Li in a thermal gradient to determine the compatibility of V-4Cr-4Ti and a multi-layer electrically-insulating coating needed to reduce the magneto hydrodynamic (MHD) force in the first wall of a lithium cooled blanket.

SUMMARY

A mono-metallic V-4Cr-4Ti thermal convection loop was operated in vacuum (~10⁻⁵Pa) at a maximum Li temperature of 700°C for 2,355 h and Li flow rate of 2-3 cm/s. Two-layer, physical vapor deposited Y_2O_3 -vanadium, electrically-insulating coatings on V-4Cr-4Ti substrates as well as uncoated tensile and sheet specimens were located in the flow path in the hot and cold legs. After exposure, specimens at the top of the hot leg showed a maximum mass loss equivalent to ~1.3µm of uniform metal loss. Elsewhere, small mass gains were observed on the majority of specimens that also showed an increase in hardness and room temperature yield stress and a decrease in ductility consistent with interstitial uptake. Specimens that lost mass showed a decrease in yield stress and hardness. Profilometry showed no significant thickness loss from the coatings.

PROGRESS AND STATUS

Introduction

One of the critical unresolved issues for the vanadium-lithium blanket concept[1,2] (and any liquid metal concept) in a deuterium/tritium fueled fusion reactor [3,4] is the need to reduce the pressure drop associated with the magnetohydrodynamic (MHD) effect of a conducting liquid flowing across the magnetic field lines One solution to the MHD problem is to decouple the structural wall from the liquid metal with an electrically insulating coating or flow channel insert (FCI).[5] This coating application requires a thin, crack-free.[6] durable layer with a relatively high electrical resistance.[7] While a "self-healing" layer is possible in corrosion where a re-passivation can occur with the re-formation of a surface oxide, this concept is not applicable to functional (i.e. electrically resistant) coatings because a defect that shorts the coating is unlikely to "heal". Therefore, a robust coating system or a FCI is needed for this application. Due to incompatibility between Li and virtually all candidate insulating oxides,[8-12] the current focus of the U.S. MHD coating program[10-12] is on evaluating the compatibility of durable, multi-layer coatings[7,13] where a vanadium overlayer prevents direct contact between the insulating oxide layer and Li. This concept shifts the compatibility concern from the oxide layer to the thin vanadium overlayer. In order to verify that a thin, ~10µm, V layer is sufficiently compatible with Li to function in a long-term situation, a mono-metallic thermal convection loop was designed and built to expose thin V overlayers to flowing Li. The loop was operated with a peak temperature of ~700°C for 2,355h.[14] Initial characterization of the coatings and V-4Cr-4Ti specimens in the loop are presented. Additional characterization of the coatings will be presented in future publications.

Experimental Procedure

A harp-shaped thermal convection loop was constructed of drawn tubing made from the large U.S. heat of V-3.8wt.%Cr-3.9%Ti (Heat#832665 made at Wah Chang, Albany, OR)[15] with an outer diameter of 19mm and a 1.6mm wall thickness. Additional details of the loop construction and operation were reported previously.[14,16] The experiment was conducted in a stainless steel vacuum chamber. Wire and

specimens, all made from the same V-4Cr-4Ti heat, formed ~80cm long chains that were placed in the hot and cold legs. The 29 specimens in each chain consisted of alternating interlocked tabs (31 x 13 x 0.9mm), which held the chain in the center of the tube, and pairs of miniature tensile specimens (type SS-3: 25 x 4 x 0.9mm). Prior to exposure, the tensile specimens were vacuum annealed for 1h at 1050°C. Specimen mass was measured on a microbalance with a ±0.01 mg/cm² error. Six of the exposed tabs had an electron-beam physical vapor deposited (EB-PVD) Y_2O_3 coating completely covered by an outer layer of unalloyed vanadium on one side.[11,12] The coatings were made in two batches[17] and the unexposed coating thicknesses are shown later in Table 2.

Sticks of Li (as-received batch: <100ppmw N, 95ppmw C and 950ppmw O)[12] totalling ~275g were loaded into the fill tank in a glove box and the tank lid was welded shut. The Li in the tank was melted to begin the experiment. A much larger than expected temperature gradient was observed during the first 1248h phase of operation. Initially, the difference between the top and bottom of the hot leg was 340°C and slowly increased to almost 400°C, Figure 1. Using thermocouples to measure the movement of a hot spot created by a pair of SiC heating elements, the Li velocity was estimated to be ~2 cm/s during the first phase. After an unexplained upset that occurred between 1248-1262h, Figure 1, the cold leg temperatures increased and the gradient was only ~225°C suggesting a faster Li velocity of >3 cm/s (based on the lower T gradient) which was similar to the velocity measured in the stainless steel test loop operated at ~550°C.[16] However, the higher cold leg temperatures during the second operation phase prevented an accurate velocity measurement. The inability to maintain the peak temperature at 700°C for the second operational phase (Fig. 1) was subsequently attributed to a loose furnace connection. One hypothesis for the high first phase T is that the Li flow was restricted by the specimen chain and that specimen movement or the chain breaking (which was not observed during disassembly) allowed more rapid Li flow during the second phase.



Figure 1. Temperatures in loop thermal wells and chamber pressure as a function of operation time for the V-4Cr-4Ti loop experiment.

After the experiment ended, the chamber was opened and the loop inverted and re-instrumented. The chamber was then pumped down and the loop was heated to ~400°C allowing the Li to drain back into the tank. The loop was then cut open in an Ar-filled glove box. The top tab specimens were not found to be located below the cross-over joints in the hot and cold leg as intended and therefore could have restricted Li flow. The specimen chains were removed from the tubing and residual Li was removed using liquid ammonia followed by soaking in ethanol and then water.

Initial characterization of the specimens and tubing included metallographic cross-sections, hardness (Vickers, 300g) measurements, chemical analysis using combustion and inductively coupled plasma analysis, and room temperature tensile testing at 10⁻³s⁻¹ strain rate. Selected specimens were examined using scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDX) analysis. The EB-PVD coatings were examined by SEM/EDX, contact profilometry and x-ray diffraction (XRD).

Results and Discussion

Figure 2 shows the mass change data for both specimen chains with the nominal temperature profiles in the hot and cold legs. Mass losses in seven specimens from the hot leg were consistent with dissolution of metal (maximum ~0.6mg/cm² is equivalent to 1µm vanadium) and/or loss of interstitials such as oxygen. Assuming linear kinetics, the maximum observed loss is the equivalent to ~2.5 mg/m²h which is similar to the rate reported previously at 538°C for V-15Cr-5Ti with Li+50ppm N in a pumped loop (1 l/min).[18] However, the results in that study were complicated by the use of a stainless steel loop. Prior results in a mono-metallic loop at 700°C reported small mass gains after 1,000h.[19]

The three specimens at the very top of the hot leg did not show a mass loss, Figure 2, which may be explained by temperature or Li flow differences. As mentioned previously, the chain was not positioned in



Figure 2. Specimen mass change for V-4Cr-4Ti specimens in the hot and cold leg of the mono-metallic loop along with the nominal temperature that the specimens saw during the two phases of operation. In the hottest section of the loop, mass losses were observed, elsewhere, small mass gains were measured.

the loop as intended and the first specimen in the chain (* in Figure 2) appeared to be above the Li flow path which may explain its high mass gain (i.e. higher interstitial pickup and/or less metal transfer). The second and third specimens appeared to be within the Li flow path although they were located above the hot leg furnace ~2cm from the hot leg thermal well where the 700°C temperature was measured. Elsewhere in both legs, all of the specimens showed a small mass gain. The location of the six EB-PVD coated specimens also are shown in Figure 2,and each had a mass gain comparable to neighboring specimens.

Chemical analyses of the interstitial contents for selected tab specimens at the top, bottom and middle of the hot and cold leg are shown in Figure 3. As expected, there was a decrease in the O content for all of the specimens and an increase in the N and C content. However, that effect was particularly strong in the hottest section where the O content decreased to 20ppmw and the N content increased to 1590ppmw. There was no significant change in the V, Cr or Ti contents measured. Table 1 shows the changes in interstitial content for each of the measured locations and the measured and calculated mass change based on the chemistry change. The small mass change observed in most of the specimens is likely associated with the uptake of N and C minus the decrease in O. However, the mass gains in the coldest parts of the loop are not explained by this uptake and may be due to a small amount of metal deposition, e.g., a 0.06 mg/cm² mass gain would be equivalent to a ~100nm layer of metal. For the highest temperature specimen analyzed from the hot leg, the large increase in N content resulted in a calculated net mass gain, suggesting that the metal loss may have been on the order of 0.8 mg/cm² or ~1.3 µm.

Figure 4 shows results from room temperature tensile tests of specimens from the hot and cold legs as well as average values for three unexposed specimens from the same specimen batch which have similar properties as those measured in prior studies.[20-22] The 0.2% yield and ultimate tensile strengths increased in specimens as the exposure temperature decreased, Figure 4a. The mass gain and



Figure 3. Measured O, C and N values for specimens at six locations in the loop. A slight drop in O and increase in C and N was observed except for the hottest location where there was a large increase in N and a decrease in O to 20ppmw.



Figure 4. Room temperature tensile properties of a subset of V-4Cr-4Ti specimens after exposure in a mono-metallic loop: (a) 0.2% yield and ultimate tensile stress and (b) uniform and total elongation. The specimen in the hottest locations that lost mass showed a decrease in strength and less loss in ductility than the other specimens that had a mass gain after exposure.

Table 1. Measured interstitial composition and mass gain data and calculated mass gain based on the interstitial composition change. The measured mass change is the average of the two tab specimens that were chemically analyzed.

Location		Measur	ed Change	e (wppm)	Mass Char	Mass Change (mg/cm ²)	
	Temperature	0	Ν	С	Measured	Calculated	
Top Hot Leg	657	-340	+1510	+120	-0.50	+0.30	
Top Cold Leg	556	-50	+80	+100	+0.06	+0.03	
Middle Hot Leg	532	-70	+230	+90	+0.06	+0.06	
Middle Cold Leg	487	-30	+30	+70	+0.04	+0.02	
Bottom Cold Leg	423	-40	+30	+20	+0.09	+0.002	
Bottom Hot Leg	416	-40	+30	+10	+0.12	0.0	
Starting content		360	80	70			

associated N and C increase for many of these specimens suggests interstitial hardening as a mechanism to increase the yield and ultimate tensile stresses. The variation with temperature is likely due to thermal ageing during the 2,355 h exposure. The specimens from the hot leg with mass losses showed a large decrease in yield strength, which is not consistent with the large N increase but is consistent with the large drop in O content, Table 1. In Figure 4b, modest decreases in the uniform and total elongations also were observed compared to unexposed specimens. These ductility values are somewhat higher than were previously reported.[19] Additional tensile specimens will be tested at 500°C to compare to prior work on Li-exposed material.[23]

Figure 5 shows the change in average hardness (from a starting value of 204±6 Hv for the starting unannealed cold-rolled material) and mass for tab specimens as a function of nominal average temperature based on their location in the specimen chain and assuming a linear temperature change between the thermal wells on the hot and cold legs. The hardness, but not the net mass change, showed a correlation with exposure temperature. Hardness values and standard deviations are based on 7 measurements across the polished ~0.9mm tab cross-section. The decrease in hardness with temperature is consistent with thermal annealing of the original cold-rolled microstructure. Figure 6 shows etched metallographic cross-sections of the hot leg tab specimens from Figure 5 and Table 1 with the surface at the top of each figure. The as-rolled microstructure is shown in Figure 5a. There was little change in the microstructure at the bottom of the hot leg at the lowest temperature, Figure 5b. The specimen exposed at ~655°C (Fig. 5d) showed a much larger re-crystallized grain size and a surface layer which appeared to be depleted in precipitates. A similar layer or recrystallization was not observed in any of the other specimens from the cold leg. The near-surface microhardness has not been investigated yet. Prior work,[18] showed a ~30µm deep microhardness gradient in V-15Cr-5Ti after exposure at 482-538°C.

Finally, Table 2 shows the profilometry data for the EB-PVD coated specimens after exposure. Batch 1 coatings were exposed at the higher temperatures because they were of higher initial quality.[17] No significant loss in thickness was detected. However, the unexposed coated specimens were concave indicating that the as-deposited coatings were under compression while the coated specimens exposed at the highest temperatures were all convex after exposure which could indicate stress relief or some type of degradation such as cracking or expansion due to reaction with Li. The EB-PVD Y_2O_3/V coatings showed no significant loss in thickness, however, further characterization is needed to determine their electrical resistance and microstructure after exposure. In order to measure the electrical resistance, a procedure needs to be developed to electrically isolate the oxide coating from the vanadium overlayer. After the resistance measurement, the coatings will be sectioned to evaluate the microstructure.



Figure 5. Average hardness measurements as a function of nominal exposure temperature along the hot and cold legs of the mono-metallic loop. The hardness decreased with exposure temperature in both legs.

Currently, a 700°C 2,350 h anneal is being conducted on several tensile specimens, a tab specimen and an unexposed MHD coating. The specimens were placed in a quartz ampoule and evacuated to limit reaction during the anneal. These specimens will provide a baseline for changes in the microstructure and



Figure 6. Light microscopy of unannealed V-4Cr-4Ti tab specimens (a) unexposed and after exposure to flowing Li (b) bottom of the hot leg (~415°C), (c) middle of the hot leg (~530°C) and (d) top of the hot leg (~655°C) where the surface grains appear depleted in precipitates.

Table 2. Profilometry data of the V/Y₂O₃ coatings on V-4Cr-4Ti substrates after exposure to flowing Li for 2,355h in a V-4Cr-4Ti loop with a maximum temperature of 700°C.

	Batch	1	Batch 2		
Location	V layer	Y ₂ O ₃ layer	V layer	Y ₂ O ₃ layer	
Unexposed	9 µm	13 µm	10 µm	17 µm	
Top Hot Leg	8	12			
Top Cold Leg	8	11			
Middle Cold Leg	7	12			
Bottom Cold Leg			10	15	
Bottom Hot Leg			9	17	
Middle Hot Leg			9	16	
As-deposited*	7.4±0.3	11.7±0.5	9.9±0.4	15.7±0.9	

* Reference 17

properties due to the temperature exposure without the effect of flowing Li.

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2.0 CERAMIC COMPOSITE MATERIALS

DIMENSIONAL AND MICROSTRUCTURAL STABILITY OF 3C-SiC IN HIGH TEMPERATURE IRRADIATION CONDITIONS—S. Kondo, Y. Katoh, L. L. Snead (Oak Ridge National Laboratory)

OBJECTIVE

The cavity swelling and progressive dislocation evolution are critical because they may cause unstable volume expansion and irradiation creep deformation, respectively. The objective of this work is to reveal the temperature and fluence dependence of the cavity swelling and dislocation development in 3C-SiC. Of importance is that both the irradiation fluence and temperature were better characterized in this experiment than in most earlier work.

SUMMARY

Microstructural analysis of 3C-SiC following neutron-irradiation at high temperatures provided quantitatively reliable data of temperature and fluence dependence of cavity swelling and dislocation evolution. Post-irradiation annealing effects on microstructural defects were also studied.

Cavities were observed for all irradiation conditions (1050-1460°C, up to 9.6 dpa) except for 1050°C, 1.4 dpa. However, the magnitude of cavity swelling was very small below ~1300°C: the largest cavity swelling observed below that temperature was only ~0.01% at 1300°C, 9.3dpa. The temperature dependent increase in the cavity swelling was observed clearly above ~1400°C. Fluence dependent swelling became plainly visible above ~1400°C, and the maximum value observed in this work was 0.25% at 1460°C, 9.6 dpa.

The dominating dislocation structure in the high temperature regime is Frank faulted loop. Minor black spots and small loop populations, which dominated the defect microstructure in lower temperature regime, were still coexisted with the Frank loops up to ~1150°C. Defect number density decreased and the size increased with increasing temperature. Significant decrease in the number density and increase in the size was observed at 1300-1460°C.

PROGRESS AND STATUS

Introduction

SiC and its composites attract a lot of interest for the nuclear application due to the low activation properties and remarkable mechanical properties at very high temperature. In recent years, many efforts have been made to evaluate irradiation effects such as dimensional instability, modification of thermal and electrical transport properties, and mechanical property changes [1]. This work focused on cavity swelling and dislocation development in the very high temperature regime, which will be primary information for clarifying the underlying mechanisms of most irradiation effects.

There are limited studies of microstructural changes in 3C-SiC at low and intermediate irradiation temperatures (<~800°C) [2-8]. Black spot defects and small loops, which are aggregates of displaced Si and C atoms, are the dominating microstructures in the temperature regime. The negative temperature dependence of saturated swelling values in 3C-SiC has been reported up to 1000°C [9], which was primarily attributed to the lattice dilation near the point defects and/or their clusters. In the high temperature regime (<~1000°C), recent self-ion- and neutron-irradiation experiments revealed that the dominant defects were interstitial-type Frank loops and cavities [10]. Cavity formation resulting from super saturated vacancy migration is a common phenomenon in most irradiated materials at elevated temperature (roughly 0.3-0.5 T_m). Recent densitometry experiments on irradiated 3C-SiC showed that the volume expansion increased with increasing temperature and fluence above ~1100°C [11,12].

Irradiation temperature		Fluence	Cavity size	Cavity density	Cavity volume fraction	Loop radius	Loop density
°C		dpa	nm	m ⁻³	%	nm	m ⁻³
1050	3C-SiC	1.4	Not detected	-	-	1.2	1.1×10^{23}
1050	3C-SiC	4.9	1.1	1.0×10^{20}	3.1×10^{-6}	1.5	1.4×10^{23}
1130	3C-SiC	1.5	1.1	1.8×10^{20}	4.3×10^{-6}	2.2	9.1×10^{22}
1130	3C-SiC	5.1	1.1	3.0×10^{20}	5.0×10^{-5}	3.3	9.1×10^{22}
1130	3C-SiC	7.7	1.1	1.7×10^{21}	6.2×10^{-5}	4.1	9.2×10^{22}
1220	3C-SiC	1.7	1.1	2.5×10^{21}	2.0×10^{-4}	2.2	1.2×10^{23}
1300	3C-SiC	1.9	1.8	5.5×10^{22}	5.9×10^{-3}	3.8	6.5×10^{22}
1300	3C-SiC	5.3	1.2	2.7×10^{23}	9.6 × 10 ⁻³	6.3	5.4×10^{22}
1300	3C-SiC	9.3	1.7	2.0×10^{23}	1.4×10^{-2}	8.5	2.7×10^{22}
1400	3C-SiC	5.6	1.7	4.7×10^{23}	3.3×10^{-2}	18	4.8×10^{21}
1400	3C-SiC	9.4	2.1	4.4×10^{23}	5.6×10^{-2}	27	2.9×10^{21}
1460	3C-SiC	1.9	3.0	3.6×10^{22}	1.3×10^{-2}	16	4.0×10^{21}
1460	3C-SiC	5.8	4.5	6.9×10^{22}	1.1×10^{-1}	28	1.2×10^{21}
1460	3C-SiC	9.6	5.7	6.6×10^{22}	2.4×10^{-1}	43	3.7×10^{20}

Table 1 Irradiation conditions and microstructural parameters for neutron-irradiated 3C-SiC.

Experimental Procedure

The material used for this work was polycrystalline 3C-SiC, which was produced by chemical vapor deposition (CVD) by Rohm and Haas Advanced Materials (Woburn, Massachusetts). The CVD material is extremely pure, with typical total impurity concentration of less than 5 wppm. The grain size is between 5 and 10 μ m in the plane parallel to the deposition substrate, with the grains elongated in the <111> growth direction perpendicular to the substrate. The material is typically free of microcracks or other large flaws, but atomic layer stacking faults on the {111} planes are common. There is no porosity in CVD SiC, and the material is generally considered to be of theoretical density (approximately 3.21 g/cm³).

Three fixed-core capsules, each containing 10 sub-cupsles, were irradiated in the High Flux Isotope Reactor, at Oak Ridge National Laboratory. The highest fluence for specimens studied here was 9.6 $\times 10^{25}$ n/m² (>0.1 MeV), corresponding to 9.6 dpa-SiC. Irradiation temperatures ranged from 1050 to 1460°C, determined by the post-irradiation inspection of melt wires inserted in both ends of each sub-capsule. Irradiation conditions and results of defect microstructures for each specimen are given in Table. 1.

Results and Discussion

Cavity microstructure in irradiated 3C-SiC are shown in Fig. 1. Very sparse (<1 × 10^{21} m⁻³) cavities near 1 nm in diameter were observed only in grain boundaries at 1050°C, 5.0 dpa. No cavities was detected at lower fluence of 1.4 dpa at 1050°C. The image shown does not represent general microstructures in the specimens but show the selected area which contains cavities. A high density (2.7 × 10^{23} m⁻³ at 9.3 dpa, 1300°C, and 4.4 × 10^{23} m⁻³ at 9.4 dpa, 1400°C) of cavity formation becomes general above ~1300°C. Most of these cavities appeared to be spherical, although the cavity size is comparable to the TEM resolution limit in this work. Faceted voids are observed at 1460°C as shown in Fig. 1, which were confirmed to be near-tetrahedron, bounded by {111}



Fig. 1 Cavity microstructures in β -SiC irradiated with neutron.

surfaces, with the corners generally truncated [10]. More detailed analysis of faceted void surfaces will be published elsewhere [13].

The estimated volume fractions of cavities (V_{cavity}/V_0) are plotted with previous neutron data [10] in Fig. 2 as a function of irradiation temperature. This shows that the small spherical cavities make only insignificant contribution to the swelling below ~1300°C (~0.01% at 1300°C, 9.6dpa). The cavity volume fractions at ~6 and ~10 dpa increase steeply with increasing temperature. Figure 3 shows the irradiation fluence dependence of cavity swelling for three temperatures. The fluence dependence becomes notable above ~1400°C. The swelling rates estimated from these plots assuming linear fluence dependence are approximately 1 × 10⁻³, 6 × 10⁻³ and 0.03 %/dpa for the temperatures ~1300, 1400, and 1460°C, respectively.



Fig.2 Irradiation temperature dependence of cavity swelling in neutron-irradiated 3C-SiC.

Fig.3 Irradiation fluence dependence of cavity swelling in neutron-irradiated 3C-SiC at three temperatures.



Fig. 4 Dislocation microstructures in 3C-SiC irradiated. Beam direction and g vectors are indicated in each image.





Fig. 5 Irradiation temperature dependence of defect number density in neutron-irradiated 3C-SiC. Displacement damage levels are indicated for the reported self-ion data.

Fig. 6 Irradiation temperature dependence of defect size in neutron-irradiated 3C-SiC.

Swelling-temperature curves generally show a peak (or two peaks), because the void size is positively and void density is negatively depended on the irradiation temperature. There is no such a peak in Fig. 2 below 1460°C. In many irradiated materials, the cavity swelling commences gradually with irradiation fluence accumulation, and the swelling rate finally reaches a steady-state level at a given temperature. The extrapolation of the fluence dependent swelling in Fig. 3 indicates an incubation fluence above ~2 dpa at 1460°C, which is likely related to continuous void nucleation and/or an immature dislocation microstructure. The negligible cavity swelling rates in SiC observed below 1300°C may be attributed to the limited vacancy mobility and the relatively stable dislocation microstructures, with high sink density as discussed below. The discrepancy in the value of cavity swelling from the earlier reports of Price might be primarily caused by the uncertainty of the irradiation conditions and/or impurity in the older material used by Price.

Fig. 4 shows examples of the dislocation microstructure in 3C-SiC irradiated at 1050, 1300, and 1460°C. Various defects including small defect clusters (so-called black spots) with unidentified configuration, small loops with various Burgers vectors, and Frank loops are formed at 1050°C as shown in Fig. 4(a). Many loops were identified to have formed on {111} planes by imaging from the {111} satellite streak near 111 spots. Most loops formed at 1300°C were identified as Frank loops by the imaging from {111} satellite streak and/or g·b contrast analysis. Above 1400°C, larger Frank loops with b = <111> were observed. Peripheries of the larger loops are predominantly hexagonal in shape, with sides parallel to <011> directions as shown in Fig. 4(c).

The defect number density and loop radius were plotted along with previous neutron and self-ion data as a function of irradiation temperature in Fig. 5, and Fig. 6, respectively. Defect density decreased and the size gradually increased with increasing temperature below ~1300°C. Both rapid density decrease and size increase were observed above ~1300°C. The black spots, which are dominant defects below ~00°C, still contribute to the defect density with small loops and Frank loops in the temperature range ~800-1150°C. The very high sink density related to the small defect clusters likely retard the significant loop growth at these lower temperatures. At 1300-1460°C, the irradiation fluence significantly affects both the defect density and size, where loops grow rapidly and develop into larger Frank loops (>~20 nm in radius). According to conventional thought,





reduced sink strength of the thermally unstable defects including small loops and cavities should allow the rapid loop growth in the very high temperature regime. The formation of dislocation networks resulting from continuous unfaulting of the Frank loops, which were not observed in the present work, might start at higher fluence as demonstrated in the self-ion irradiated SiC [8].

Figure 7 shows the defect microstructures before and after post irradiation annealing at 1500°C for 1 hour. Measured loop radius and number density are shown in each image. Both the radius and density were not significantly changed after annealing, except that the number density of smaller loops decreased slightly. Generally, smaller loops can be removed easily because of the more excess free energy (dislocation line tension) per interstitial. For a similar reason, smaller voids may be removed by annealing. Senor et al. reported the absence of cavities in 3C-SiC irradiated to 0.9×10^{25} n/m² at 1100°C, whereas cavities were observed following subsequent annealing at 1500°C for 1 hour [7]. In contrast, annihilation of voids by annealing for specimen irradiated at 1130°C was observed. Further studies are required to clarify the annealing mechanisms of irradiated SiC.

CONCLUSIONS

The temperature and fluence dependence of cavity swelling and dislocation development in CVD SiC irradiated with fast neutrons at high temperatures (1050-1460°C, up to 9.6 dpa) were evaluated using transmission electron microscopy. The cavity swelling was very limited below 1300°C (<0.01% at 1300°C, 9.3 dpa). Temperature and fluence dependent swelling became visible above ~1400°C. The maximum value of the cavity swelling was 0.25% at 1460°C, 9.6 dpa, but this appeared to be below the peak swelling temperature. Frank loops were the dominant dislocation structure in this temperature regime, and the number density decreased and the size increased with increasing irradiation temperature. The loop microstructures depended less significantly on both the irradiation temperature and fluence below 1200°C. A significant decrease in the number density and increase in the size were observed at 1300-1460°C.

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EFFECT OF NEUTRON IRRADIATION ON DC ELECTRICAL CONDUCTIVITY OF SILICON CARBIDE CERAMICS AND COMPOSITES FOR FUSION FLOW CHANNEL INSERT APPLICATIONS—Y. Katoh, S. Kondo, L. L. Snead (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this work is to help addressing the electrical conductivity issue for the silicon carbide-based flow channel insert in lead-lithium blanket of fusion breeding reactors; specifically to establish control schemes for electrical conductivity of SiC composites by identifying the conduction mechanism in composite structures and to address neutron irradiation effect on electrical conductivity in SiC composites and constituents.

SUMMARY

High purity chemically vapor-deposited silicon carbide (SiC) and 2D continuous SiC fiber, chemically vapor-infiltrated SiC matrix composites with pyrocarbon interphases were examined for temperature dependent (RT to 800°C) electrical conductivity and the influence of neutron irradiation on it. In the 2D composites, trans-thickness electrical conductivity was dominated by bypass conduction via interphase network at relatively low temperatures, whereas conduction through SiC constituents dominated at higher temperatures. The Influence of neutron irradiation on electrical properties appeared very strong for SiC, resulting typically in by orders lower ambient conductivity and steeper temperature dependency. Through-thickness electrical conductivity of neutron-irradiated 2D SiC composites with thin PyC interphase will likely in the order of 10 S/m in the typical operating temperature range for flow channel inserts. Mechanisms of electrical conduction in the composites and irradiation-induced modification of electrical conductivity of the composites and their constituents are discussed.

PROGRESS AND STATUS

Introduction

There have been several fusion breeding blanket designs employing lead-lithium eutectic liquid as both the breeding material and the primary or secondary coolant and assuming the use of flow channel inserts (FCI) as the insulating components in the coolant ducts. Such blanket designs were proposed in the EU advanced lead-lithium blanket concept [1] and the US ARIES-ST [2], and the adopted in proposed US dual-cooled lead-lithium (DCLL) test blanket module (TBM) [3], China dual functional lithium-lead (DFLL) TBM [4] for the International Thermonuclear Experimental Reactor (ITER), and EU power plant conceptual study (PPCS) Model C [5]. The dual-coolant type blanket designs incorporating insulating FCI are attractive because they can rely on industrially more experienced steels as the structural materials while using the liquid coolant at temperatures well beyond the limits for steels.

Key requirements for FCI have been identified as 1) adequate thermal insulation, 2) adequate electrical insulation, 3) chemical compatibility with lead-lithium, 4) leak-tightness against lead-lithium, 5) mechanical integrity under rather severe secondary stresses, and 6) maintain above requirements throughout operation in harsh conditions of fusion blankets. The operating conditions involve irradiation by fusion neutrons, developing flow conditions coupled with temperature and field gradients, and mechanical

loadings such as those induced by plasma instability events. One study of magnetohydrodynamic (MHD) and thermal analysis suggests an optimum combination of thermal and electrical conductivities ~2 W/m-K and 5-100 S/m, respectively, for the US DCLL TBM [6]. The maximum operating temperatures are ~470°C for ITER TBM and >700°C envisioned for demonstration reactors.

Silicon carbide (SiC)-based materials are presently the primary candidates as the materials for FCI, based on the proven neutron irradiation tolerance in terms of structural and mechanical integrity [7] and chemical stability in stagnant lead-lithium at elevated temperatures [8]. Irradiation and chemical stabilities have been demonstrated for high purity, crystalline SiC in forms of monolith or continuous fiber-reinforced composites. Main technical issues remaining for SiC-based FCI are 1) to address electrical conductivity issues, 2) to address secondary stress issues, and 3) to secure adequate thermal insulation. The present work is intended to help addressing the first issue: to establish control schemes for electrical conductivity of SiC composites by identifying the conduction mechanism in composite structures and to address neutron irradiation effect on electrical conductivity in SiC composites and constituents.

Experimental Procedure

Materials used were chemically vapor-deposited (CVD) SiC with the manufacturer-claimed purity (except nitrogen) >99.9995% (Rohm&Haas Advanced Materials, Woburn, MA) and continuous SiC fiber composites with two-dimensional (2D) woven fabric architectures, chemically vapor-infiltrated (CVI) SiC matrices, and fiber-matrix interphases consisting of pyrocarbon (PyC) or PyC/SiC multilayers. SiC fibers used were Hi-Nicalon[™] Type-S (Nippon Carbon Co., Tokyo) and Tyranno[™]-SA3 (Ube Industries, Ltd., Ube, Japan). Architectures of the composites used are summarized in Table 1. The interphase deposition and matrix infiltration were performed by Hypertherm High-Temperature Composites, Inc. (Huntington Beach, CA). The primary impurity in both CVD SiC and CVI SiC matrices are nitrogen.

Neutron irradiation was performed in flux trap positions of High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory. The neutron dose and irradiation temperature were in ranges 1.4 - 8.1 dpa and $400 - 1120^{\circ}$ C, respectively.

Both faces of composite samples were ground flat into fabric layers prior to irradiation. Electrical resistivity measurement was performed in a high vacuum furnace in 4-probe configuration for monolithic specimens or in 2-probe configuration for composite specimens in through-thickness orientation. For the 2-probe measurement, the specimen faces were metalized by heat treatment to make sufficiently low resistivity ohmic contacts. The interface was confirmed to be $<1x10^{-6}$ ohm-m² after heat treatment at $>550^{\circ}C$.

Results and Discussion

Result of through-thickness electrical conductivity measurement on the non-irradiated composite materials is shown in Fig. 1. All three composites shown in Table 1 were tested in a non-irradiated condition. Total thickness of the multilayered interphase is ~500 nm and ~100 nm of that is occupied by PyC layers in total. All the materials exhibited ohmic conduction. In all three composites, with increasing temperature, electrical conductivity stays fairly constant until it starts to increase at ~400°C. The through-thickness electrical conductivity at <~400 °C were several S/m with substantial variations by both materials and specimens, whereas it seems to converge to ~20 S/m at 1000°C.



Fig.1. Unirradiated electrical conductivity of various 2D continuous SiC fiber, chemically vapor-infiltrated SiC matrix composites. Data labels indicate fiber type (TySA for Tyranno-SA3 or HNLS for Hi-Nicalon Type-S) and interphase (PyC for pyrocarbon or ML for PyC/SiC multilayer, followed by thickness in nanometer). T/T and I/P stand for through-thickness and in-plane, respectively. Data by Youngblood were taken from Ref. [9].

Material designation	HNLS/ML	TySA/PyC150	TySA/PyC50
Reinforcement	SW Hi-Nicalon™ Type-S 0/90°	PW Tyranno [™] -SA3 0/90°	PW Tyranno [™] -SA3 0/90°
Interphase	$\begin{array}{c} 5x(PyC_{20nm}\!/SiC_{100nm})\\ Multilayered \end{array}$	PyC _{150nm}	PyC _{50nm}
Matrix	CVI SiC	CVI SiC	CVI SiC
Electrical conductivity (20°C) [S/m]			
In-plane, estimated interphase contribution	250	550	180
In-plane, experiment	200	360	150
Through-thickness, experiment	5.5 (±0.8 for 8 samples)	4.5	2.6
Efficiency of through-thickness bypass	2.8%	1.2%	1.7%

Table. 1. Constitution and non-irradiated electrical conductivity for 2D composites.

The temperature dependence of non-irradiated through-thickness electrical conductivity for composites is qualitatively resembles that of in-plane conductivity of a very similar material as shown in Fig. 1 [9]. The in-plane conductivity is obviously dictated by bypass conduction through PyC interphase [9, 10]. Moreover, the temperature dependence of through-thickness conductivity below ~400°C is consistent with those for typical near-isotropic carbon materials [11], but is very different from those for typical CVD SiC. Therefore, one can conclude that the through-thickness conduction in the low temperature regime is primarily through the interphase.

In 2D composites, it can be assumed that $\sim 1/2$ of the interphase films is oriented in favor of through-thickness bypass conduction, but a small fraction is contributing to the macroscopic conduction due to the poor interconnection. Considering $\sim 1/2$ of the interphase films also contributes to in-plane conduction in one of the fiber directions, through-thickness interphase bypass efficiency may be defined as

$$\eta = 2\sigma_t / f_i \sigma_i \approx \sigma_t / \sigma_{ip} \tag{1}$$

where σ and *f* are electrical conductivity and volume fraction, the subscripts, *t*, *ip*, and *i*, denote through-thickness, in-plane, and interphase, respectively. The η values should be dependent on interphase thickness and packing density of fabrics, and were estimated to be ~1% for the present monolayered interphase and ~3% for the multilayered interphase (Table 1). Obviously, the multilayered interphase gives a higher chance to interphase for transverse bridging over multiple fibers.

In the high temperature regime, steeper temperature dependence obviously indicates the dominance of contributions from SiC constituents. Thus, composites can be considered a parallel circuit of imperfect interphase network and SiC. A transition to the SiC-dominated conduction occurs when the apparent conductivity through SiC becomes comparable with that of the interphase bypass. The transition temperature obviously depends not only on the interphase bypass efficiency but also on electronic properties of SiC, which vary by many orders with impurity elements and concentrations.

In addition, the composite makes a serial circuit of "fabric layer composite" discussed above and SiC when 1) the composite faces are not ground into fabric layers, 2) any two fabric layers are electrically separated with SiC matrix, or 3) composite is over-coated with SiC. In such cases, SiC constituents dictate electrical conduction at all temperatures. A typical example is through-thickness conduction of the HNLS/PyC composite in Fig. 1 [9].

Figure 2 summarizes the through-thickness electrical conductivity of irradiated composite materials and the bulk electrical conductivity of irradiated CVD SiC. The irradiated materials also exhibited ohmic conduction property. The composite specimens tested were HNLS/ML irradiated at 800°C to 1.4 dpa and 1120°C to 8.1 dpa. Electrical conductivity of the composite specimen irradiated at 800°C exhibited temperature dependence similar to those for non-irradiated composites. The composite specimen irradiated at 1120°C behaved rather anomalously, showing electrical conductivity continuously increasing from ambient to high temperatures.



Fig. 2. Neutron-irradiated electrical conductivity of 2D Hi-Nicalon Type-S SiC fiber, chemically vapor-infiltrated SiC matrix, pyrocabon/SiC multilayered interphase composite and chemically vapor-deposited SiC. Data label indicates material, irradiation temperature and dose.

The irradiated CVD SiC specimens exhibited steeply temperature-dependent electrical conductivity. Regardless of irradiation temperature in a range 400-1020°C, all three specimens showed the same activation energy for the controlling process at >~200°C, implying the energy level of ~375 meV for the common responsible defect. Higher irradiation temperatures resulted in lower electrical conductivity at all temperatures. Ambient temperature electrical conductivity decreased from the typical non-irradiated value of 1-1000 S/m by a few to several orders as shown in Fig. 3, depending strongly on irradiation temperature. Comparison of temperature dependence at relatively high temperatures between the CVI composites and CVD SiC, controlling mechanism for electrical conductivity may be significantly different.



Fig. 3. Effect of neutron irradiation temperature on ambient temperature electrical conductivity of high purity, chemically vapor-deposited SiC.

Conduction in non-irradiated CVD SiC at room or higher temperatures is governed by non-primary impurities. Neutron irradiation lowered electrical conductivity very significantly, Fig. 2. This is consistent with the observation by Kanazawa et al [12] who reported reduction in both carrier density and mobility after low dose neutron irradiation to N-doped 6H and 4H SiC, and may be reasonable considering the ionic properties of Frenkel defects in SiC [13]. However, the roles of radiation defects are not limited to carrier trapping, because irradiation at lower temperatures with higher defect concentration resulted in higher ambient electrical conductivity. The electrical conduction at elevated temperatures is likely to be governed by defects of single type, with an electronic level ~375 meV, regardless of irradiation temperature. Considering the irradiation temperature range, the responsible defect must be readily produced at 400°C, stable at 1020°C, and stable in configuration between the two temperatures. These conditions eliminate possibility for either type interstitial, Si vacancy, and perhaps interstitial clusters. The electronic level coincides with the defect level of V_{Si} -V_c in 3C-SiC, 0.38 eV above E_v, obtained by Li and Lin-Chung [14]. Importantly, non-irradiated and irradiated SiC are very different electronic materials because all of carrier density, carrier mobility, and electronic level of controlling feature are different.

Neutron irradiation in HFIR produces small concentration of transmutation products in SiC such as P from ³⁰Si. The effect of transmutation doping on as-irradiated electronic properties is considered negligible, because the concentrations of transmutation dopants are very small compared to the those of self defects [15]. However, this may not be the case for fusion neutron spectrums, by which much greater amount impurities such as AI, Mg, and Be will be produced [16].

The two irradiated composite specimens exhibited dissimilar temperature dependence of through-thickness electrical conductivity. The electrical conduction in the specimen irradiated at 800°C is

obviously dominated by the interphase bypass at most temperatures, whereas the one irradiated at 1120°C likely involve the interphase network which is electrically detached in through-thickness direction. The conduction property of the 1120°C-irradiated specimen is also dissimilar with those of the irradiated CVD SiC samples, suggesting influences of much higher impurity concentrations in the CVI SiC matrices or contributions from the interphase and/or fibers.

The 800°C-irradiated composite specimen exhibited electrical conductivity slightly higher than that for non-irradiated composites. PyC interphases in CVI SiC/SiC are often microstructurally similar to glassy carbon rather than near-isotropic graphite. Present result seems reasonable, considering the reported electrical conductivity increase by neutron irradiation for glassy carbon [17]. However, electrical conductivity decrease by typically after neutron irradiation is commonly observed for graphitic carbon [18], being consistent with the observed decrease in in-plane electrical conductivity for irradiated uni-directional CVI SiC/SiC with PyC interphase [10]. The effect of neutron irradiation on electrical conductivity of PyC interphase in SiC/SiC remains unclear, though it is not as dramatic as of SiC.

Conclusions

Electrical conduction mechanism in 2D woven-fabric SiC/SiC composites with conductive PyC interphase was identified; 1) through-thickness conduction within the stacked fabric layers is typically accommodated by the interphase bypass network at relatively low temperatures, 2) over-coating and/or internal layers of semiconducting SiC, if present, add serial resisters to the through-thickness circuit, 3) in-plane conduction is governed by conduction through axial interphases at relatively low temperatures, and 4) conduction through SiC constituents dominates at high temperatures.

Neutron irradiation influences the composite electrical conductivity by modifying electrical properties of both PyC and SiC constituents. Electrical conductivity of PyC interphase is relatively insensitive to irradiation and may decrease or increase, depending on its starting microstructure. Irradiated SiC is electronically a different material from non-irradiated SiC. Semiconducting properties of SiC become governed by radiation defects after neutron irradiation, resulting in steeper temperature dependence of electrical conductivity of irradiated high purity SiC is likely negligible in fission neutron irradiation. However, transmutation effects on electronic properties are potential critical issues for SiC-based FCI for DEMO, which will receive high dose irradiation of fusion neutrons.

Through-thickness electrical conductivity of neutron-irradiated 2D SiC/SiC with thin PyC interphase will likely in the order of 10 S/m in the typical operating temperature range for FCI. Applying SiC over-coating is beneficial in reducing electrical conductivity at relatively low temperatures in expense of more significant irradiation effect and steeper temperature dependence. Electrical conductivity tailoring by engineering interphase structure and configuration in composite materials appears feasible.
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MICROSTRUCTURES OF CHEMICALLY VAPOR-DEPOSITED SILICON CARBIDE AFTER IRRADIATION CREEP DEFORMATION—Y. Katoh, S. Kondo, L. L. Snead (Oak Ridge National Laboratory)

OBJECTIVE

The present work is intended to help understand the irradiation creep mechanisms in beta-phase SiC, by examining the influence of externally applied stress in the order of 100 MPa on microstructural development during neutron irradiation to relatively low doses.

SUMMARY

Microstructures of silicon carbide were examined by transmission electron microscopy (TEM) after creep deformation under neutron irradiation. Thin strip specimens of polycrystalline and monocrystalline, chemically vapor-deposited, beta-phase silicon carbide were irradiated in High Flux Isotope Reactor to 0.7 - 4.2 dpa at nominal temperatures 640 - 1080°C in an elastically pre-strained bend stress relaxation configuration with the initial stress of ~100 MPa. Irradiation creep caused permanent strains of 0.6 to 2.3 x 10^{-4} . Tensile-loaded near-surface portions of the crept specimens were examined by TEM. The main microstructural features observed were dislocation loops in all samples, and appeared similar to those observed in samples irradiated in non-stressed conditions. Slight but statistically significant anisotropy in dislocation loop microstructure was observed in one irradiation condition, and accounted for at least a fraction of the creep strain derived from the stress relaxation. The estimated total volume of loops accounted for 10 - 45% of the estimated total swelling. The results imply that the early irradiation creep deformation of SiC observed in this work was driven by anisotropic evolutions of extrinsic dislocation loops and matrix defects with undetectable sizes.

PROGRESS AND STATUS

Introduction

Beta phase SiC in fibrous composite forms, which is often referred to by SiC(f)/SiC composite, is considered for applications in fusion and fission energy systems. SiC/SiC composites have been studied as advanced options for blanket structures of magnetic and inertial fusion systems [1]. They are also recently considered suitable materials for insulating liners of liquid metal flow channels for certain fusion blanket types, along with other materials such as monolithic and porous SiC [2]. Moreover, SiC/SiC composites are considered the promising materials for control rod sleeves of helium-cooled reactors, and a potential advanced fuel cladding material for light water reactors and gas-cooled and salt-cooled reactors [3-6]. For these applications, benefit of using SiC/SiC composites comes primarily from the added reliability owing to fibrous reinforcement, in addition to the various advantages inherent to SiC.

Irradiation creep is an important phenomenon for materials for radiation services, because it is a major contributor to potential dimensional instability of materials under irradiation at such temperatures that thermal creep is not anticipated. Although irradiation creep often determines irradiated lifetime of metallic structural components, it is not necessarily undesirable for brittle materials like ceramics for functional applications because it may relax and/or redistribute stresses. For SiC-based nuclear components, the

latter function of irradiation creep can be very important, particularly when a significant temperature gradient exists and the secondary stresses developed by differential swelling can be severe [7].

Studies on neutron irradiation creep of SiC have so far been extremely limited and insufficient. Price published the result of the irradiation creep study on CVD SiC in 1977 [8]. In that work, elastically bent strip samples were irradiated in a fission reactor, and the linear-averaged creep compliance was estimated to be in the order of 10^{-38} [Pa·n/m² (E > 0.18 MeV)]⁻¹, or 10^{-7} [MPa·dpa]⁻¹, at 780 - 1130°C. In a recent publication, Katoh et al. concludes that creep strains for CVD SiC were dominated by transient creep at temperatures below ~950°C whereas steady-state creep is likely at higher temperatures with an compliance of $1.5 \pm 0.8 \times 10^{-6}$ [MPa·dpa]⁻¹ [9]. The present work is intended to help understand the irradiation creep mechanisms in SiC, by examining the influence of externally applied stress in the order of 100 MPa on microstructural development in beta phase SiC during neutron irradiation to relatively low doses.

Experimental Procedure

Materials used were high purity, polycrystalline CVD SiC (Rohm and Haas Co., Advanced Materials, Waborn, Massachusetts, USA) and monocrystalline 3C-SiC (Hoya Advanced Semiconductors Technologies, Inc., Tokyo, Japan). The manufacturer-claimed purity of the polycrystalline material is >99.9995%, whereas the monocrystalline wafer was n-type doped with nitrogen (~1x10¹⁹ cm³ carrier density) but otherwise of very high purity. Thin strip samples with dimensions of 25 mm x 1 mm x 50 μ m were prepared. The monocrystalline samples were with {100} surface orientation and were machined so that the longitudinal direction was parallel with one of the <011> orientations.

In a bend stress relaxation (BSR) irradiation creep experiment, thin strip samples were elastically bent to a fixed radius during irradiation. The initial and final stresses, σ_0 and σ_a , respectively, are calculated using the measured initial (constrained) bend radius (R_0), the unconstrained residual bend radius after irradiation (R_a), specimen thickness (t) and literature values for temperature dependent elastic modulus (E).

$$\sigma_0 = \frac{Et}{2R_0}, \quad \sigma_a = \frac{Et}{2} \left(\frac{1}{R_0} - \frac{1}{R_a} \right) \tag{1}$$

The irradiation was performed in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (Oak Ridge, Tennessee, USA) to a maximum neutron fluence of 4.2 x 10^{25} n/m² (E > 0.1 MeV). An equivalence of one displacement per atom (dpa) = 1 x 10^{25} n/m² (E>0.1 MeV) is assumed hereafter. The nominal irradiation temperatures were 640 - 1080°C. Details of the irradiation technique and the result of creep strain measurement are published elsewhere [9].

Thin foil specimens for TEM examination were prepared from the tension side of the flexurally deformed samples utilizing a sectioning and back-thinning process. In this process, the tension side surface was first removed by $\sim 1 \ \mu m$ to eliminate the layer which might have been affected by surface effects, followed by perforation from the compression side of the specimen. Thus, the areas for TEM examination were applied approximately 96% of the maximum flexural stress on the strip samples in an almost uni-axial tensile mode during irradiation. Argon ion beam accelerated to 3 keV used for both processes at a milling angle of ~ 6

degrees. TEM examination was performed using Philips Tecnai 20 operated at 200 kV.

Results and Discussion

The irradiation and stress conditions for the specimens examined by TEM are listed in Table 1, along with a summary of irradiation creep strains and microstructural features. A polycrystalline sample was examined for the irradiation condition of 640° C / 3.7 dpa, whereas monocrystalline samples were examined for the conditions of 1030° C / 0.7 dpa and 1080° C / 4.2 dpa.

		CR4RH	CR7SX	CR8SX
Matarial		R&H CVD Poly-beta	Hoya Monocrystalline	Hoya Monocrystalline
Material		SiC	3C-SiC	3C-SiC
Tirr-nominal	°C	640	1030	1080
Fluence-nominal	dpa	3.7	0.7	4.2
Initial/final stress	MPa	87/46	86/57	101/0
Creep strain		1.12×10^{-4}	0.63×10^{-4}	2.29×10^{-4}
Defects observed		Tiny loops & BSD*	Mostly Frank loops	Frank loops
Average defect diameter	nm	~3.9	~3.3	~12
Defect number density	m ⁻³	$\sim 2.8 \times 10^{23}$	$\sim 2.1 \times 10^{23}$	$\sim 3.8 \times 10^{22}$
Estimated swelling by loops		$\sim 1.1 \times 10^{-3}$	$\sim 5.1 \times 10^{-4}$	~1.4x10 ⁻³
Estimated unstressed swelling		$\sim 1.1 \times 10^{-2}$	$\sim 1.5 \times 10^{-3}$	$\sim 3 \times 10^{-3}$

Table. 1. Summary of microstructural data.

After irradiation at 640°C to 3.7 dpa, the observed microstructural defects were stacking faults and tiny spot-like clusters. For this sample, the initial and final stresses were 87 and 36 MPa, respectively. Figure 1 presents a weak beam dark field image of the polycrystalline specimen with the beam direction *B* near [011] and the diffraction vector g parallel to [200]. The stacking faults were distanced each other by 50 - 500 nm as typical in as-deposited CVD SiC, and are not believed to have been modified during irradiation. The spot-like clusters mostly appear as loops at higher magnifications and are presumably of the same type(s) as previously observed in CVD SiC irradiated at 800°C [10, 11]. An anisotropy analysis was not carried out for these loops, because their Burgers vectors or habit planes had not been identified.



Fig.1. Weak beam dark field image of the tensile side of chemically vapor deposited polycrystalline SiC specimen irradiated at ~640°C to 3.7 dpa under initial/final stress of 87/46 MPa. $B \sim [011]$, g = [200], g/4g. Arrow indicates the stress axis.

Neutron irradiation at 1030°C to 0.7 dpa produced tiny (typically a few nanometers in diameter) dislocation loops as the only defects observed in the monocrystalline specimen by conventional TEM. The initial stress of 86 MPa relaxed to 57 MPa at the end of irradiation for this sample. To identify characteristics of these loops, a visibility test with different diffraction vectors was performed. In Fig. 2, weak beam dark field images at an edge of the wedge (001) foil are compared in diffraction conditions $g = \begin{bmatrix} \overline{2}20 \end{bmatrix}$ (A), g = [040] (B), and g = [220] (C). If loops are of Frank faulted type with Burgers vector of a/3<111>, in theory, all loops should be visible using the [040] diffraction and a half of them visible in the other two conditions. Note that the visible loops using $\begin{bmatrix} \overline{2}20 \end{bmatrix}$ and the ones visible using [220] are exclusive each other. If all clusters are perfect loops with Burgers vector of a/2<110>, the diffraction conditions $g = \begin{bmatrix} \overline{2}20 \end{bmatrix}$, [040], and [220] images 5/6, 2/3, and 5/6 of the entire loop population, respectively. Fig. 2 indicate that a substantially greater number of loops along the edge are seen with g = [040] than with g = <220. Moreover, $g = \begin{bmatrix} \overline{2}20 \end{bmatrix}$ and g = [220] conditions image partial populations of the loops which are almost exclusive each other. Therefore, it is likely that the dislocation loops produced in this irradiation condition are mostly Frank faulted loops.



Fig. 2. Weak beam dark field images of the tensile side of chemically vapor deposited monocrystalline SiC specimen irradiated at ~1030°C to 0.7 dpa under initial/final stress of 86/57 MPa. Images (A), (B), and (C) were taken from the exactly identical area with $B \sim [001]$, $g = \lfloor \overline{2}20 \rfloor$, [040], and [220], respectively. Loops imaged with strong contrast are surrounded by solid symbols, whereas those with no or weak contrast are surrounded by dashed symbols.

The thin foil specimen was taken from the tension side subsurface of the crept sample, as described in the previous section. In this discussion, crystallographic coordination assumes the surface normal to [001] and the stress axis parallel with [110]. Within four {111} Frank loop habit planes, $(\overline{1}11)$ and $(1\overline{1}1)$ planes are in parallel with the stress axis, whereas (111) and $(11\overline{1})$ planes intersect with it at an angle of ~35 degrees. For convenience sake, hereafter we call the former two planes "zero-stress" loop planes and the latter two planes "finite-stress" loop planes.

In Fig. 3, weak beam dark field images of the 1030° C / 0.7 dpa specimen are compared for diffraction vectors g = [220] (A) and $g = [2\overline{20}]$ (B) within the same area. The elliptical symbols drawn on Thompson tetrahedra indicate {111} planes on which the supposedly visible Frank loops are located. The arrows in white represent the axis of tensile stress applied during irradiation. Obviously, only loops on the finite-stress planes are supposedly imaged in Fig. 3 (A), whereas the rest or loops on the zero-stress planes are seen in Fig. 3 (B), assuming all loops are of Frank faulted type. No difference in loop number density or size between the finite-stress and zero-stress orientations could be noticed.



Fig. 3. Weak beam dark field images of the tensile side of chemically vapor deposited monocrystalline SiC specimen irradiated at ~1030°C to 0.7 dpa under initial/final stress of 86/57 MPa. Images (A) and (B) were taken from the identical area. Imaging conditions are $B \sim [001]$, g = [220] (A) and $B \sim [001]$, $g = \begin{bmatrix} 2\overline{2}0 \end{bmatrix}$ (B). Arrows indicate the stress axis [110]. Elliptical symbols shown on Thompson tetrahedra indicate loop planes imaged.

Frank faulted loops also were the dominant microstructural features observed in the monocrystalline specimen following neutron irradiation at 1080°C to 4.2 dpa. The initial tensile stress of 101 MPa had completely been recovered to ~0 MPa before the end of irradiation. Loop to loop interactions have already occurred at limited locations in this specimen, however, majority of the loops remained unreacted. The loops were clearly lying on {111} planes, and the presence of intense <111> satellite streaks in selected area diffraction patterns in the absence of stacking faults (other than Frank loops) confirmed the abundance of Frank faulted loops. The streak images of edge-on loops on two different {111} planes are shown in Fig. 4. These micrographs were taken with $B \sim [011]$, and satellite streaks along $\begin{bmatrix} 11\overline{11} \end{bmatrix}$ (A) and $\begin{bmatrix} 1\overline{11} \end{bmatrix}$ (B), as indicated by the shaded planes on the inset Thompson tetrahedra. Hence, the micrograph (A) shows Frank loops on one of the two finite-stress loop planes and the micrograph (B) shows those on one of the two zero-stress loop planes. Again, there is no significant difference in loop characteristics between the two populations.



Fig. 4. Streak images of the tensile side of chemically vapor deposited monocrystalline SiC specimen irradiated at ~1080°C to 4.2 dpa under initial/final stress of 101/0 MPa. Images (A) and (B) were taken from the identical area. Images were from $[11\overline{1}]$ satellite streak (A) and from $[1\overline{11}]$ satellite streak (B) at $B \sim [011]$. Arrows and shaded planes on Thompson tetrahedra indicate the stress axis [110] and loop planes imaged, respectively.

Loop characteristics of the finite-stress and zero-stress loop planes are quantified and summarized in Table 2. For the irradiation condition 1030°C / 0.7 dpa, loop number density appeared ~20% higher on the finite-stress loop planes than on the zero-stress planes, whereas the average loop sizes were about the same. The difference in number density is rather minor but statistically significant, considering the fact that more than 300 loops were counted in each diffraction condition from two different areas. The loop number density was higher on the finite-stress loop planes for nearly all sizes, as compared for size distribution in Fig. 5. For this irradiation condition, it should be noted that the quantification of loop sizes involves substantial uncertainty due to the small sizes and the foil drifting during the TEM image recording. On the other hand, for the irradiation condition 1080°C / 4.2 dpa, loop sizes were quantified with much more confidence because most of the loops were larger than 10 nm in diameter. In this condition, both the loop number density and the average loop size appeared comparable on the finite-stress and the zero-stress loop planes within statistical uncertainties. The loop size distributions may appear slightly different but are actually about the same when smoothed.

			CR7SX		CR8SX			
Tirr-nominal	°C		1030		1080			
Fluence-nominal	dpa		0.7		4.2			
Initial/final stress	MPa		86/57		101/0			
		Finite-stress	Zero-stress	A11 (111)	Finite-stress	Zero-stress	All	
(Loop planes)		{111}	{111}		{111}	{111}	$\{111\}$	
		planes	planes	plattes	planes	planes	planes	
Average loop radius	nm	1.6	1.7	1.7	6.0	6.0	6.0	
Defect number density	m ⁻³	1.2×10^{23}	9.7×10^{22}	2.1×10^{23}	1.8×10^{22}	1.9×10^{22}	3.8×10^{22}	
Estimated swelling		$2 \text{cm} 10^{-4}$	2.5×10^{-4}	5.1×10^{-4}	7.0×10^{-4}	7.4×10^{-4}	1.4×10^{-3}	
by loops		2.0X10	2.5X10 5.1X10		7.0X10	7.4X10	1.4X10	
Unstressed swelling								
estimated from	$\sim 1.5 \times 10^{-3}$ $\sim 3 \times 10^{-3}$							
literature data								

Table 2. Comparison of loop microstructures on different loop planes.



Fig. 5. Comparison of size distribution for loops with Burger's vector near-parallel and normal to tensile stress axis in chemically vapor deposited monocrystalline SiC specimen irradiated at ~1030°C to 0.7 dpa under initial/final stress of 86/57 MPa (A) and at ~1080°C to 4.2 dpa under initial/final stress of 101/0 MPa (B).

Comparison with microstructural development during unstressed irradiation

In neutron-irradiated high purity CVD SiC, it has been reported that tiny non-faulted dislocation loops dominates the microstructures at irradiation temperatures <~800°C to a dose level of at least ~8 dpa [10], whereas Frank faulted loops dominates at >~1100°C until dislocation interactions become significant [10, 12, 13]. There should be a transition from the non-faulted loop domination to the faulted loop domination likely between ~800 and ~1100°C, although the lowest temperature for Frank faulted loops to develop

could be even lower according to other reports [14, 15]. In the present work, as shown in Figs. 1 - 4 and Table 1, microstructural defects which had been produced by neutron irradiation under tensile stress and were observed in conventional TEM were tiny non-faulted dislocation loops at 640°C / 3.7 dpa, tiny dislocation loops most of which are likely Frank loops at 1030°C / 0.7 dpa, and fairly well-grown Frank loops at 1080°C / 4.2 dpa. These observed microstructures were those anticipated to develop during non-stressed neutron irradiation.

In Fig. 6, average radius and number density of dislocation loops observed in the creep-deformed samples are graphically compared with the data from the non-stressed irradiation. The 640°C / 3.7 dpa and the 1030°C / 0.7 dpa data points fit in the temperature-dependence data bands for non-stressed irradiation. The 1080°C / 4.2 dpa data point for loop number density significantly deviates from the data band. However, it is unlikely to have been caused by the applied stress, because the loop characteristics did not differ between planes with finite and zero stress components. Considering the fact that the loop number density data point is located at the lower edge of the data band, the most likely reason for the rather anomalously rapid loop growth is a deviation of actual irradiation temperature from the nominal one.



Fig. 6. Average loop radius and loop number density in chemically vapor deposited SiC irradiated under external stresses; comparison with literature data for unstressed conditions.

Anisotropy in loop development

The above observations imply that applied stress in the magnitude range studied in this work do not impose very significant influences on the species, number density, and size of the irradiation-produced defects in SiC. On the other hand, in the 1030°C / 0.7 dpa sample, loop population on the habit plane with

finite normal and shear stress components was by ~20% greater than that on the plane with zero normal and shear stress components, which is statistically significant.

In ion-irradiated CVD SiC, a very significant anisotropy in the distribution of Frank loops has been reported by Kondo, et al [16]. In their experiment, Rohm & Haas high purity CVD SiC samples were irradiated with 5.1 MeV silicon ions at 1400°C to ~34 dpa, and it was found that number density of the Frank loops produced on individual {111} planes is clearly correlated with an angle of the loop plane relative to the irradiated surface. This anisotropy was attributed primarily to the constraint against lateral expansion due to the shallow thickness of irradiated layer as compared to the sample thickness, in contrast to the free expansion allowed along the surface normal. Based on the present result and the Kondo work, it is likely that external stress causes an anisotropic Frank loop development. Although it is difficult to estimate the magnitude of lateral compressive stress developed during the ion irradiation, it could be significantly higher than the stress levels applied in the present work, considering that volumetric swelling of ion-irradiated SiC at 1400°C is roughly estimated to be ~0.4% and the Young's modulus ~410 GPa [17]. The difference in extent of anisotropy between the two works may have been caused by difference in stress magnitude, irradiation temperature, dose rate, or other factors.

In the present work, anisotropy in the loop microstructure was not detected in the 1080°C / 4.2 dpa sample, in spite that it was apparent in the sample irradiated at a slightly lower temperature to a lower dose. The potential explanations for this apparent discrepancy include: 1) dislocation interactions already significant in the 1080°C / 4.2 dpa sample cancelled the stress-induced anisotropy which may had existed at lower doses (calculated mean dislocation line spacing is ~15 nm compared to ~12 nm mean loop diameter), 2) substantial neutron dose after significant stress relaxation cancelled the anisotropy (0.7 dpa at 1030°C already relaxed 1/3 of the initial stress), and 3) stress effect is substantially different at the two temperatures (particularly the actual temperature difference may have been more significantly).

Comparison of microstructural data with macroscopic strain

In such a condition that 1) the majority of vacancies surviving mutual annihilation stay in the matrix, 2) interstitials are mobile enough and clusters only into extrinsic dislocation loops, and 3) microstructural sinks of other types are not present, the number of interstitials clustering into loops approximately equals the number of vacancies left in the matrix. In this case, macroscopic swelling should approximately correspond with the total loop volume fraction, and if the swelling is anisotropic, the strain components decomposed along the loop normals should roughly correspond with the volume fractions of loops on individual loop planes.

However, in this work, both the measured creep strain and the unstressed volumetric swelling seem to be significantly greater than those estimated based solely on loop microstructures. In fact, for the 1030° C / 0.7 dpa condition, the strain estimated from the microstructural data normal to the loop plane with the finite stress is by only ~1x10⁻⁵ greater than that normal to the loop plane with zero stress (Table 2). From the anisotropic loop microstructure data, strain along the stress axis is calculated to be by ~5x10⁻⁶ greater than the average linear strain. Uncertainty in this estimated loop contribution to the creep strain is large because a small change in loop radius results in large change in it. Nevertheless, the anisotropic swelling due to anisotropic loop development likely accounts only for a fraction of the measured creep strain of $6.3x10^{-5}$ (Table 1). Similarly, the magnitude of swelling estimated from the microstructural data accounts for

10 – 45% of the swelling values typically anticipated for SiC irradiated without stress application in otherwise corresponding conditions (Table 1). Such substantial discrepancies of the estimated loop volume from the macroscopic swelling have been historically reported at relatively low temperatures at which vacancies are believed to be practically immobile, and attributed to the assumed presence of defect clusters which are not visible by conventional TEM techniques [10, 18].

Thermal creep, particularly the primary and/or transient creep, of high purity, crystalline SiC has been studied and often attributed to grain boundary-related phenomena (such as grain boundary diffusion and grain rearrangement) and grown-in defects including stacking faults [19, 20]. However, in the present work, high-purity polycrystalline and monocrystalline SiC samples were irradiated in a BSR configuration side by side, and there observed relatively minor difference between the two materials in stress relaxation behavior. The monocrystalline sample was not only free from grain boundaries but also contained very few stacking faults or no line dislocations in a pre-irradiation condition. Both materials possess the theoretical mass density of beta-phase SiC, implying very low concentrations of grown-in vacancies.

In the monocrystalline samples, likelihood of the migrating irradiation-produced point defects to escape to the surface is negligible even if one does not assume the likely presence of invisible defects, because the mean dislocation inter-spacing of the visible loops alone is calculated to be <10 nm for the case of 1030°C / 0.7 dpa irradiation. Therefore, annihilation or trapping of migrating point defects are possible only at the matrix defects or clusters. In this microstructural condition, defects contributing to irradiation creep have to be matrix defects and/or clusters. Because the defects visible in TEM accounted only for limited fractions of the irradiation creep strains, the present result suggests that invisible matrix defect clusters could be the major contributors to creep. Visible loops may have played a rather supplemental role to irradiation creep (and swelling) at least in conditions studied in this work, although the relative loop contribution may change at higher stresses or higher temperatures. The contributing invisible clusters can only be speculated and possibly are small SIA or vacancy clusters and complex clusters involving antisite defects [21].

Conclusions

High density non-faulted and faulted dislocation loops, respectively, were produced in high purity beta-phase CVD SiC during neutron irradiation to 3.7 dpa at ~640°C and 0.7 or 4.2 dpa at 1030 - 1080°C in a bend stress relaxation configuration with the initial stresses ~100 MPa. The dislocation loop microstructures were both qualitatively and quantitatively similar to those typically develop under irradiation without application of external stresses.

In the monocrystalline samples, resolved stress components were zero for two of the four faulted loop planes and were finite for other two planes. Difference in loop number density between the two sets of planes was apparent only in 1030°C / 0.7 dpa condition. On the other hand, averages and distributions of loop size were not significantly different between the two sets of planes in any irradiation condition.

The estimated creep strain due to the anisotropic loop microstructure did not fully account for the measured macroscopic creep strain. Similarly, volumetric swelling values estimated from the loop microstructures accounted for less than a half of the typical macroscopic swelling values for irradiated SiC. These observations imply significant contributions to both irradiation creep and swelling from matrix defects which were not observed by TEM.

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MODELING SiC/SiC COMPOSITES WITH OFF-AXIS FIBERS¹ – C. H. Henager, Jr. (Pacific Northwest National Laboratory², Richland, WA 99336, USA)

OBJECTIVE

This work updates modeling results for fiber composites having other orientations than 0/90. The work of Cox et al. has been used to derive a fiber bridging law for off-axis fibers that can be used to help model SiC/SiC composites fabricated into tubular geometries.

SUMMARY

A time-dependent fiber-bridging model that accounts for fiber orientation has been developed and its predictions are compared to strength and crack growth data for a braided weave composite. The level of agreement suggests that existing models of off-axis bridging fibers are not adequate for fusion reactor designs using SiC/SiC composites in off-axis orientations.

PROGRESS AND STATUS

Introduction

SiC is an excellent material for fusion reactor environments, including first wall plasma facing materials and breeder-blanket modules. In the form of woven or braided composites with high-strength SiC fibers it has the requisite mechanical, thermal, and electrical properties to be a useful and versatile material system for fusion applications [1-7]. The use of SiC-reinforced composites for fusion reactors or other nuclear applications will not be restricted to 0/90 aligned fiber architecture in all cases. It is important to understand the role of fiber orientation in the strength, toughness, and time-dependent properties for such materials. The use of high-strength ceramic fibers for composites is predicated on optimizing the strength, fracture resistance, and retained strength in aggressive environments, which argues for the best use of fiber strengths, namely on-axis loading for full load transfer to the high-strength fibers. Relatively few researchers have systematically studied the effects of fiber orientation on composite properties [8-10], and none have, to the best of our knowledge, performed any time-dependent testing of composites with off-axis or inclined fiber orientations.

Experimental Procedure

Materials tested

The SiC/SiC materials that were tested at PNNL are 1) a 5-harness satin weave, 8-ply, Hi-Nicalon Type-S fiber composite that was purchased in 2004 from GE Power Systems³ and 2) A Hypertherm⁴ composite purchased in 2006 that is $\pm 55^{\circ}$ braided weave, 10-ply plate, Hi-Nicalon Type-S fiber composite. The 5-harness satin weave 0/90 composite from GE Power Systems was manufactured for PNNL in 2002 with a bulk density of 2.69 g/cm³ and 40% nominal fiber volume fraction and was fabricated using isothermal chemical vapor infiltration (ICVI). A 150-nm thick pyrocarbon (PyC) interface was applied to the Type-S fibers prior to ICVI processing. The Hypertherm materials were also made with Type-S Hi-Nicalon fibers but coated with a 150 nm PyC, (100 nm CVI SiC, 20 nm PyC)₄ multi-layer interface applied prior to CVI matrix deposition. These materials had a nominal fiber volume fraction of 30%, a bulk density of 2.9 g/cm³, and a 380-µm thick outer seal coat of SiC.

Mechanical property testing

¹ Poster presentation at ICFRM-13, Nice, FR, 2007.

² PNNL is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

³ http://www.gepower.com

⁴ Hypertherm HTC Inc. (Huntington Beach, Calif.)

The peak load fracture toughness, termed K_Q , using single-edge notched beams (SENB) of each composite material was determined at ambient temperature and also at elevated temperature based on ASTM C-1421 (see Table 1).

Composite Material-	Fixture⁵		Sample					
Sample								
	Support Span	Loading Span	Span (L)	Depth ⁶ (d)	Width (W)			
0/90 5-harness satin weave – SENB ⁷	40	20	50	5	2.1			
$\pm 55^{\circ}$ braid – SENB ⁷	40	20	50	6.1	3.6			

Model development

Analysis of bridging fibers aligned normal to the stress axes is well developed in the composite literature. We generally use shear-lag model with slip interface traction that results in a non-linear force displacement law. For non-aligned fibers we require a fundamentally different relation between force and displacement to account for fiber bending and so-called snubbing friction. Cox [8] has developed a forcedisplacement law that we will evaluate for off-axis ceramic fibers. Cox derived the following linear relation for fiber deflection due to bending and including snubbing friction effects:

$$\mu_{e}\left(-\cos\phi + \cos(\theta_{0} + \phi) + \frac{P\left(\frac{-P\cos\phi + e^{-\frac{\theta_{0}\mu_{e}}{P}}(P\cos\phi - \mu_{e}\sin\phi)}{\mu_{e}} + \sin(\theta_{0} + \phi)\right)}{\mu_{e}}\right)}{\mu_{e}}$$

$$W_{defl} = \frac{2r_{f}(P^{2} + \mu_{e}^{2})\tau_{1}}{2r_{f}(P^{2} + \mu_{e}^{2})\tau_{1}}$$
(1)

where *W* is the fiber deflection, *P* is the force, ϕ is the fiber inclination angle, θ_0 is the bending angle, μ_e is the snubbing friction term, and τ_I is the conventional sliding friction term. Plus, there is a term for elastic stretch of the fiber that is non-linear as before:

$$W_{el} = \frac{1 + e^{\frac{2\theta_0\mu_e}{P}} (\mu_e - 1) \cos\phi}{8E_f r_f^2 \mu_e \tau_1}$$
(2)

Snubbing friction refers to the increase in friction as the inclined fiber is pulled and bends out of the ceramic matrix, much like the friction due to pulling a rope around a smooth edge. Such friction is highly localized but greatly modifies the fiber force-displacement law. The conventional force law is matched to the new force law when $\phi = 0$ as shown in Figure 1 and Figure 2 shows the new force law when ϕ is not equal to zero. In this case the bridging fiber becomes stiffer with increasing ϕ .

⁵ All dimensions are in mm in Table 1.

⁶ Sample surfaces in depth direction were left as received and were not polished.

⁷ a/W values were 0.16 for SENB samples.



Figure 1. Force displacement law based on shear-lag model, denoted as 90 Deg curve, is matched to the new force law labeled $\phi = 0$ by adjusting μ_e and τ_1 in Eq. 2 since Eq. 1 is zero when $\phi = 0$.



Figure 2. Force displacement laws are compared when ϕ is not equal to zero. With increasing ϕ the bridging force law decreases W_{el} and increases W_{defl} to give a "stiffer" bridge but now one that is part bending.

The bridging model requires a fiber stress function, which is constructed by partitioning the fiber force between tension and bending as:

$$\sigma_{br} = \frac{F_{br} \cos\phi}{2r_f} + \frac{3F_{br} \sin\phi M}{4r_f^2}$$
(3)

where the first term corresponds to our previous tensile orientation stress when $\phi = 0$ and the second term is the bending term accounting for the moment of inertia for a 2D bridge in our model [11]. We can

put a lower bound on M using the COD but M may be larger than that due to interactions with the SiC matrix that act to increase the moment arm. In the new model, F_{br} is calculated using Eqs. 1 and 2 based on the fiber deflection required to remain a bridging fiber in the dynamic crack bridging model [11]. We then make use of Eq. 3 to compute the stress on the bridging fiber to track fiber failure as a function of fiber displacement, which now includes bending due to fiber inclination angle.

Results

Figure 3 shows the results of the SENB toughness measurements, reported as K_{Q} , for each material. The braided weave material has a fracture toughness of approximately one-third of that of the 0/90 composite. Can we rationalize this data with the Cox bridging model that we have constructed? Our tensile bridging model predicts fracture toughness quite accurately using typical composite data and average fiber strength of 2.5 GPa. If we use those parameters and vary the fiber inclination angle according to our implementation of the Cox equations, then we predict the following, where $\phi = 35^{\circ}$ as defined by Cox. In Figure 4 we show the results of these calculations for inclined fiber composites based on our implementation of the Cox model. Three cases are shown in Figure 4, including no snubbing friction, a snubbing friction ratio of 200:1 relative to the interfacial shear friction term, and snubbing, plus a doubling of the fiber bending moment due to matrix spallation during fiber deformation and bending.



Figure 3. SiC-composite fracture toughness, K_Q , for (a) 0/90 satin-weave material and (b) ±55 braided weave material showing the large difference in measured toughness at ambient and at 1373K.



Figure 4. Predicted fracture toughness as a function of fiber inclination angel using a fiber strength of 2.5 GPa, which is the same strength used in our model for 0/90 oriented composites. The experimental data point lies below all three curves.

In general, the model cannot account for the observed decrease in toughness due to fiber inclination. This suggests either a refinement to the model is required or that more data should be obtained on composites with similar fiber volume fractions and processing conditions. However, microstructural observations help support some of the model assumptions. Matrix spallation is observed which complicates the determination of the bending moment that a fiber experiences. Figure 5 shows SEM images of fiber fractures from the braided weave composite material illustrates matrix spallation as evidenced by the exposed fiber channels and apparent shear failure of the fracture fibers as evidenced by the fracture inclination angle.



Figure 5. SEM micrographs of \pm 55 braided weave fracture surfaces showing matrix spallation and fiber shear fracture features. In (a) and (b) we observe fiber channels exposed due to spallation. In (b) we observe fiber shear fracture features.

Conclusions

A new force displacement law for inclined bridging fibers in SiC/SiC composites has been developed based on a model by Cox for the force required to pull out an inclined fiber from an elastic matrix. The modified fiber-bridging model is not able to fully account for observed fracture toughness data for a braided fiber composite. Additional data is required to further test the model. Several critical model assumptions, however, were verified by fractography.

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JOINING SIC/SIC COMPOSITES FOR FUSION APPLICATIONS¹ – C. H. Henager, Jr. (Pacific Northwest National Laboratory², Richland, WA 99336, USA)

OBJECTIVE

This work updates joining results on SiC-based materials using solid state displacement reactions between Si and TiC powders.

SUMMARY

The use of SiC composites in fusion environments may require joining of plates using non-mechanical joints, such as reactive joining or brazing. One promising joining method is the use of solid-state displacement reactions between Si and TiC to produce $Ti_3SiC_2 + SiC$. Such joints, while stronger than the SiC-composite interlaminar shear strength, which is a critical metric for joint performance, requires pressure and bonding at elevated temperatures. We are exploring the processing envelope for this joint in advance of the US-Japan TITAN collaboration so that we can produce viable joints to undergo irradiation studies in HFIR. Joining pressure appears to require almost 30 MPa at 1673K in order to produce strong and dense joints.

PROGRESS AND STATUS

Introduction

SiC is an excellent material for fusion reactor environments, including first wall plasma facing materials and breeder-blanket modules. It is low-activation, temperature-resistant, and radiation damage tolerant compared to most materials. In the form of woven or braided composites with high-strength SiC fibers it has the requisite mechanical, thermal, and electrical properties to be a useful and versatile material system for fusion applications, especially since microstructural tailoring during processing allows control over the physical properties of interest [1-7]. However, it is difficult to mechanically join large sections of such materials using conventional fasteners so the analog of welding is being pursued for these ceramic materials [2, 6, 8-15]. Such methods include metallic brazes [9, 16], glass ceramics [8, 17], preceramic polymers [15], and displacement reactions [2]. This paper reports on the current status of SiC and SiCcomposite joining for fusion applications based on displacement reactions between Si and TiC. This has been used to produce bulk composite material consisting of SiC-Ti₃SiC₂, with small amounts of TiC determined by the phase equilibria conditions [18].

Experimental Procedure

Joints are made using a tape cast powder consisting of mixtures of TiC and Si powders, which were 99.99% purity having average diameters less than 45 μ m with a TiC:Si ratio of 3:2. Tapes were about 200 μ m thick and were cut to shape and applied between two Hexaloy SiC coupons cut to a rectangular parallelepiped shape 20mm x 4mm x 2mm in size. Joints were formed by heating the coupon sandwiches in argon to 1673K at 10K/min and holding for 2 hours at 30 MPa applied pressure. These joints were dense and approximately 12 μ m thick. Joints made at lower temperatures and using less pressure were not fully dense and were approximately 100 μ m thick. Binder burnout in air at 600K followed by heating in argon resulted in oxidation of the TiC and Si powders, which retarded the displacement reaction progress and prevented the desired phase formation. No joint strength data were generated yet.

¹ Poster presentation at ICFRM-13, Nice, FR, 2007.

² PNNL is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

Results

Figure 1 shows an optical micrograph of a joint processed at 1673K for 2 hours. The joint is dense and 12 μ m thick, which is in the target range of less than 20 μ m in thickness to minimize joint volume fraction. Figure 2 is a scanning electron micrograph of a region of a joint processed at 1573K that shows the resulting microstructure of the joint as a result of the displacement reaction. The dark needles are SiC and the gray matrix is the Ti₃SiC₂ phase. This is the target microstructure for this work where the SiC needle phase reinforces the Ti₃SiC₂ matrix phase in an interpenetrating manner. Figure 3 shows the entire joint as processed at 1573K and 30 MPa, which illustrates the need to process the joint at higher temperatures to ensure the proper joint density, such as that shown in Figure 1.



Figure 1. Optical micrograph of Ti₃SiC₂+SiC joint between Hexaloy SiC coupons.



Figure 2. Scanning electron micrograph of a region of a Ti_3SiC_2+SiC joint between Hexaloy SiC coupons showing the desired microstructure that develops during the displacement reaction between TiC + Si.



Figure 3. Scanning electron micrograph of a Ti_3SiC_2+SiC joint between Hexaloy SiC coupons processed at 1573K showing the an undesirable amount of joint porosity and thickness exceeding 100 μ m.

Conclusions

Solid-state reaction joining was partially optimized by processing tape cast TiC+Si joints in argon at 1673K and 30 MPa bonding pressure using Hexaloy SiC coupons. Joints with desirable microstructures and thicknesses have been obtained. Further work is underway to refine these parameters, such as reducing the pressure but still retain full joint density.

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COMPATIBILITY OF INTERFACES AND FIBERS FOR SIC-COMPOSITES IN FUSION ENVIRONMENTS¹ – C. H. Henager, Jr. and R. J. Kurtz (Pacific Northwest National Laboratory², Richland, WA 99336, USA)

OBJECTIVE

This work surveys the literature regarding corrosion of SiC and SiC-composites relevant to Fusion Energy systems and applies a crack bridging model based on several known scenarios to suggest future work that will be required to understand the limits of corrosion on these materials.

SUMMARY

The use of SiC composites in fusion environments is predicated on stability under neutron irradiation, on outstanding high-temperature mechanical properties, and on chemical inertness and corrosion resistance. However, SiC is susceptible to many forms of corrosion in water and in water vapor where silica formation is required as a protective layer because silica forms stable hydroxides that are volatile, even at low temperatures. SiC composites have an additional concern that fine-grained fibers and weak interfaces provide the required fracture toughness, but these components may also exhibit susceptibility to corrosion that can compromise material properties. In this work we examine and review the compatibility of fibers and interfaces, as well as the SiC matrix, in proposed fusion environments including first wall, tritium breeding, and blanket modules and module coolants.

PROGRESS AND STATUS

Introduction

SiC is an excellent material for fusion reactor environments, including first wall plasma facing materials and breeder-blanket module materials. It is low-activation, temperature-resistant, and radiation damage tolerant compared to most materials. In the form of woven or braided composites with high-strength SiC fibers it has the requisite mechanical, thermal, and electrical properties to be a useful and versatile material system for fusion applications, especially since microstructural tailoring during processing allows control over the physical properties of interest [1-11]. Chemical and environmental compatibility with fusion and blanket cooling environments appear to be positive [1, 5, 12, 13] but uncertainties remain primarily due to inadequate testing of SiC_f/SiC materials in flowing Pb-Li and due to uncertainty in final composite architecture designs for fusion.

Although SiC is stable up to high use temperatures, there are issues with regard to corrosion resistance and chemical reactivity of SiC that require elaboration for fusion applications. In many respects, the thorough testing of SiC/SiC in high-temperature environments has been disappointing due to the reactivity of SiC with water and water vapor, especially flowing gases. Unfortunately, this has virtually eliminated Si-based ceramics from consideration in combustion and/or engine environments. Fundamentally, Si is too reactive with hydrogen and oxygen and the formation of protective silica scales is lacking in these environments [14-24].

This paper reports on the current status of SiC and SiC-composites for fusion applications from the perspective of SiC corrosion issues in water, water vapor, low-pressure oxygen, and Pb-Li. The

¹ Paper submitted to J. Nuclear Materials, ICFRM-13 Proceedings.

² PNNL is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

inhomogeneous nature of SiC-composites is discussed with regard to corrosion issues of the composite materials and specifically the vulnerability of the high-strength SiC fibers and tailored interphase in the presence of matrix cracks in the SiC matrix [25, 26].

Corrosion of SiC

Research at NASA Lewis Research Center and at Oak Ridge National Laboratory has demonstrated the disruptive nature of water and water vapor on the protective silica film on SiC during high-temperature exposures [14, 16, 18-24, 27]. Figure 1 is a micrograph from the work of Tortorelli and More [22] showing the effects of water vapor on silica film morphology on α -SiC. The work at NASA [14, 18-21, 27] has developed the fundamental understanding of parabolic-linear oxidation of Si-based ceramics in flowing atmospheres containing water vapor. At high temperatures, SiC and Si₃N₄ react with water vapor to form a SiO₂ scale, which also reacts with water vapor to form a volatile Si(OH)₄ species. These simultaneous reactions, one forming SiO₂ and the other removing SiO₂, are described by parabolic-linear kinetics. A steady state, in which these reactions occur at the same rate, is eventually achieved, after which the oxide found on the surface is a constant thickness, and recession of the underlying material occurs at a linear rate. This data has indicated that Si-based ceramics are essentially unsuited for engine environments unless they can be coated with an environmental barrier coating. Although these chemical conditions are not relevant to fusion the lessons to be learned here are very relevant to the blanket module concepts that have SiC-composites in flowing liquid metal coolants, such as Pb-Li.



Figure 1. SiO₂ scales on sintered a-SiC after exposure at 1200°C for 100 h at 10 atm in (a) air 15% H_2O and (b) 100% air. Arrows in (a) denote dense vitreous SiO₂ layer [22].

Recent research to understand the behavior of SiC in high-temperature water for advanced reactor concepts has shown that CVD β -SiC is prone to pitting corrosion at 573K in deoxygenated water [28-30].

Figure 2a is an SEM micrograph of a large pit observed on the surface of CVD SiC after 2000 hours of exposure. Figure 2b is a compilation of the surface chemistry data obtained in the SEM using EDS methods that show the loss of Si that is observed in the pitting process. Similar chemical reactions have been suggested for the dissolution of silica in water, as are proposed for the gas phase, and which has been a topic of scientific study for some time by Tomozawa and co-workers [31-34]. Thus, silica is lost in the form of silicon hydroxides from the surface of the SiC and carbon is comparatively enriched at the surface (Fig. 2b). The average Si content on the surface decreases relative to C but for the pit interiors the Si decrease is much greater.



Figure 2. (a) SEM images of large pit showing complex fractal-like pit morphology and (b) plot of average Si composition in atomic % as a function of time and location on the surface of the CVD SiC. The data points have been shifted slightly along the x-axis (time) for clarity.

Corrosion of SiC-composites

Unfortunately, much less information exists for SiC-composites in fusion reactor conditions, including firstwall applications and tritium breeding blankets. Reasons for this vary but include a lack of standardized material, lack of specifications for the environments, and lack of space in flowing liquid coolant test loops. Optimistically, the good news for SiC-composites is that SiC appears to be compatible with Pb-Li coolants. Pint's research with β -SiC helps establish the compatibility of SiC with Pb-Li coolants below 1373K [1], while studies by Yoneoka et al. [35] and Barbier et al. [36] suggest that SiC-composites also have little interaction with Pb-Li coolants. However, this data is preliminary and only involves static exposures, not flowing. Pint discusses concerns regarding fiber and interphase corrosion and the need for a seal coating [1]. This is also suggested by the work of Barbier where Pb-Li ingress into voids in the SiC-composite was observed [36], which suggests wetting of the SiC by the Pb-Li liquid occurs during exposure.

Even with a seal coating, the conservative approach is to consider a cracked seal coat and Pb-Li ingress to the SiC-composite. We consider the corrosion issues with a SiC_f/SiC composite consisting of a finegrained SiC fiber and a pyrocarbon interphase. Without specific degradation data in Pb-Li environments, a time-dependent bridging model is useful to understand fiber and fiber/matrix interphase degradation. The degradation mechanisms of SiC-fibers are thermal creep cavitation causing stress rupture [37] and irradiation creep, and these processes have been treated in prior studies [38]. For the current study, a static bridging model was developed based on the dynamic model physics [39, 40]. We consider fiber strength reductions and fiber/matrix degradation due to environmental damage in first wall and breeder blanket applications.

The model is first calibrated using single-edge-notched beam (SENB) data for a 5-harness satin weave, 0/90 Type-S fiber, CVI-SiC-composite manufactured by GE Power Systems³, which has a peak load fracture toughness of $K_{Q} = 22.9$ MPa \sqrt{m} at ambient temperature and an ultimate strength in 4-point bending of 750 MPa [41]. Table 1 lists the input parameters and we show that if the fiber fracture strength is assumed to be 2.5 GPa that a good agreement with measured K_{Q} is achieved for an interfacial shear strength value of 15 MPa.

Parameter	Value
SENB width	5.5 mm
SENB notch length	1.0 mm
CVI-SiC modulus	4.6 x 10 ⁵ MPa
Hi-Nicalon Type-S SiC fiber modulus	4.2 x 10 ⁵ MPa
Composite modulus	1.81 x 10⁵ MPa
Bridging fiber volume fraction	0.2
Fiber radius	7 microns
Interfacial shear stress (t)	15 MPa
Fiber fracture strength	2500 MPa

Table 1. Parameters for static and dynamic bridging model

We examine the effect of loss of fiber strength due to an unspecified interaction with a corrosive liquid or gas. The results of this are presented in Figure 3 and show that a loss of fiber strength from 2.5 GPa to 1.85 GPa will reduce the SiC-composite toughness to an unacceptable level. Based on fiber creep data for the Type-S fiber we can calculate the approximate time to reach 1% creep strain at 1073K to be in excess of 5 x 10^5 hours, which drops to about 12,000 at 1173K and only 400 hours at 1273K. This assumes the existence of a bridged crack in the composite under a moderate load. Operation at 800C or 1073K would assure a long lifetime with respect to creep rupture only if no significant fiber degradation due to the fusion environment occurs. Thus, flowing Pb-Li tests on SiC fibers are required to demonstrate that no degradation occurs over thousands of hours.

³ http://www.gepower.com



Figure 3. Parametric plot of SiC-composite fracture toughness as a function of fiber fracture strength. This plot illustrates the decrease in fracture toughness expected due to a loss of fiber strength due to corrosion or environmental degradation.

The second parametric study is an interaction between the environment and the fiber/matrix interphase. This is problematic since the interphase that will be selected is not known so we assume a thin pyrocarbon interphase with an interfacial shear strength of 15 MPa as suggested by the bridging model. We consider interactions between the environment and the interphase that cause an increase in bonding [42-49] and use the static bridging model to calculate fracture toughness due to changes in the interfacial shear strength. Figure 4 shows that if the interfacial shear strength is increased from 15 MPa to above 40 MPa the composite fracture toughness will fall below the acceptable limit of 15 MPa \sqrt{m} . Thus, the fiber/matrix interphase materials must also be unaffected and this may represent the most vulnerable part of the SiC/SiC composite material system. This result suggests that tests in flowing Pb-Li be coordinated with post-test fracture toughness measurements on composite materials.



Figure 4. Composite fracture toughness as a function of interfacial shear strength for debonding, t, showing the loss of toughness due to an increased shear strength such as oxidation embrittlement reactions at the interphase.

The final parametric study involves an area that has been previously address by the dynamic bridging model when oxidation removal of a thin carbon interphase was treated, which is relevant for fusion first wall exposures and low oxygen partial pressures or volatilization reactions in flowing Pb-Li in blanket modules. Interphase removal due to chemical reactions causes a decrease in bridging effectiveness and loss of crack growth resistance. These calculations are performed using the dynamic crack bridging model and allowing the oxidation of the thin pyrocarbon interface to proceed in order to simulate a volatile reaction. These results are shown in Figure 5 and illustrate the large effect of even very small recession rates. A recession rate at the interface of 3×10^{-9} m/s can cause an additional crack extension of 1-mm over one year for a hypothetical bridged crack in SiC/SiC, which may be unacceptable. Such issues will require greater knowledge of component design and operating parameters than is presently available.



Figure 5. Crack extension during 1-year operation due to recession of fiber/matrix interphase, which here is reaction of pyrocarbon with oxygen at 1373K. This parametric plot illustrates the sensitivity of a bridged crack to interphase removal due to volatilization.

Conclusions

The most important conclusion from this overview study of compatibility issues for SiC-composites in fusion environments is that there is a critical lack of data for SiC-composites in flowing Pb-Li environments. Notwithstanding the apparent unreactivity of SiC and SiC/SiC with Pb-Li in static tests, this paper has pointed out the complexity of the SiC/SiC material system with a CVI-matrix, a fine-grained, high-strength fiber, and a weak, debonding fiber/matrix interphase, which raises concerns for the behavior of this system in a potentially corrosive environment. Fortunately, SiC appears to be compatible with Pb-Li but this needs to be verified in flowing environments. The fibers and fibers coated with typical interphase materials also need to be studied in this manner. Finally, SiC/SiC composites need to be exposed in flowing Pb-Li collects within the pores of uncoated SiC/SiC is of some concern at this point but further tests are required. The use of mechanical property modeling, as used here, can guide the experimentation and establish needed confidence levels for the research.

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3.0 FERRITIC/MARTENSITIC STEELS AND ODS STEELS

ON THE ROLE OF ALLOY COMPOSITION AND PROCESSING PARAMETERS IN NANOCLUSTER FORMATION AND DISPERSION STRENGTHENING IN NANOSTRUCTURED FERRITIC ALLOYS -M. J. Alinger and G. R. Odette (University of California Santa Barbara) and D. T. Hoelzer (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this research was to develop an understanding of the role of composition and processing parameters on nanofeature (NF) formation and dispersion strengthening in nanostructured ferritic alloys (NFA).

SUMMARY

An extensive experimental study to characterize the sequence-of-events that lead to the formation of a very high density of Y-Ti-O solute nanoclusters (NFs) in mechanically alloyed (MA), hot isostatically pressed (HIPed) ferritic stainless steels is reported. Yttria and O dissolve in the Fe-14Cr3W(0.4Ti) powders during MA. The dissolved Y and O, and when present Ti, subsequently precipitate during hot consolidation. The number densities and volume fractions of the NF decrease, and their radii increase, with increasing consolidation temperature. The NF form at 850 and 1000°C in both attritor and higher energy SPEX milled alloys containing Y, both with and without Ti additions. SPEX milling produces higher volume fractions of NFs and higher hardness in these cases. The presence of Ti refines the NFs, and both Ti and high milling energy (SPEX versus attritor) are necessary for the formation NFs at the highest consolidation temperatures of 1150°C. Microhardness trends closely mirror the effects of the compositional and processing variables on the NFs. However, the precise structure and composition of the NFs are not well understood. Indeed, their character varies, depending on the alloy composition and processing variables. The NFs appear to range from coherent solute enriched zones, or sub-oxides, to complex oxide phases.

PROGRESS AND STATUS

Introduction

The development of alloy systems for structural applications at elevated temperatures in high-energy neutron environments poses a complex materials challenge. Such alloys must manifest long-term stability of both their microstructure and mechanical properties. Microstructural stability includes the ability to successfully manage high levels of both transmutation product helium and excess vacancies and self-interstitial atom defects, that result from the displacement of atoms from their lattice positions, while also minimizing residual radioactivity. Additionally, advanced alloys must balance fracture toughness at lower temperatures with high creep strength at elevated temperatures. In combination, these requirements present a unique opportunity to use a materials science based approach to alloy design and development.

Pioneering work by Fisher [1] and researchers in the US breeder reactor program [2] in the nineteen eighties showed that mechanical alloying (MA) of Fe-14Cr-Ti-Mo powders with Y_2O_3 , followed by hot consolidation, produces ultra fine, nm-scale precipitates or solute clusters that yield both high static and creep strength, as well as radiation damage resistance. Outstanding research to develop these alloys by Ukai and co-workers in Japan has continued up to the present [3-14].

Ukai et al. first recognized the importance of dissolved Ti in refining the Y_2O_3 precipitates [3], attributing this to reactions leading to the formation of Y_2TiO_5 oxides. Since then, various transmission electron microscopy techniques have been used to characterize NFA microstructures and to identify the Y-Ti-O features, typically at larger sizes of several nm [11, 15-23]. These studies have shown the presence of the pyrochlore complex oxide, $Y_2Ti_2O_7$, as well as Y_2TiO_5 and Y_2O_3 [9,11,17,18,20]. Mechanical property and TEM studies have also shown that the NFAs are resistant to radiation damage and that the Y-Ti-O features are both stable under irradiation and effective in trapping helium [2,22,24-30].

However, recent atom probe tomography (APT) studies [31-36] indicate that the smallest Y-Ti-O features differ from these complex oxides in that: a) their solute Ti plus Y metal to oxygen atom ratio is typically greater than 1; b) they have high to very high Ti to Y ratios up to 3/1, or more; and, in some cases, c) they may also contain considerable quantities of Fe. Small angle neutron scattering (SANS) measurements, which are a major focus of the work reported here, have shown that the nature of the Y-Ti-O features depends on the processing time-temperature history [37,38]. The SANS studies show that magnetic to nuclear scattering ratios and volume fractions of the Y-Ti-O features are also sometimes inconsistent with complex oxides, especially for processing paths with a slow ramp heat up to the nominal consolidation temperature. The APT and SANS results suggest that the smallest Y-Ti-O features may be sub-oxide, or even coherent GP zone-type, transition phases. Given this complexity, we will hereafter refer to the small, 1-3 nm diameter, Y-Ti-O features as nano-clusters (NFs).

Mechanical alloying also produces nanometer scale grain structures and high dislocation densities in the milled powders. The grains grow or recrystallize and the dislocations partially recover during hot consolidation, mainly depending on the processing temperature and the presence or absence NFs [12,19]. Hence, we will refer to these materials as nanostructured ferritic alloys (NFAs), to distinguish them from more conventional oxide dispersion strengthened (ODS) alloys, that generally contain coarser scale incoherent Y_2O_3 particles. The very high creep strength of NFAs has been attributed the presence NFs, although this remains to be fully demonstrated [2,3,9,14,28,39-41].

However, the effects of alloy composition and processing path on the sizes, number densities, volume fraction and basic character of NFs have not been well understood. The objective of this research was to develop a systematic knowledge base to guide processing to tailor microstructures and optimize the mechanical properties for particular applications. Specifically we will address the following two key questions:

- 1. What is the sequence-of-events leading to the formation of NFs?
- 2. What are the compositional and processing variables that control the characteristics of various types of NFs and other nm-scale features?

These questions were addressed by characterizing a set of model alloys, primarily using microhardness and SANS techniques. The model alloy powders were mechanically alloyed by ball milling and, with one exception, consolidated by hot isostatic pressing (HIPing) at temperatures from 850 to 1150°C. Other publications will address the time-temperature kinetics of formation of NFs, their thermal stability and their relation to alloy strength.

Experimental

Alloys

The series of model alloys used in this study represent variants of two commercial vendor NFAs, INCO 14Cr-Y-Mo-Ti-O MA957 and Kobe Steel 12Cr-Y-W-Ti-O, that we refer to as J12WYT. Both alloys contain Y equivalent to ≈ 0.25 to 0.30 wt.% Y₂O₃. These 12-14 wt.% Cr-Ti plus W or Mo alloys lie outside the γ -loop, hence, are classified as ferritic stainless steels, with good corrosion/oxidation resistance deriving from their high Cr content. The specific base model alloy composition used in this study is: 14 wt.% Cr, 3 wt. % W (a low activation replacement for Mo at mass ratio of about 2/1 to give approximately equal atomic fractions), 0.25 wt. % Y₂O₃ (note the Y in the alloy designations below generally refers to a Y₂O₃ source) and 0.4 wt% Ti. We refer to this base alloy composition alloy as U14YWT. The W provides solid solution strengthening, while Y, Ti and O collectively produce dispersion strengthening. Iron and yttrium are essentially immiscible, normally forming an intermetallic Fe₁₇Y₂ phase in dilute Y-Fe alloys. In the presence of dissolved O, Y₂O₃ (yttria) particles might be expected to replace Fe₁₇Y₂, simply based on their respective formation energies. Further, it might also be expected that the addition of Ti would lead to the formation of complex oxides, like Y₂Ti₂O₇ (pyrochlore) [42,43].

Table 1 shows the compositions of the model and commercial vendor alloys [38]. The model alloy matrix includes sequential additions of Ti, Y and O, where the latter two elements were introduced by ball milling elemental or alloyed powders with Y_2O_3 or metallic Y. The sequential solute addition matrix, described

further below, serves two main purposes. First, this approach allows determining the effects of both the individual and combinations of solutes on the hardness of NFAs. Second, the sequence of solute additions provides control alloys for SANS studies to evaluate to effect of a specific alloy modification on the NFs.

	Alloy Element (wt%)						Milling	Consolidation		
Alloy ID	Cr	Ti	W	Y_2O_3	Al	Mo	Y	Technique	Process	Temperature(°C)
MA957	14	1	-	0.30	-	0.3	-		Hot Ext.	1150
J12YWT	12	0.4	3	0.25	-	-	-		Hot Ext.	1150
PM2000	20	0.5	-	0.50	5.5	-	-		Hot Ext.	1150
U14Y	14	-	-	0.25	-	-	-	SPEX	HIP	850, 1000, 1150
U14YT	14	0.4	-	0.25	-	-	-	SPEX	HIP	850, 1000, 1150
U14YW	14	-	3	0.25	-	-	-	SPEX	HIP	850, 1000, 1150
U14YWT	14	0.4	3	0.25	-	-	-	SPEX	HIP	850, 1000, 1150
U14Y(M)T	14	0.4	-	-	-	-	0.2	SPEX	HIP	850, 1000, 1150
U14	14	-	-	-	-	-	-	SPEX	HIP	850, 1000, 1150
U14T	14	0.4	-	-	-	-	-	SPEX	HIP	850, 1000, 1150
U14W	14	-	3	-	-	-	-	SPEX	HIP	850, 1000, 1150
U14WT	14	0.4	3	-	-	-	-	SPEX	HIP	850, 1000, 1150
O14Y	14	-	-	0.25	-	-	-	Attritor	HIP	850, 1000, 1150
O14YT	14	0.4	-	0.25	-	-	-	Attritor	HIP	850, 1000, 1150
O14YWT	14	0.4	3	0.25	-	-	-	Attritor	HIP	850, 1000, 1150
O14YWTX	14	0.4	3	0.25	-	-	-	Attritor	Hot Ext.	850

Table 1 The NFA Compositions (wt%) and Processing Parameters

The individual solute additions include Y, W and Ti. The paired additions include Y plus Ti, W plus Ti and W plus Y; the base alloy contains all three solutes, Y plus W plus Ti. One U14YT alloy, designated Y(M)T, was processed by milling the alloy powder with metallic Y, rather than Y_2O_3 . As discussed below, all of these U-alloys were SPEX milled in small batches at the University of California Santa Barbara (UCSB). Table 1 also shows a series of alloys that were attritor milled at Oak Ridge National Laboratory (ORNL), designated by the letter O, with additions of Y, Y plus Ti and Y plus W plus Ti. Both U- and O-alloy powders were consolidated by HIPing at temperatures 850, 1000 and 1150°C. Finally, one O14YWT alloy, designated as O14YWTX, was extruded, rather than HIPed, at 850°C.

Mechanical Alloying

Iron and yttrium are essentially immiscible. Thus conventional melt processing techniques are not viable for dissolving Y into a Fe rich matrix. Further, even if Y could be dissolved in a Fe matrix, internal oxidation to form dispersed phases would be inhibited by Cr scales and Iow O solubility. Thus, one obvious approach to incorporating Y into Fe-rich matrix is mechanical alloying (MA) by ball milling Fe-rich alloy powders with yttria (Y_2O_3). Ball milling results in severe deformation and fragmentation mixing of fine powders by multiple energetic impacts between much larger hardened balls that are agitated to a significant kinetic energy by a variety of shaking processes. Two Y_2O_3 incorporation paths can be envisioned. In one case, the Y_2O_3 would be taken up in the metal powders as highly refined oxide fragments. The other possibility is that the Y_2O_3 is actually mechanically dissolved in the Fe-rich matrix by the combination of fragmentation and severe deformation. Highly supersaturated metallic solutions can be produced in this fashion [44]. The direct mixing-dissolution mechanism is not as obvious for brittle oxide powders. However, at small sizes, Y_2O_3 fragments might be diced to the atomic scale by a massive number of dislocation intersections. As shown later in this paper, the Y-O dissolution process appears to be dominant in the MA of Y_2O_3 with Fe-Cr-Ti powders. An excellent review of mechanical alloying can be found in Reference 45. Two different methods for mechanical alloying iron-based powders with Y_2O_3 were used in this study: attritor milling (at ORNL) and the SPEX 8000 mixer-milling (at UCSB). The SPEX milling was performed in a stainless steel vial with hardened 0.95 cm diameter steel balls sealed in a dry argon atmosphere using a 10/1 ball to powder weight ratio (BWR). The powders were milled in 10 g batches for 8 h at ambient temperature with forced air-cooling. The attritor milling was also performed in an argon atmosphere in a water-cooled vessel, using ≈ 5 mm diameter steel balls with a 10/1 BWR. In this case the powders were milled for 80 h in 200 g batches. Note all steps involving powder handling were carried out in glove box with a dry Ar atmosphere.

Hot Consolidation

Both hot isostatic pressing (HIPing) and hot extrusion were used to consolidate the MA powders. In the case of HIPing, the powders were loaded in low carbon steel cans that were evacuated to 2.5×10^{-6} Torr and degassed at 300° C for 24 h prior to final weld sealing of a crimped exhaust tube. The various U-alloys in Table 1 were HIPed in 50 to 100 g batches. One HIP can typically contained a stack-up of 3 alloy powders separated by Y_2O_3 discs. The HIPing was performed at 200 MPa for 3h at 850, 1000 and 1150° C. The canned powders were ramped to temperature at 15° C/min and slowly cooled following the 3 h HIP period. The powders consolidated by extrusion were contained in low alloy steel cans and vacuum degassed at 400° C for 2 h. The sealed cans were then rapidly furnace heated to 850° C, thermally equilibrated, extruded through a die with a 7:1 reduction ratio and air-cooled. 2D. Characterization Techniques

In this work, characterization of the microstructural evolution, with emphasis on the NFs, was performed using various techniques, including: atom probe tomography (APT), small angle neutron scattering (SANS) and microhardness measurements. Selected combinations of these techniques were used to assess the effects of alloy composition, mechanical alloying (milling) parameters and consolidation conditions.

Small Angle Neutron Scattering

Small angle neutron scattering (SANS) was used to characterize the NFs. SANS is particularly useful in this case since the nm-scale features scatter neutrons at high angles (q values - see below), in a region that is otherwise dominated by low intensity uniform incoherent scattering [46]. The measurements were carried out on the 8 m SANS instrument (NG1) at the National Institute of Standards and Technology at an average neutron wavelength of $\lambda = 0.5$ nm. As illustrated in Figure1 a strong ≈ 1.7 tesla magnetic field applied in the horizontal direction permitted measurement of both nuclear, $d\Sigma/d\Omega(q)_n$, and magnetic, $d\Sigma/d\Omega(q)_m$, neutron scattering cross sections, where the total scattering cross section $d\Sigma/d\Omega(q,\phi)$ is

$$\frac{d\Sigma}{d\Omega}(q,\phi) = \frac{d\Sigma}{d\Omega}(q)_n + \sin^2\phi \frac{d\Sigma}{d\Omega}(q)_m$$
(1)

Here, ϕ is the angle with respect to the magnetic field direction and q is scattering vector that is related to λ and the scattering angle, 2 θ , as

(2)

$$q = 4\pi \sin\theta/\lambda$$

The number of neutrons scattered at q and ϕ were measured with a 64 by 64 cm position sensitive ³He detector with a pixel size of ≈ 5 mm. By locating the detector 2 m from the specimen and rotating it $\approx 5^{\circ}$ off the beam axis, the maximum q was $\approx 3 \text{ nm}^{-1}$ for ϕ from 0 to 45°; the maximum q decreased to $\approx 2 \text{ nm}^{-1}$ at $\phi = 90^{\circ}$.


Figure 1 Experimental configuration used in the SANS measurements showing the incident beam and specimen in an applied magnetic field producing a 2D scattering pattern on the position sensitive detector.

The d Σ /d Ω (q, ϕ) were determined as follows. The detector counts at a pixel location associated with measurements of background radiation and counts from parasitic neutron scattering were subtracted from the measured total, thus giving the number of neutron counts associated with the sample itself, $I_s(q, \phi)$. The corresponding $I_w(q, \phi)$ for a water standard, with a known d Σ /d Ω (q, ϕ)_w, was also measured. The calibrated d Σ /d Ω (q, ϕ)_s is given by

$$\frac{d\Sigma}{d\Omega}(q,\phi)_{s} = \frac{d\Sigma}{d\Omega}(q,\phi)_{W}\left[\frac{n_{s}}{n_{W}}\right]\frac{t_{s}}{t_{W}}\left[\frac{\phi t_{s}}{\phi t_{W}}\right]\frac{I_{s}(q,\phi)}{I_{W}(q,\phi)}\right]$$
(3)

Here the n, t and ϕ t are the number of atoms, the fraction of neutrons transmitted through the sample and the total fluence of neutrons, for the sample (S) and water standard (W), respectively.

The absolute cross-sections were averaged over specified detector q and ϕ ranges (typically, $\phi = 0\pm 30$, 45 ± 15 and 80 ± 10). The scattering cross sections for the nanometer features associated with the variable of interest, $d\Sigma/d\Omega(q,\phi)_f$, were determined by subtracting a corresponding control cross section, $d\Sigma/d\Omega(q,\phi)_c$. For example, as illustrated in Figure 2, subtracting the $d\Sigma/d\Omega(q,\phi)_c$ for 12WT from the $d\Sigma/d\Omega(q,\phi)_s$ for J12YWT was used to assess the effect of adding Y_2O_3 to an alloy containing W and Ti. The SANS data analysis based on other choices of controls resulted in generally similar conclusions [38].



Figure 2. Illustration of the SANS data analysis procedure that subtracts control $d\Sigma/d\Omega$ data (U12WT1150) from that for specimen (J12YWT) to identify the scattering associated with NFs.

The d Σ /d Ω (q, ϕ)_f is determined by the number density (N), radius (r), volume fraction (f), shape (taken as non-interacting spheres) and scattering length density (ρ) difference between the nm-scale features (ρ_f) and the matrix (ρ_m) they are embedded in, $\Delta \rho = \rho_f - \rho_m$, where $\Delta \rho$ is the scattering contrast factor. For specified features and specified size (r),

$$\frac{d\Sigma}{d\Omega}(q,\phi) = Nf^2 (\Delta \rho)^2 |S(qr)|^2$$
(4)

Here, S(qr) is a small angle scattering form factor that depends on the feature shape [46]. The ρ_f and ρ_{m} , and $\Delta\rho$, differ for nuclear versus magnetic scattering. The nuclear scattering ρ^{nuc} depends on the compositions of the feature and the matrix and their average atomic volumes V, respectively, as

$$\rho^{nuc} = \sum_{i} \frac{b_i X_i}{V} \tag{5}$$

Here b_i is the isotope averaged scattering length for element i, X_i is the atom fraction of that element in the feature or matrix. Thus the matrix and scattering feature compositions and average atomic volumes must be known to determine $\Delta\rho^{nuc}$. The magnetic scattering length density ρ_f^{mag} was taken as 0 for the NFs composed of Ti, Y and O and the ρ_m^{mag} corresponded to the Fe-14Cr composition of the matrix. Thus even if the composition of the scattering feature is not known, the magnetic $\Delta\rho^{mag}$ can be specified with good precision. The assumption that $\rho_f^{mag} = 0$ was tested by measuring the variation of $d\Sigma/d\Omega(q)_{mag}$ with temperature. The observed decrease in $d\Sigma/d\Omega(q)_{mag}$ with increasing temperature could be entirely explained by the corresponding decrease in the saturation magnetization of the Fe-Cr-W matrix, consistent with the hypothesis that $\rho_f^{mag} = 0$.

The d Σ /d Ω (q)_{mag} was determined from the d Σ /d Ω (q, ϕ) data for the entire detector based on a best fit for magnetic to nuclear scattering ratio, M/N = [$\Delta \rho^{\text{mag}}$]²/[$\Delta \rho^{\text{nuc}}$]², as

$$\frac{d\Sigma}{d\Omega}(q)_{mag} = \frac{d\Sigma}{d\Omega}(q,\phi) / \left[N/M + \sin^2(\phi) \right]$$
(6)

Alternatively, the $d\Sigma/d\Omega(\phi)$ data was q and ϕ averaged over a large q range (typically, 0.8 - 1.8 nm⁻¹) for 8 to 10 average $\sin(\phi)^2$ values from \approx 0 to 1. The average $d\Sigma/d\Omega(\phi)$ were then least squares fit to determine the M/N as

$$\frac{d\Sigma}{d\Omega}(\phi) = \frac{d\Sigma}{d\Omega_{nuc}} \left[1 + \frac{M}{N} \sin^2(\phi) \right]$$
(7)

Here, $d\Sigma/d\Omega_{nuc}$ and M/N are the best-fit parameters.

Of course the nm-scale features have a distribution of sizes, r. In this analysis, the distribution was described by a lognormal function, as parameterized by a mode radius, r_m , and a distribution width parameter β [38, 47]. The r_m and β were found by least square fitting Equation 4, modified to account for the lognormal size distribution, to the reduced $d\Sigma/d\Omega(q)_{mag}$ data. Note, the lognormal is used for convenience and due to the fact that it does not admit negative values of r, and the degree to which it is an approximation of the actual distribution is believed to have negligible effects on the results, especially when compared to other sources of uncertainty. The r_m and β are related to the average nm-scale feature r, <r> (actually <r> = {<r³>}^{1/3}) as

$$r = \langle r \rangle = r_m \exp\left(\frac{3\beta^2}{4}\right) \tag{8}$$

Note that r depends on the shape, but not magnitude of $d\Sigma/d\Omega(q)_{mag}$. The corresponding nm-scale feature N and f scale with $d\Sigma/d\Omega(q)_{mag}$ and are given by

$$N = \left(\frac{3}{4\pi}\right)^2 \left[\frac{\exp\left(-9\beta^2\right)}{r_m^6 \rho_{mag}^2}\right] \frac{d\Sigma}{d\Omega_{mag}}(0)$$
(9)

$$f = \left(\frac{3}{4\pi}\right) \left[\frac{\exp\left(-6.75\beta^2\right)}{r_m^3 \rho_{mag}^2}\right] \frac{d\Sigma}{d\Omega_{mag}} (0)$$
(10)

Here, $d\Sigma/d\Omega_{mag}(0)$ is the magnetic scattering at q = 0. Note different combinations of r_m and β can give nearly equivalent fits to the $d\Sigma/d\Omega(q)_{mag}$ data. This covariance has little effect on f and only a modest effect on r, but this has a significantly larger effect on N.

The analysis described above is applicable when there is only one type of scattering feature. However, in some cases it is not possible to fit the $d\Sigma/d\Omega(q)_{mag}$ with a single lognormal distribution, which indicates the presence of multiple scattering features. The presence of multiple features with different sizes is also suggested by a significant q-dependence of the M/N ratio. In such cases, the fitting can be carried out for two features with different r_m , β and M/N parameters.

SANS was also performed on unconsolidated powders. Precisely weighed quantities of milled powders were loaded in pure 1100 Al capsules with thin windows that were sealed with an O-ring in a dry-Ar glove box. The neutron beam was masked to be slightly larger than the capsule powder pocket and slightly smaller than the O-ring diameter. Empty container runs were used to characterize the parasitic scattering from the Al capsules. In the data reported here, the annealed powder data had the same time-temperature history as the HIPed alloys.

The results of the SANS measurements are described below. More detailed description of the SANS data collection, reduction and analysis procedures can be found in Reference 38 and 47.

Microhardness

Diamond pyramid Vickers microhardness measurements (kg/mm²) were performed with a LECO M-400A semi-automated testing instrument. The microhardness values for the consolidated alloys with 0.05 μ m diamond surface finish, at a 1000 g load, were based on the average of a minimum of five indents. Microhardness measurements were also performed on milled powders mounted in bakelite and flat polished to a 0.05 μ m diamond finish. Individual indents were made on the particles that were on the larger end of the powder size distribution. However, the actual dimensions of the mounted, flake shaped powders were not known, and some were rather thin. Thus the load for powder indentations was reduced to 50 g. The powder microhardness measurements that were anomalously low were eliminated, since this is an indication that the particle was too thin to provide an accurate measurement.

Atom Probe Tomography

Atom probe tomography (APT) specimens were prepared by standard electropolishing methods [48]. The APT characterizations was performed at the Oak Ridge National Laboratory (ORNL), with the assistance of Dr. Mike Miller, on the Imago local electrode atom probe (LEAP), as part of the SHaRE program. The measurements were performed at a specimen temperature of 50–60 K, pulse repetition rate of 100 kHz, and a pulse fraction of 20% of the standing voltage. The atom maps were analyzed using Imago and ORNL's in-house software. All NF compositions quoted in this paper are atom fractions.

RESULTS

The results section is divided into three sections. The first describes the characterization of the as-milled powders to determine the key mechanisms occurring during this stage of processing. The second section describes the effects of milling, thermal history and compositional variables on the NFs in consolidated alloys. The NFs formed in base alloy powders annealed with the same time temperature history as the HIP cycle are also compared to the consolidated alloys. The final section describes what is known about the character of the NFs.

Characterization of the As-milled Powders

The hardness of several as-milled powders (designated by a P, such as U14YWTP) are shown in Figure 3 along with that for the unmilled 14Cr powders. The error bars represent one standard deviation measures of the data scatter. The severe deformation imparted by mechanical alloying results in high hardness for both milling techniques and all alloy compositions. The high strength is associated with both small crystallite sizes (e.g., \approx 20 to 24 nm in U14YTP and U14YWTP, respectively) and high lattice strains (e.g., 0.48 to 0.64% in 14YTP and P14YWTP, respectively) as measured with X-ray diffraction (XRD) methods [38,49]. The SPEX milled powders were \approx 20% harder than the attritor milled powders, consistent with the higher energy of former milling method that leads to the larger lattice strains and smaller crystallite sizes [38]. The addition of Ti to U14YP (U14YTP) powders results in a small increase in hardness but there is little additional effect of the addition of W (U14YWTP). Notably the SPEX milled powders containing both Y and Ti reach remarkable hardness levels of \approx 1000 kg/mm², which is roughly equivalent to a uniaxial flow stress of 3000 MPa.

No oxides were observed in the as-milled powders by XRD [38]. This is consistent with the SANS data in Figure 4, showing $d\Sigma/d\Omega$ versus q² plots at 45° to the applied magnetic field. The 45° curves are presented because they have the highest q range, and include both the nuclear and about 50% of the magnetic scattering contributions. Scattering curves for the unmilled 14WT and the U14YWT alloy HIPed at 850°C are compared to those for the various as-milled powders. Figure 4a shows 45° scattering curves for milled U14YWTP (filled circles), O14YWTP (filled diamonds) and U14WTP (filled triangles) powders. Figure 4b shows the corresponding as-milled powder scattering curves for U14YTP (filled squares), U14Y(M)TP (filled inverted triangle), U14YP (filled right triangle), U14WTP (filled triangles). The scattering curves for all the as-milled powders are similar, and are somewhat higher than those for the un-milled U14WT (open triangles) and U14 powders (not shown). The milling induced scattering may be due to solutes, including O introduced during milling and very small sub-nm solute clusters, as well as contributions from the high dislocation density and small grain sizes. The increase in scattering at lower q

in the U14YTP may indicate the presence of low number density of larger scattering features, perhaps as the result of incomplete dissolution of Y_2O_3 , incorporation of Cr_2O_3 oxide scales during milling, or additional oxidation of the powders prior to SANS. Note some of the differences in the magnitudes of the as-milled scattering curves may also be due to uncertainties in the mass of the powder actually probed by the neutron beam.



Figure 3. Hardness of the SPEX and attritor as-milled powders showing the effects of the additions of Y, Ti and Y, Ti, W.



Figure 4. SANS scattering curves at 45° for unmilled 14WT powders and the U14YWT alloy HIPed at 850°C compared to the corresponding scattering curves for the various as-milled powders.

Irrespective of the small differences, however, analysis of these results show the extra scattering at higher q after milling is from very small features with sizes equivalent to radii of ≈ 0.5 nm or less. In stark contrast, the scattering curve for the U14YWT HIPed at 850°C (unfilled circles) shows a high number density of nm-scale precipitates formed during hot consolidation, as indicated by the large bulge in the $d\Sigma/d\Omega$ curve between $q^2 \approx 1$ and 6 nm⁻². Thus the SANS data suggest that most of the Y, Ti and O are dissolved into the Fe-14Cr alloy matrix during both SPEX and attritor ball milling, forming highly

supersaturated solid solutions, along with some very small sub nm solute clusters or Y-O and/or Ti-O complexes. The major corollary conclusion from the milling study is that the NFs form during hot consolidation and or powder annealing. The detailed kinetics of precipitation will be discussed in detail in a future publication.

The effect of annealing on the hardness of the powders is shown in Figure 5 for 1 h anneals in 75°C increments between 850 and 1150°C for the SPEX milled powders and in 150°C increments for the attritor milled powders. Annealing involved increasing the temperature at a rate of 15°C/min (equivalent to the HIP ramp), holding at the designated temperature for 1 h, and air-cooling. The Figure 5a shows that the SPEX milled U14P hardness recovers completely after annealing at 850°C. The recovery in the U14YTP and U14YWTP powders increases with increasing annealing temperature. However, the residual hardening in the powders with both with Y and Ti is still significant after the 1150°C anneal. Both the pre and post milling hardness is lower in the U14YWP powder, with Y but not Ti. Figure 5b shows the corresponding results for the attritor milled powders. The general annealing trends are similar, but the overall hardness is lower in the attritor milled powders.



Figure 5. Hardness as a function of 1 h annealing at temperature from 850 to 1150°C for: a) SPEX and b) attritor milled powders.

The effect of 1150°C HIPing of un-milled versus SPEX milled 14Cr powders on SANS 45° scattering curves is shown in Figure 6. The scattering at low q is increased slightly by the milling. Again, this is probably due to oxidation and impurity pickup during milling, possibly leading to a limited amount of internal Cr oxidation, or incorporation of oxide layers in the milled powders.

Powder Consolidation

The consolidation path has a very important influence on the as-processed microstructure. The most obvious difference between the two consolidation techniques used in this study is that hot extrusion produces anisotropic elongated and textured grains, while HIPing produces more equiaxed microstructures. However, there are also variations in the time-temperature history and mechanical deformation that may also influence the NFs, as well as the dislocation and grain structures in the two cases, even at the same nominal consolidation temperature. Thus, the effects of the two milling and two consolidation methods were compared for MA 14YWT. In addition to the UCSB and ORNL model alloys, two NFAs produced by commercial vendors, INCO MA957 and Kobe Steel J12YWT, were also characterized.



Figure 6. SANS 45° scattering curves showing the small effect of milling on the 45° scattering curves for U14(Cr) alloys HIPed at 1150°C.

Figure 7 shows the effect of HIP consolidation temperature on the nm-scale precipitates in the baseline model alloy, U14YWT, including the NF size (r), number density (N), volume fraction (f), as well as the alloy microhardness (H). As expected, the NF N and f decrease, while the corresponding r increases, with increasing HIPing temperature. The NF parameter ranges for HIPing at 850 to 1150°C were $r \approx 1.2$ to 1.7 nm, f ≈ 2.2 to 0.6% and N ≈ 2.6 to 0.3×10^{24} /m³. In the case of the alloy HIPed at 1150°C, it was necessary to fit r, f, N and M/N parameters for both a small NFs (r ≈ 1.7 nm) and a much larger, nominally an oxide type feature, with r ≈ 11.4 nm. Because the larger features are near the limits of resolution for the SANS configuration used in this study, they are not discussed further; hence, our primary focus is on the NFs. Note, the larger precipitates, that were also observed for several other alloy conditions, are better characterized by TEM [19]. Figure 7 also shows that the hardness of U14YWT decreases from 635 to 344 kg/mm² with increasing HIPing temperature from 850 to 1150°C



Figure 7. SANS r, f, N and H data showing the effect of HIP consolidation temperatures of 850, 1000 and 1150°C on the UCSB base alloy U14YWT.

Figure 8 compares the r, f and N of the NFs in the HIPed U14YWT with those that form in annealed U14YWTP powders subject to the same ramped time temperature history. Clearly, the NFs are similar in the two cases, indicating that the deformation that occurs during HIPing has little effect on the Y-Ti-O clustering-precipitation process.



Figure 8. SANS r, f, N and H data showing that the NFs formed in HIPed alloys and annealed powders are very similar.

Figure 9 shows a 3-dimensional APT map for U14YWT HIPed at 1150°C with a grain boundary at the center of the map that is slightly enriched in Cr and W, as shown in Figure 9b and c, along with trace amounts of impurity C and N as shown in Figure 9d and e. However, there is no evidence of carbide/nitride formation, or of the presence of any other second phases, like Fe₂W-Laves, Cr rich α ' or σ -phases, or Fe₁₇Y₂. Further, there was no evidence of the presence of dissolved, or finely precipitated, Ar milling gas in the APT data. As shown in Figure 9f to j, the Y, Ti and O do not segregate to the grain boundaries; instead, these elements either remain dissolved, or are associated with the NFs. Figure10 shows the average composition of the NFs in U14YWT HIPed at 1000°C is ≈ 0.17 Y, 0.28 Ti, 0.33 O and 0.22 Fe, Cr and W. The composition of the NFs found in U14YWT HIPed at 1000 and 1150°C is very similar in to those previously observed by Miller in both MA957 and J12YWT [33-35]. However, unlike the commercial vendor alloys, the NFs in U14YWT and other model alloys were not homogeneously distributed. The heterogeneous distributions of NFs found in this study are similar to those found in other model alloys analyzed by Miller [36]. Section 3D provides a more detailed discussion of the Composition and character of the NFs.

The SANS results for attritor milled O14YWT powders, both HIPed and hot extruded at 850°C, are shown in Figure 11. The hot extruded alloy has a somewhat larger NF f and N compared to the HIPed alloy. However, the latter is slightly harder. Hot extrusion results in more deformation than HIPing, and produces texture and grains that are elongated in the extrusion direction. As shown in Figure 12, the SPEX milled powders HIPed at 850 and 1000°C contain a higher N and f of similarly sized (r) NFs compared to the attritor milled alloys. However, no NFs are observed in the attritor milled alloy HIPed at 1150°C. In contrast, the SPEX milled alloy HIPed at 1150°C contains NFs (as well as some coarser oxides), but with lower f and N and larger r than for HIPing at lower temperatures. It should be noted these differences are not intrinsic to the mechanical alloying method, since, subsequent to these measurements, NFs were observed in more recent batches of attritor milled powders HIPed at 1150°C.



Figure 9. Atom probe tomography (APT) atom maps for U14YWT1150.



Figure 10. The average precipitate composition in U14YWT HIPed at 1000°C as determined by APT.



Figure 11. SANS r, f, N and H data showing the effect of HIP versus hot extrusion consolidation at 850°C for O14YWT. The results for U14YWT are also shown for comparison.



Figure 12. SANS r, f, N and H data showing the effect of SPEX versus attritor milling at a) 850, b) 1000, and c) 1150°C.

The critical effects of alloy composition in SPEX milled alloys are shown in Figure 13a for HIPing at 850°C and in Figure 13b for HIPing at 1150°C. All the alloys contain Y. Two other alloys add either W or Ti and a third contains both W and Ti. In the case of HIPing at 850°C, all of the alloys contain NFs with similar r, but with f and N that increase somewhat with the addition of Ti. The hardness is also significantly higher

in the alloys with Ti, and is also larger in the alloys with W, especially the one with Y and Ti. In the case of HIPing at 1150°C, NFs do not form in alloys without Ti. Rather, the Y-bearing alloys without Ti, contain a significant volume fraction of much larger features. Increase in hardness with the addition of Ti of the alloys HIPed at 1150°C is less than for HIPing at 850°C, and adding W appears to lead to a small degree of softening in this case. These results are generally consistent with previous TEM and APT results reported by showing a larger number of smaller NFs in Ti bearing alloys processed at 1150°C [2,19, 33]. As discussed elsewhere the relationship of N, r and f to the alloy hardness is consistent with accepted models of dispersed barrier strengthening [38]. Thus, both Y and Ti are necessary for the formation of NFs at higher consolidation temperatures.



Figure 13. SANS r, f, N and H data showing the effect of alloy chemistry for alloys HIPed at 850°C (a) and 1150° C (b).

Figure 14 shows the effect of SPEX milling U14T powders with metallic Y (U14Y(M)T) versus Y_2O_3 oxide powders (U14YT) followed by HIPing at 850°C. The similarity of the r, N and f in the two cases indicates that the intentional addition of oxygen is not essential to the formation of the NFs, at least at this lower consolidation temperature. This is likely due to oxygen pick-up during MA.



Figure 14. SANS r, f, N and H data showing the minimal effect of milling with yttrium metal (Y) versus yttria (Y_2O_3) on r, N, f.

Figure 15 compares the NFs in U14YWT HIPed at 1150°C to those found in commercial vendor alloys MA957, J12YWT (reported to be hot extruded at 1150°C). SANS controls for these NFAs were fabricated by SPEX milling and 1150°C HIP consolidation of Y-free powders with otherwise similar compositions to the vendor alloys. Note SANS measurements were also carried out for PM2000 but NFs were not found in this case (not shown). However, the r, f and N in the UCSB base model alloy U14YWT are similar to those in MA957 and J12YWT.



Figure 15. SANS r, f, N and H data comparing U14YWT1150, MA957 and 12YWT.

The SANS results on J12WYT can be compared to APT data on the same alloy reported by Miller [33,35]. The nominal average APT radius is slightly larger than the corresponding r from SANS and the NF number density is substantially higher than the N from SANS. However, the small differences in the radius are likely due to the local APT magnification effect, and the APT technique samples a much smaller volume of material than SANS, hence, may not account for spatial fluctuations in the NF number densities. Miller reports that he typically uses data from the regions that are richest in the features being probed [50]. Indeed, using the nominal radius and local number density from the APT data would produce a nominal volume fraction of NFs that is far too high to be physical. Thus, the overall agreement between the two techniques is reasonable.

However, there is one significant difference between the HIPed model and the commercial vendor alloys that is not shown in Figure 15. That is, the magnetic to nuclear scattering ratios (M/N) are \approx 1.2 for MA957 and 0.9 for J12YWT, are much lower than the M/N > 2 for U14YWT. The significance of this observation is briefly discussed in Section 3D below, and will be addressed in more detail in future publications.

The results in Sections 3A and 3B can be summarized as follows:

1. MA dissolves Y and O in the Fe alloy powder matrix.

2. The dissolved Y, O and, when present Ti, precipitate during hot consolidation in the form of NFs and larger oxide phases, depending on the alloy composition and processing time-temperature history.

3. The NF f and N decrease and their size (r) increases with increasing HIPing temperature.

4. Hot extrusion versus HIPing at 850°C has a modest effect on the NFs.

5. NFs form in alloys containing Y and Y plus Ti HIPed at 850 and 1000°C.

6. Ti is necessary to form NFs during HIPing at 1150°C.

7. NFs form in SPEX milled, but not attritor milled, alloys containing Y and Ti during HIPing at 1150°C; however, this is not the case for more recent batches of attritor milled powders, also HIPed at 1150°C.

8. Milling with metallic Y produces similar NFs in powders milled with Y₂O₃ during HIPing at 850°C.

9. The NF f, N and r in the baseline U14YWT alloy HIPed at 1150°C are similar to those in the commercial vendor MA957 and JY12YWT alloys that were hot extruded at the same temperature.

The microhardness data on the various alloys in the preceding sections is of direct interest as a metric of strength, and also reflects the underlying micro/nano-structural variations. Figure 16 summarizes the microhardness data trends for various alloys and processing conditions. The addition of Ti or W alone, or in combination, does not have a large systematic effect on hardness. The addition of Y does increase hardness, but the alloys with the highest hardness contain both Ti and Y. There is also a systematic effect of higher hardness for SPEX milled powder alloys compared to those consolidated from attritor milled powders. Finally, as expected, the hardness in alloys with Y and Y plus Ti, decreases with increasing consolidation temperature. These observations are consistent with the conclusion that, while they are not the only source of hardening relative to the control alloys, NFs are necessary for significant strengthening, at least low test temperatures. The quantitative relation between the NFs and microhardness will be presented in a future publication.



Figure 16. Summary of the hardness trends for a) alloys consolidated at 850°C, b) 1000°C, c) 1150°C and d) commercial vendor alloys.

The Composition and Character of the NFs

The results of the systematic SANS measurements show that the NF form by clustering and precipitation of Ti, Y and O from solid solution. As expected, the number densities and volume fractions of the NFs decrease and their radii increase with higher HIPing temperatures. However, we have not yet addressed the nature of the NFs. Information on the composition of the NFs is contained in the SANS magnetic to nuclear scattering ratio, M/N, which is given by

$M/N = (\rho_f^{nuc} - \rho_m^{nuc})^2 / (\Delta \rho_m^{mag})^2$	(11a)
$ \rho_{\rm f}^{\rm nuc} = \Sigma_{\rm i} X_{\rm if} b_{\rm i}^{\rm nuc} / V_{\rm f} $	(11b)
$\rho_{m}^{nuc} = \Sigma_{i} X_{im} b_{i}^{nuc} / V_{m}$	(11c)
$\rho_{\rm m}^{\rm mag} = b_{\rm m}^{\rm mag} / V_{\rm m}$	(11d)

Here, the ρ^{nuc} are the average nuclear scattering length densities, the b_i^{nuc} are the isotope averaged nuclear scattering length of the element i, the X_i are the atom fractions of element i, the V are the average atomic volumes in the NFs (f) and matrix (m), respectively. The ρ_m^{mag} is the magnetic scattering length density of the Fe-14Cr-3W matrix, which was taken as 0.82 times that for unalloyed Fe at 23°C. Thus, the M/N depends on the composition of the NFs.

The nominal M/N for the common complex Y-Ti oxides are shown in Table 2, along with the measured values for NFs in U14YWT and the commercial vendor alloys J12YWT and MA957. The corresponding maximum volume fractions of the oxides, f_{max} , are limited by mass balances, and can be estimated assuming all the Y is precipitated as

$$f_{max} = X_{vf}(V_f/V_m)$$

(12)

The f_{max} for the common complex oxides are also show in Table 2 along with the measured values.

Table 2 Computed and Measured NF M/N Ratios and Volume Fractions or Maximum Computed	Volume
Fractions	

Oxide/Alloy	M/N	f or f_{max} (%)
Y ₂ TiO ₅	1.60	0.57
YTiO ₃	2.14	0.61
$Y_2Ti_2O_7$	1.04	0.87
U14YWT-850	2.50	2.18
U14YWT-1000	2.30	1.31
U14YWT-1150	2.10	0.65
J12WYT	0.90	0.69
MA957	1.20	0.65

The SANS data for both the J12YWT and MA957 are reasonably consistent with a $Y_2Ti_2O_7$ pyrochlore complex oxide phase. The corresponding SANS data for U14YWT HIPed at 1150°C is consistent with the YTiO₃ complex oxide. However, the volume fractions of the U14YWT alloys HIPed at 850 and 1000°C are too high to be explained by the presence of these oxide phases alone, and the M/N are somewhat higher than for the oxides shown in Table 2, especially at 850°C. The combination of high f and M/N suggest that the NFs may contain Fe.

Note, that the high f and M/N in the HIPed versus the extruded alloys are associated with differences in the temperature cycle experienced in powder consolidation in the two cases. In the case of HIPing, the powders were slowly heated to the consolidation temperature over a period of about 1 h, thereby allowing precipitation to occur at lower temperatures. In contrast the MA957 and J12YWT extrusions were rapidly heated to 1150°C, thus they experience less low temperature precipitation. This conclusion was confirmed by SANS studies of powders that were heat-treated both with ramp anneals that simulated the HIP cycle, and fast anneals that were closer to the temperature cycle experienced by the extruded alloys. The f = 0.44% and M/N = 0.94 for fast annealing of the U14YWTP powder at 1100°C are consistent with SANS data for J12YWT. The results of the powder annealing T-t precipitation kinetics study will be reported elsewhere.

The amount of Fe that rationalizes the high M/N and f_{max} can be estimated assuming a nominal value for V_f/V_m , that all the Y is in the NFs with a specified metal to oxygen atom ratio, M/O. Taking $V_f/V_m = 1$ and M/O = 2.5 (typical of that found in APT - see below) yields Fe contents of 0.36, 0.31 and 0.25 for U14YWT HIPed at 850, 1000 and 1150°C, respectively. The corresponding fractions of Y are 0.06, 0.1 and 0.16, resulting in Ti/Y ratios of 3, 1.9 and 1.25 at 850, 1000 and 1150°C, respectively. Of course other compositions derive from different assumptions about V_f/V_m and M/O.

In principle, the NF compositions can be precisely measured by APT. A fractional composition of ≈ 0.18 Y, 0.27 Ti, 0.33 O and 0.22 Fe and Cr was observed in the U14WYT HIPed at 1000°C. Note, the metal to oxygen atom ratio (M/O) of ≈ 2 and the Y plus Ti solute (S) to oxygen atom ratio (S/O) of ≈ 1.36 are inconsistent with any known oxide phase. Assuming V_f/V_m = 1, the maximum volume fraction for this composition is f_{max} = 0.69%. This is less than measured by SANS (1.31%). The corresponding calculated M/N ratio is ≈ 1.34 is also much less that the measured value of 2.3.

Miller et al have carried out APT measurements on MA957 and J12YWT that were extruded at 1150°C [33-36], as well as a MA Fe-14Cr-3W-0.4Ti-0.25Y₂0₃ (O14YWT) extruded at 850°C [35]. The fractional compositions of the NFs in these alloys are summarized in Table 3. The calculated M/O, S/O, Ti/Y from the APT measurements are summarized in Table 4, which also shows the corresponding M/N and f_{max} assuming V_f/V_m = 1 and that f_{max} is limited by the total amount of Y, and the cases for NF with very low Y content, Ti as well.

Alloy	Y	Ti	0	Fe + Cr	Ref
U14YWT*	0.17	0.28	0.33	0.22	this work
MA957	0.15	0.33	0.40	0.12	XX
J12YWT	0.09	0.20	0.24	0.47	XX
J12YWT	0.08	0.42	0.40	0.10	XX
J12YWT	0.06	0.39	0.42	0.13	XX
O14YWT**	0.06	0.42	0.46	0.06	XX
Aver.	0.10	0.34	0.37	0.19	-
Aver. W/o Fe	0.13	0.42	0.45	-	-

Table 3 Summary of NF Fractional Compositions Derived From APT

* HIPed at 1000°C; ** Extruded at 850°C

Alloy	M/O	S/O	Ti/Y	M/N	f_c
U14YWT*	2.00	1.36	1.50	1.34	0.69
MA957	1.50	1.21	2.20	0.87	0.81
J12YWT	3.17	1.21	2.20	2.30	1.25
J12YWT	1.24	1.14	5.25	0.55	1.20
J12YWT	1.38	1.07	6.50	0.53	1.20
O14YWT**	2.17	2.00	6.70	0.56	1.20

Table 4 Calculated M/N Based on APT Compositions, Metal to Oxygen, Solute to Oxygen, Titanium to Yttrium Ratios and Measured and Estimated Maximum Volume Fractions

* HIPed at 1000°C; ** Extruded at 850°C

Taken at face value, the APT M/O and S/O ratios suggest that the NFs are not a known complex oxide phase. The APT composition based calculated M/N for MA957, and the more recent data on J12YWT, are also lower than those measured by SANS. However, decreasing the APT M/O ratio closer to a stiochiometric value of less than 1 and increasing either the atomic density or Fe content of the NFs, increases the M/N ratio closer to the measure values. Indeed, modest combinations of these adjustments provide reasonable consistency between the APT and SANS results for the commercial vendor alloys. Note, that precise APT measurement of the dominant matrix element (Fe) content of nm-scale features is difficult, since this depends on the interface structure and how the cluster boundary is located in the APT data analysis. While the APT S/O and Ti/Y ratios should be reliable, if present, oxides are non-conducting phases and variations in the field emission processes may perturb the measured atomic ratios. Further, the interpretation of M/N ratios from SANS studies is complicated by a number of factors, including the assumptions made in defining a control alloy (e.g., 14WT for 14YWT).

Transmission electron microscopy (TEM) studies have shown the presence of nm-scale features down to about 2 nm diameter or smaller [2,3,9,11,21-23]. The association of these imaged features with Y-Ti-O enriched and Fe depleted regions has been confirmed by energy filtered TEM (EFTEM) [22]. While EFTEM resolution limits are as low as 1 nm for very thin foils, but typically \approx 2-3 nm, and interpretation of the TEM results has been complicated by specimen preparation challenges, like artifacts produced by ion milling and FIBing, as well as surface deposits formed during electropolishing. Notably, TEM studies of somewhat larger NF (> 5 - 7 nm) in alloys similar to those studied in this work have confirmed the presence of Y₂Ti₂O₇ pyrochlore and Y₂TiO₅ oxides [3,9,11,18,20].

Thus additional work will be needed to clarify the nature and composition of the NFs over a range of sizes, using a variety on advanced high-resolution microanalytical tools. However the current state of understanding of the character of the NFs can be summarized as follows.

1. SANS data for extruded alloys (and fast annealed powders described in detail elsewhere) are consistent with the formation of nm-scale complex oxides like Y_2TiO_3 and $Y_2Ti_2O_7$. These are also likely candidates for the small NFs found in TEM studies, although this will require further confirmation. At larger sizes, TEM studies have clearly identified the presence of complex oxides.

2. Taken at face value, the M/O and S/O ratios that are greater than 1 found in APT studies are not consistent with known complex oxides. Further, the corresponding Ti/Y ratios are much larger than expected for any oxide phase. These NFs may be non-equilibrium sub-oxide transition phases.

3. NFAs that are produced by HIPing, with a slow heat up period, contain larger volume fractions of NFs at lower nominal consolidation temperatures and generally have higher M/N ratios than alloys that are rapidly heated. This is tentatively attributed to a significant Fe content in the NF (25 to 35%) that may be due to precipitation at lower temperatures during heat up. These NFs may also be non-equilibrium sub-oxide transition phases, or even coherent solute enriched zones.

4. Resolution of the character and composition of various NFs will require additional research.

Concluding Remarks

This study provided significant insight on the sequence of events leading to the formation of NFs in MA, hot consolidated ferritic stainless steels. Yttria is dissolved in the metallic powders during MA. The dissolved Y and O, and when present Ti, precipitate during hot consolidation. The N and f of NFs decrease, and their r increase, with higher consolidation temperatures. At 850 and 1000°C, the NFs form in both attritor and SPEX milled alloys with Y, both with and without Ti additions. SPEX milling produces higher volume fractions of NFs and higher hardness in these cases. The presence of Ti refines the NFs, and both Ti and Y as well as high milling energy are necessary for the formation NFs at the highest consolidation temperatures of 1150°C. The microhardness of the consolidated alloys also track the effects of the compositional and processing variables on the NFs. However, the precise structures and compositions of the NFs are still not well understood. The varied character of the NFs appear to range from coherent solute enriched zones, or sub-oxide particles, to complex oxide phases.

Acknowledgements

The research carried out in our work was built on the pioneering contributions of J. Fisher (INCO), the inventor of MA NFAs, as well as that of both Dr. M. Hamilton (PNNL) and her co-workers in the US Breeder Reactor Materials Program and Professor S. Ukai (currently at Hokkaido University) and his collaborators in Japan. The authors gratefully acknowledge Doug Klingensmith (UCSB) for his contributions to the SANS measurements, Professor Brian Wirth (UC Berkeley) for his help in analysis of the SANS data and both Dr. Mike Miller and Kaye Russell for their guidance the APT studies. We acknowledge the support of the National Institute of Standards and Technology, US Department of Commerce, Center for Neutron Research in providing the SANS facilities used in this work. Research at the Oak Ridge National Laboratory SHaRE User Center was sponsored by the Division of Materials Sciences, U.S. Department of Energy (DOE), under contract DE-AC05-000R22725 with UT-Battelle, LLC. The overall research effort at UCSB was supported by DOE Office of Fusion Energy Science (Grant # DE-FG03-94ER54275) and the I-NERI DOE Office of Nuclear Energy through a subcontract with ORNL (Grant # 400014112).

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Embrittlement of Irradiated F82H in the Absence of Irradiation Hardening—R. L. Klueh (Oak Ridge National Laboratory), K. Shiba (Japan Atomic Energy Agency), and M. A. Sokolov (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this work is to develop an understanding of the effect of irradiation on microstructure and mechanical properties of ferritic/martensitic steels for fusion applications and to use that knowledge to develop steels with improved properties.

SUMMARY

Neutron irradiation of 7-12% Cr ferritic/martensitic steels below 425–450°C produces microstructural defects and precipitation that cause an increase in yield stress. This irradiation hardening causes embrittlement, which is observed in a Charpy impact or fracture toughness test as an increase in the ductile-brittle transition temperature. Based on observations that show little change in strength in steels irradiated above 425–450°C, the general conclusion has been that no embrittlement occurs above these temperatures. In a recent study of F82H steel, significant embrittlement was observed after irradiation at 500°C. This embrittlement is apparently due to irradiation-accelerated Laves-phase precipitation. Observations of the embrittlement in the absence of hardening has been examined and analyzed with thermal-aging studies and computational thermodynamics calculations to illuminate and understand the effect.

PROGRESS AND STATUS

Introduction

The effects of neutron irradiation on the mechanical properties of commercial and reduced-activation ferritic/martensitic steels have been studied extensively [1-9]. Below 425–450°C, irradiation damage hardens the steels, causing an increase in yield stress and ultimate tensile strength and a decrease in ductility [1-5]. Irradiation hardening affects toughness, and the effect is observed qualitatively in a Charpy impact test as an increase in the ductile-brittle transition temperature (DBTT) and a decrease in upper-shelf energy (USE) [6-11]. The magnitude of the shift varies inversely with irradiation temperature, similar to the variation in hardening.

For irradiation above 425–450°C, the tensile properties are generally unchanged, although there may be enhanced softening over that caused by thermal aging alone, depending on fluence and temperature [3-5]. In this paper, embrittlement of F82H at irradiation temperatures above the hardening regime will be examined and discussed.

Experimental

The reduced-activation steel F82H (nominally Fe-7.5Cr-2.0W-0.15V-0.02Ta-0.09C) was irradiated in the High Flux Isotope Reactor (HFIR) in the normalized-and-tempered condition [12,13]. Normalization involved austenitizing at 1050°C to transform the steel to austenite, after which it was air cooled to form 100% martensite. Tempering was at 750°C for 1 h.

One-third-size pre-cracked Charpy (PCVN), Charpy V-notch (CVN), and 0.18T disk-compact fracturetoughness [DC(T)] specimens were irradiated in HFIR to \approx 3-5 and 20 dpa at 300 to 500°C [12,13]. The PCVN, CVN, and DC(T) specimens were tested to determine the transition temperature before and after irradiation. Tensile specimens were irradiated to 4.7 dpa and 20 dpa at 300 and 500°C and tested at -100°C, room temperature, and at the irradiation temperature [12].

Results

A large increase in yield stress was observed after irradiation at 300°C to 4.7 and 20 dpa, with most of the change occurring for the 4.7 dpa irradiation [12,13]. There was only a slight further increase after 20 dpa [Fig. 1(a)]. Irradiation at 500°C to 4.8 and 20 dpa had no effect on yield stress [12].



Figure 1. The (a) transition temperature as a function of irradiation temperature and (b) yield stress as a function of test temperature for F82H irradiated in HFIR in the range 250-500°C [13]

Fracture toughness transition temperature shifts were evaluated with the master curve methodology [12], and the shifts showed a pronounced effect of irradiation temperature [Fig. 1(b)]. The greatest effect occurred for the lowest temperature irradiations, with the shift decreasing with increasing temperature. Unexpectedly, there was a shift of 33°C for the 5 dpa CVN specimen irradiated at 500°C, and this was corroborated by a 38°C shift for the 20 dpa CVN specimen [13].

Analysis

Based on thermal-aging observations of F82H discussed below, it is postulated that the increase in transition temperature in the absence of irradiation hardening can be traced to irradiation-accelerated Laves-phase [(Fe,Cr)₂W] precipitation. For normalized-and-tempered F82H tempered at 750°C, the major precipitate is chromium-rich $M_{23}C_6$ with a small amount of MX, where M is vanadium and tantalum rich, and X is carbon and nitrogen. Calculations with the computational thermodynamics program JMatPro [14] predicted 1.9 wt % $M_{23}C_6$ and 0.06 wt % MX form during tempering at 750°C, with little change as temperature is decreased. Laves phase is predicted to be stable below ~650°C. The calculations indicate an abrupt cutoff temperature for Laves: at ~640°C, where 1.22% Laves is predicted, after which it drops to zero by ~650°C. However, M_6C is predicted to form below 756°C and increase to 1.15% at 650°C, where it then drops abruptly to zero at 639°C. Calculated amounts of Laves, $M_{23}C_6$, M_6C , and MX present at 400-800°C are shown in Fig. 2.

Shiba thermally aged tensile and Charpy specimens of F82H for 1000, 3000, 10000, and 30000 h at 400 (aged 30000 h only), 500, 550, 600, and 650°C. Although aging caused a reduction in room-temperature strength that was quite large at the highest aging temperatures and longest times [Fig. 3(a)], there was an adverse effect on impact properties [Fig. 3(b)] [15,16]. The largest strength decreases occurred at 600 and 650°C; at 650°C, a 33% decrease occurred after 30000 h.



Figure 2. Equilibrium amounts of M₂₃C₆, Laves phase, M₆C, and MX precipitates calculated to form in F82H steel at 400–800°C. Calculations were made with the computational thermodynamics program JMatPro.



Figure 3. The (a) yield stress and (b) ductile-brittle-transition temperature as a function of aging time at 500, 550, 600, and 650°C [15,16].

Despite the large decrease in strength after aging at 650°C, the largest increase in Charpy DBTT (105°C) also occurred at this temperature after 30000 h. The DBTT also increased at the other temperatures, with the magnitude of the increase decreasing with decreasing aging temperature. The change was relatively small at 400 and 500°C, even after 30000 h.

Extracted precipitates from normalized-and-tempered and thermally aged specimens were analyzed by xray diffraction and EDX analysis using SEM and TEM [15,16]. For aging times up to 3000 h, the total amount of precipitate increased at 600 and 650°C. After 10000 and 30000 h, the largest increase in the amount of precipitate occurred at 600°C. The EDX analysis indicated that the largest elemental increases in the precipitate were tungsten, iron, and chromium, all three of which are expected to be present in Laves phase; M_6C will be tungsten rich. X-ray diffraction of the precipitate verified the presence of Laves phase at 550, 600, and 650°C after aging for 10000 h. TEM observations indicated Laves phase formed on $M_{23}C_6$ particles on prior-austenite grain boundaries and lath boundaries. When the total amount of precipitate calculated with JMatPro (the sum of the two curves in Fig. 2) is compared to the measured precipitate after 30000 h, the effect of kinetics versus equilibrium is evident (Fig. 4). Equilibrium was reached by 30000 h at 650°C [15], and it is being approached after aging 30000 h at 600°C. Significant amounts of precipitate formed at 550°C, but because of the reduced kinetics at 400 and 500°C, little precipitate formed at these aging temperatures, even after 30,000 h. Much more is to be expected with longer aging times. However, from observations on the increase in transition temperature that occurred during irradiation of F82H at 500°C in HFIR, it is concluded that irradiation accelerates precipitation kinetics, thus causing embrittlement, even though there was no irradiation hardening.



Figure 4. Amount of extracted precipitate in normalized-and tempered F82H steel thermally aged 30000 h at 400, 500, 550,600, and 650°C compared to calculated equilibrium amount of $M_{23}C_6$, Laves, M_6C , and MX phases. Amounts extracted and calculated for steel tempered at 750°C are indicated by N&T (E) and N&T (C), respectively.

Discussion

The observations of embrittlement of F82H in the absence of irradiation hardening appeared to be caused by Laves-phase precipitation that occurred during irradiation. Fracture in steels is generally initiated at precipitate particles and/or inclusions with the critical stress to propagate a crack being inversely proportional to crack length [17,18]. If it is assumed fracture initiation occurs at a Laves-phase particle and the crack length at initiation equals the diameter of a particle, then fracture stress will decrease with increasing precipitate size.

In the HFIR experiment containing the F82H-IEA heat that was irradiated to 5 and 20 dpa at 500°C, the F82H-IEA heat with a different heat treatment (F82H-HT2), ORNL 9Cr-2WVTa steel (Fe-9.0Cr-2.0W-0.25V-0.06Ta-0.11C), and JLF-1 steel (Fe-9.0Cr-2.0W-0.20V-0.07Ta-0.10C) were also irradiated at 500°C (Table 1) [19]. The latter two steels have compositions only slightly different from F82H. All of

Material	Dose (dpa)	DBTT (°C)	ΔDBTT (°C)	Grain Size No.
F82H-IEA	5	-54	30	2.2
	20	-46	38	5.5
F82H (HT #2)	5	-92	9	6.5
ORNL 9Cr-2WVTa	5	-78	16	6
JLF-1	5	-66	19	6

Table 1. Shift in transition temperature of steels irradiated in HFIR at 500°C

these steels had a positive $\Delta DBTT$, but they all had a smaller $\Delta DBTT$ after the 5 dpa irradiation at 500°C than the F82H-IEA heat. Laves phase in an amount similar to that in F82H is calculated to form at 500°C in all of these tungsten-containing steels.

The objective of the different heat treatment for F82H was to obtain a smaller prior-austenite grain size than the large grain size of F82H-IEA. After austenitizing at 920°C instead of 1050°C, the estimated ASTM grain size number increased from 3.3 to 6.5, corresponding to average grain sizes of ≈114 and ≈38 µm, respectively. The ORNL 9Cr-2WVTa and JLF-1 steels had ASTM grain-size number 6, corresponding to ≈45 µm. They had smaller Δ DBTTs than the F82H-IEA, although they were somewhat larger than F82H-HT2.

Laves phase forms preferentially on prior-austenite grain boundaries, but the amount of Laves formed does not depend on grain size. Therefore, if the $\Delta DBTT$ at 500°C is caused by Laves phase, the difference in the F82H with different heat treatments could be the result of the different grain sizes, assuming all else remains the same. If most of the Laves forms on prior-austenite grain boundaries, then a smaller grain size would provide a larger area for heterogeneous nucleation. This would be expected to result in a larger number of smaller precipitates, which could explain the observations based on the proposed crack-nucleation mechanism.

Thermodynamics calculations indicate that the amount of Laves phase in the reduced-activation steels at 500°C depends mainly on tungsten content, and since ORNL 9Cr-2WVTa and JLF-1 contain 2% W similar to the F82H, similar amounts of Laves are predicted for these steels as for F82H. ORNL 9Cr-2WVTa and JLF-1 have similar compositions, and they have similar prior-austenite grain sizes, which are smaller than that of F82H-IEA. The Δ DBTTs for the two steels at 500°C are similar and somewhat higher than for F82H-HT2 and about half that of F82H-IEA (Table 1). With time at temperature or for higher irradiation doses, the Laves phase precipitation will be completed, and the particles will coarsen. It is expected that this will have a major effect on toughness, but needs to be determined by long-time thermal aging and/or higher-dose irradiation experiments.

Odette and co-workers [20,21] discussed fracture under similar circumstances to those presented in this paper, which they labeled non-hardening embrittlement (NHE). To describe the behavior, a multiscale model based on a model proposed by Ritchie, Knott and Rice [22], which is "based on the observation that cleavage occurs by the propagation of microcracks emanating from brittle trigger-particles, like large grain boundary carbides…" [21]. They write that, "Local stress–strain concentrations due to incompatible matrix particle deformation cause some of the brittle ceramic trigger-particles to crack."

Summary and Conclusions

In the past, irradiation-effects studies in ferritic/martensitic steels have focused on temperatures where irradiation hardening occurs (<425-450°C) that is accompanied by embrittlement caused by a reduction in toughness. Embrittlement due to irradiation-enhanced precipitation in the absence of irradiation hardening has received relatively little attention.

In this report, F82H steel was embrittled when irradiated at 500°C where no hardening occurred in a tensile test. The embrittlement was attributed to Laves-phase precipitation. It occurred for a relatively low dose (≈20 dpa) and a relatively low temperature (500°C). Because of the low dose (relatively short thermal exposure time) and relatively low temperature for extensive precipitation, the ultimate effect of the precipitates on properties has yet to be determined. Therefore, need exists for high-dose irradiations at higher temperatures (500-600°C) than most previous irradiation experiments.

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4.0 COPPER ALLOYS

No contributions.

5.0 REFRACTORY METALS AND ALLOYS

THE INFLUENCE OF NEUTRON IRRADIATION AND TRANSMUTATION IN FFTF ON THE MICROSTRUCTURAL AND MICROCHEMICAL DEVELOPMENT OF Mo-41Re AT 470-730°C – D. J. Edwards and F. A. Garner (Pacific Northwest National Laboratory, Richland, WA, USA)^{*}

OBJECTIVE

The object of this effort is to determine the response of Mo-Re alloys to neutron irradiation.

SUMMARY

Specimens of Mo-41 wt% Re irradiated in the Fast Flux Test Facility (FFTF) experience significant and non-monotonic changes in density that arise first from radiation-induced segregation, leading to non-equilibrium phase separation, and second by progressive transmutation of Re to Os. As a consequence the density of Mo-41Re initially decreases and then increases thereafter.

Beginning as a single-phase solid solution of Re and Mo, irradiation of Mo-41 wt% Re over a range of temperatures (470-730°C) to 28-96 dpa produces a high density of thin platelets of a hexagonal close-packed phase identified as a solid solution of Re, Os and possibly a small amount of Mo. These hcp precipitates are thought to form in the alloy matrix as a consequence of strong radiation-induced segregation to Frank loops. Grain boundaries also segregate Re to form the hcp phase, but the precipitates are much bigger and more equiaxed in shape. Although not formed at lower dose, continued irradiation at 730° C leads to the co-formation of late-forming Chi–phase, an equilibrium phase that then competes with the preexisting hcp phase for rhenium.

PROGRESS AND STATUS

Introduction

The search for materials to serve as structural components of proposed nuclear energy or spacecraft devices has led to the exploratory irradiation of a wide variety of metals and alloys. Molybdenum and its alloys, including those of the Mo-Re system, have been proposed as potential candidates for such service because of their inherently high melting point and strength, room temperature fabricability, and an acceptable match with the coefficients of thermal expansion for carbon and tungsten in fusion first wall applications.

There have been a number of studies[1-24] on the Mo-Re system and its behavior after neutron or charged particle irradiation, but insufficient data have been published on the microstructural and transmutation-induced microchemical evolution that causes degradation of physical and mechanical properties, especially at high neutron exposures, high temperatures and very high Re levels. Only a few of the above-referenced studies examined the post-irradiation microstructure.

Singh and coworkers [11, 12] investigated the microstructure and mechanical properties of Mo-5%Re irradiated in the DR-3 reactor to ~0.16 dpa at temperatures of 50-450°C and observed only dislocation loops. There were no precipitates or voids under these conditions. Chakin and coworkers [13] also investigated Mo-Re alloys at 15, 20, 30 and 41% Re irradiated in the SM-2 reactor to relatively low neutron exposures at temperatures of 120-160°C. They also did not observe any precipitates, but only dislocation loops.

Hasegawa et al. [14] investigated Mo-5 wt% Re irradiated in the FFTF fast reactor at five temperatures ranging from 373-800°C and dose levels of 7-34 dpa. They observed small voids under all irradiation

^{*} Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830.

conditions studied but precipitates were formed only in specimens irradiated above 520°C. They also observed plate-like precipitates but they did not identify their crystal structure or composition.

In a later paper involving Mo-5Re and Mo-41Re (wt%) from the same irradiation series, Hasegawa and coworkers showed that increasing the Re content from 5 to 41% led to a suppression of void formation at 41wt% Re in FFTF for doses ranging from 7 to 34 dpa depending on irradiation temperature, but the precipitation became much more pronounced and complicated [16]. There were (1) relatively large needle or thin plate precipitates at 373°C, (2) fine needle or rectangular type precipitates at 406, 519 and 600°C, and (3) large blocky and plate type precipitates at 800°C. The precipitates were not identified in this study, but it was noted by Hasegawa that Garner and coworkers [21] had previously identified the plate-type precipitates as being a Re-rich hcp phase at 645 and 730°C.

Nemoto and coworkers [17] extended the studies of Hasagawa, irradiating Mo-Re alloys at 2, 4, 5, 10, 13, and 41 wt% Re, concluding that at ~20 dpa in FFTF sigma phase and Chi-phase precipitates were formed in all specimens irradiated in the range 406-800°C, regardless of whether the Re content was low (2, 4, 5, 10, 13 wt%) or high at 41 wt%. However, their conclusion was based primarily on comparisons with more extensive microscopy in a similar parallel study in FFTF conducted on W-26 wt% Re [19]. Nemoto and coworkers did not identify the hcp phase in Mo-41Re that was observed by Garner and coworkers at somewhat higher doses [21], however. This difference in conclusion produces some uncertainty concerning the identity of the precipitate phases forming in Mo-Re at the 41 wt% Re level. Addressing this uncertainty is the primary focus of this paper.

The identification of Chi-phase precipitates in relatively dilute Mo-5Re by Nemoto is noteworthy since the equilibrium phase diagram shown in Figure 1 predicts that only a solid solution should exist at that composition and temperature range [25]. Therefore a very strong radiation-driven mechanism to produce segregation is required to reach the 86-88 wt% Re levels characteristic of Chi-phase in the unirradiated condition. Although somewhat less segregation is need to produce sigma phase (~65-80%) it is also surprising that Nemoto observed sigma phase in his irradiation series since the phase diagram in Figure 1 would predict that sigma would form only above 1125°C.



Figure 1. Equilibrium phase diagram for the Mo-Re system (from ref. 25).

In Mo-Re alloys containing Re at 13, 42 and 45 wt%, radiation-induced segregation and precipitation have been observed by Erck and Rehn [22-24]. Their ion irradiation experiments yielded high concentrations of Re at or near the foil surfaces and grain boundaries, and produced Chi-phase precipitates in >40 wt% Re specimens irradiated at temperatures greater than 750°C.

The works of Erck and Rehn, Hasegawa and Nemoto lead to the conclusion that Mo-Re alloys are susceptible to radiation-induced segregation and precipitation depending on several parameters, including composition, heat treatment, dose level, dose rate and irradiation temperature.

The issue of phase stability becomes even more important when the effects of transmutation are considered. Greenwood and Garner [26] have shown that Mo-Re alloys will transmute strongly to Mo-Re-Os-Ru-Tc alloys in a wide variety of neutron spectra, especially in highly thermalized spectra of light water reactors such as HFIR or SM-2. In a recent paper by Busby and coworkers, for example, a low dose of only 0.72 dpa in Mo-41 wt% Re irradiated in HFIR resulted in a transmuted composition of Mo-24Re-17Os [18].

As shown in Figures 2a and b, Greenwood and Garner also demonstrated that while fast reactor spectra in general led to much lower rates of transmutation, the spectral sensitivity of resonances in the epithermal range is strong enough that large differences in transmutation rates per dpa can occur between in-core and below-core regions of the FFTF reactor [26]. In a later experimental study by Garner and coworkers on pure Re irradiated in EBR-II and FFTF it was shown that relatively small spectral differences between in-core regions of the two fast reactors could significantly impact the interpretation of the data [27]. One consequence of increasing Os formation in Re is a reduced lattice parameter that induces significant and progressive densification of the evolving alloy.



Figure 2. Transmutation of (a) Re and (b) Mo in FFTF showing a strong sensitivity of transmutation to axial position in reactor. Note that doses were quoted in terms of dpa for pure Fe, reflecting the large number of elements examined in ref. 26. In these FFTF studies Mo would experience only 87% of the dpa received by pure Fe.

These position-dependent differences in transmutation rate make it difficult to confidently combine and correlate data vs. dpa from different core locations without inadvertently conducting an unrecognized two-variable experiment. The chemical properties of Re and Os are sufficiently different that the progressive in-growth of Os probably will influence both the lattice parameter change and the phase stability of the evolving alloy.

In order to assess the combined impact of irradiation-induced segregation and transmutation on swelling, phase stability and microstructural evolution, pure Mo and Mo-41 wt% Re were irradiated side-by-side in

FFTF. The density changes and microstructural results on pure Mo were published earlier [28]. Some of the microstructural results on Mo-41 wt% Re cited earlier was published earlier by Garner, Greenwood and Edwards [21], with the complete microstructural results presented in this paper.

Experimental Procedure

Specimens of Mo-41Re (wt%) were irradiated in the form of standard 3mm diameter microscopy disks after preparation in two starting conditions. These conditions were a) annealed one hour at 760°C, followed by aging for two hours at 320°C and b) 20% cold-worked, and followed by aging for two hours at 320°C.

The Mo-4Re and Mo specimens were enclosed in stainless steel "weeper" packets which allowed contact with reactor sodium. At each irradiation temperature two identically-loaded packets were irradiated sideby-side in the Fast Flux Test Facility (FFTF), with one packet removed at the end of the first cycle and the other after the second cycle. Unirradiated archive material was available for comparison.

The temperatures in the Materials Open Test Assembly (MOTA) were actively controlled to remain within $\pm 5^{\circ}$ C of the target level throughout the irradiation. As shown in Table 1 irradiation proceeded at target temperatures of 471, 569, 645, and 730°C to two exposure levels, with dpa levels varying with target temperature. Two doses of 41 and 96 dpa were reached in capsules irradiated at 420°C. In the latter stages of the 96 dpa irradiation at 420°C, however, there was an over-temperature event followed by irregular and lower than target temperature sequences as described in reference 21. Therefore less confidence is placed in data generated in the second segment of the irradiation conducted at 420°C.

Temp °C	Fluence*	dpa Fe	dpa Mo	annealed	cold-worked
471	8.45	32.2	28	2.26	0.06
471	11.8	43.7	38	-0.28	-0.25
420	12.3	47.2	41	0.33	-0.08
420	27.6	110.8	96	0.11	0.28
569	10.6	40.8	35	0.72	1.14
569	16.9	65.8	57	0.82	0.12
645	10.6	40.8	35	0.66	0.043
645	16.9	65.8	57	1.41	0.15
730	10.6	40.8	35	1 45	0 47
730	15.9	40.0 61.5	53	0.07	-0.49

Table 1. Density decreases (%) measured in Mo-41 wt% Re

Fluences quoted in units of 10²² n/cm² E>0.1 MeV

The dpa levels cited here were calculated for pure Mo calculated using the SPECTER code [29]. It is difficult to calculate more accurate dpa levels for Mo-Re and Mo-Re-Os alloys due to the lack of threshold energy data for Re and Os, and the dose/time dependence of the composition due to transmutation. Attempts to estimate the doses for the heavier Mo-41 Re alloy using Ta as a surrogate for Re, using a threshold displacement energy of 90 eV as recommended in ASTM E521, yields a reduction of ~28% from the dose experienced by pure molybdenum. This estimate ignores the progressively increasing contribution of Os with continued irradiation, however. Earlier studies by Hasegawa and Nemoto also faced the problem of how to calculate dpa for Mo-Re-Os alloys. They also chose to quote their dpa levels in terms of pure Mo and used the calculations cited in reference 29.

The initial and post-irradiation densities for all of the different conditions were determined by an immersion technique known to be accurate to 0.2% change in density. JEOL 1200EX and 2000ES transmission electron microscopes (TEM) were used in the analysis of the microstructure of selected specimens. Specimens for TEM were polished at room temperature and ~30 volts using a 20% sulfuric and 80% ethanol electrolyte in a Tenupol electropolishing unit.

Discussion

Density decreases as large as 2% were observed after irradiation, varying with irradiation temperature, starting state of the alloy and dpa level. There is no easily discernible pattern to the density changes that develop in response to variations in temperature, starting state and dpa level.

As shown in Figure 3 the density changes observed in four of the five irradiation sequences exhibited an "overshoot" behavior for both starting conditions [21]. A similar behavior was also observed in pure Mo and was shown to be due to the competing kinetics of early void nucleation and the subsequent approach to a saturation state by void shrinkage associated with the development of a highly ordered void lattice [28]. Since the "overshoot" behavior was observed in both pure Mo and Mo-41Re, there was initial speculation that a similar process involving void lattices might also have occurred in Mo-41 wt% Re. The expectation was found to be incorrect, however.



Figure 3a. Irradiation-induced density changes observed at 420°C in Mo-41 wt% Re irradiated in FFTF (ref. 21). Ann refers to annealed and aged while CW refers to cold-worked and aged starting conditions.



Figure 3b. Irradiation-induced density changes observed at 471-730°C in Mo-41 wt% Re irradiated in FFTF (ref. 21). Ann refers to annealed and aged while CW refers to cold-worked and aged starting conditions.

Electron microscopy of the unirradiated Mo-41Re specimens showed that both the cold-worked and aged and the annealed and aged specimens were single phase solid solutions of Mo and Re. This may indicate that the diffusion kinetics were too slow at the 320°C ageing temperature to produce the equilibrium χ -phase (Chi- phase) predicted in the phase diagram for the Mo-Re system (Figure 1). In addition, the composition of Mo-41 wt% Re is such that very little of the Chi-phase is predicted to be present according to the phase diagram. No significant dislocation density was observed in either the annealed and aged or the cold-worked and aged specimens. The lack of dislocations in the cold-worked and aged material suggests that the ageing treatment at 320°C was sufficient to fully anneal the alloy. However, the lack of dislocations in either starting condition does not provide an explanation of why the radiation-induced density changes were different in the two starting conditions.

Due to the extensive precipitation that occurred during irradiation, selective electropolishing of the matrix appeared to have occurred in all specimens. This selective removal hindered the compositional analysis somewhat, especially that of the matrix.

Examination of the irradiated specimens revealed very few voids, certainly an insufficient number of voids to account for the observed decrease in density. Instead, for those specimens irradiated at temperatures of 420-730°C, TEM analysis revealed a dense, complex microstructure with the dominant feature consisting of a high density of thin precipitate platelets in the interior of bcc Mo-rich grains. These precipitates overshadowed all other microstructural features such that no definitive measurements could be of voids, dislocation loops or dislocation line segments.

Examples of the precipitate microstructure of the irradiated specimens are shown in Figures 4-6 and 10, demonstrating qualitatively that the platelets increase in size as the irradiation temperature increases. Electron diffraction (Figure 7) showed these precipitates to possess a hexagonal close-packed (hcp) crystal structure with lattice parameters of $a_0 = 0.284$ nm and $c_0 = 0.453$ nm, near that of pure Re within experimental error.

The diffraction pattern shown in Figure 7a was taken \sim 7° off of the <111>_{Mo} zone axis, demonstrating the orientation relationship derived for the hexagonal precipitates in the interiors of the grains as approximately:

 $\{011\}_{Mo} || \{0001\}_{Re} <111>_{Mo} || <21 10>_{Re}$

Subsequent tilting experiments confirmed the orientation relationship. In some cases, however, the precipitates were aligned such that the precipitate zone axis was superimposed on the matrix $<111>_{Mo}$ zone axis. The reason for this remains unclear, but it may be related to localized misorientation of the precipitates since the electropolishing tended to etch away the supporting Mo-rich matrix. The diffraction patterns shown in Figures 7b and c, respectively, were taken on the Mo <011> and <001> zone axes. The extra spots and streaks in the <011> diffraction patterns could not be indexed, and are assumed to be a consequence of double diffraction and the thinness of the precipitate platelets.



Figure 4. Irradiation-induced precipitation observed at temperatures of a) 420°C at 96 dpa, b) 569°C at 57 dpa, c) 645°C at 57 dpa, and d) 730°C at 53 dpa in annealed and aged Mo-41 wt% Re.

In contrast to the results of Nemoto and coworkers no sigma phase precipitates were observed in Mo-41 wt% Re at any temperature or dose examined in this study. However, in the second irradiation segment at 730°C and 53 dpa an additional precipitate phase was occasionally found that possessed a much different appearance compared to the hcp phase. Examination of the specimens irradiated in the first irradiation segment to 35 dpa at 730°C did not show any evidence of these precipitates, indicating that higher temperature, as well as higher dose and time at temperature are probably required to form this phase.

In Figure 5c there are a number of these precipitates that are much larger and more equiaxed in appearance than the hexagonal phase. These particles were identified as bcc MoRe₃ (Chi-phase)

proposed by Knapton [30]. SAD patterns for the Chi-phase are shown in Figure 8, demonstrating that the precipitates possess a cube-on–cube orientation relationship with the molybdenum matrix, which agrees with the work of Erck and Rehn [22-24]. The lattice parameter was measured to be ~0.96 nm, almost identical to that measured separately by Knapton and by Erck and Rehn.



Figure 5. Microstructures for the cold worked and aged Mo-41 wt% Re irradiated at a) 471°C and 28 dpa, b) 645°C and 35 dpa, and c) 730°C and 53 dpa. Large Chi-phase precipitates in c) appear to be growing at the expense of the smaller hcp precipitates.

The hexagonal precipitates in the regions surrounding the large Chi-phase precipitates at 53 dpa appear to be smaller in size, indicating that the hexagonal precipitates may be dissolving to form the Chi-phase. A large number of the hcp phase precipitates still exist, however, and many of them have sizes approaching that of the Chi-phase.

Selective electropolishing of the matrix made it relatively easy to obtain the composition of the precipitate phases but correspondingly harder to measure the composition of the matrix. The composition of the Chi-phase precipitates at 730°C to 53 dpa was measured to be approximately 45% Re, 15% Os and 40% Mo by weight. EDS analysis of the hcp precipitates showed the composition at approximately 75% Re, 17% Os, and 8% Mo by weight in the same specimen. Typical examples of the EDS spectra from the two phases are given in Figure 9.

The 8-9 wt% Mo measured in the hcp precipitates can not be confidently accepted and may reflect the inclusion of some matrix in the precipitate analysis. An accurate composition for the matrix could not be obtained because of the high density of precipitates and the lack of suitably large enough matrix volumes. Denuded zones were generally observed near grain boundaries and were the only regions free of

precipitates. Although these regions were much higher in molybdenum, their compositions are not confidently thought to be representative of the matrix.



Figure 6. Microstructures of Mo-41 wt% Re where a) and c) correspond to the cold-worked and aged specimens irradiated at 471°C and 730°C, respectively, while b) and d) correspond to the annealed and aged specimens irradiated at 471°C and 730°C, respectively. The dpa level at 427°C is 28 dpa and is 35 dpa at 730°C.

An additional difficulty encountered in determining the ratio of Re to Os involved overlap of photon peaks between the Re and Os, as shown in Figures 9a and b. However, the L_a peaks at 8.68 and 8.92 keV for Re and Os, respectively, were separated enough to allow an estimate to be made of the Os content.

Although Greenwood and Garner [26] predicted that Tc and Ru should be present at several tenths of a percent because of transmutation of the molybdenum, none of the EDS spectra contained peaks from either element detectable above the photon background arising from radioactivation. Taking spectra from thick regions, which included both the matrix and the precipitates, also did not yield any evidence of Tc and Ru. The peaks for the two elements should be easily separable at the higher energies if they are present in resolvable amounts. However, the selective electropolishing of the molybdenum matrix may have lowered the amount of Tc and Ru to levels below the detection limit. A similar observation concerning the absence of Tc and Ru signals was made by Hasegawa and coworkers on specimens irradiated in FFTF to 11-34 dpa [14].


Figure 7. Diffraction patterns from the hexagonal phase in the cold worked and aged Mo-41 wt% Re irradiated at 730°C and 35 dpa. The diffraction pattern in a) was taken \sim 7° off the <111> zone axis. The remaining two diffraction patterns b) and c) were taken exactly on the zone axes <011> and <001>, respectively.

As a general trend, it was observed that the lower the irradiation temperature, the smaller the size of the hcp precipitates and the higher their number density. The Chi-phase precipitates tend to be larger and fewer in number in the cold-worked and aged specimens compared to the annealed and aged specimens.





Figure 8. Selected area diffraction patterns from the cubic Chi-phase in the cold worked and aged Mo-41 wt% Re irradiated at 730°C and 53 dpa, demonstrating the cube-on-cube orientation relationship with the Mo matrix. The diffraction pattern in a) is on the <111> zone axis, while b) an c) were both taken on the <011> zone axis. Note that b) contains diffraction spots for both the hexagonal phase as well as the cubic Chi-phase. The pattern in c) shows one variant of the Chi-phase precipitate.



Figure 9. EDS measurements of a) a hexagonal precipitate and b) Chi-phase precipitate in the Mo-41 wt% Re irradiated at 730°C and 54 dpa.

Figure 10 shows that the grain boundaries were sometimes found to be associated with extensive precipitation of a thick, equiaxed phase. Analysis of these grain boundary precipitates showed that they were also the Re-rich hcp phase.



Figure 10. Examples of the grain boundary hcp precipitates in specimens irradiated under the following conditions: a) 645°C, 35 dpa, annealed and aged, b) 730°C, 35 dpa, annealed and aged, and c) 730°C and 53 dpa, cold-worked and aged. Large grain boundary hcp precipitates in c) appear to be growing at the expense of the smaller hcp precipitates.

Results

The Mo-Re equilibrium phase diagram predicts that at 400-700°C Mo-41 wt% Re in the unirradiated condition should be comprised of a eutectoid mixture with a small fraction of Chi-phase imbedded in a solid solution of bcc Mo-Re. However, the TEM results show that the unirradiated Mo-41 wt% Re specimens were in fact single phase. This failure to reach the anticipated equilibrium state is attributed to the rather low aging temperature and short aging time, as well as the close proximity to the phase boundary. Indeed, Leonard and coworkers showed that 1100 hour aging of Mo-41 wt% Re in this temperature range resulted in no precipitation, while similar aging of Mo-47.5 wt% Re resulted in both sigma-phase and Chi-phase precipitation. [5].

In the irradiated Mo-41 wt% Re specimens of the current study, however, it was observed that the nonequilibrium hexagonal-closed-packed phase was very easily formed at all conditions examined. This reflects a tendency toward radiation-induced segregation of Re so strong as to produce a phase that should exist only on the far right of the Mo-Re phase diagram. The segregation is so strong as to also bypass the formation of the slower-forming equilibrium Chi-phase.

The observation that the equilibrium Chi-phase can also form at 730°C after sufficiently high dose and time agrees qualitatively with Erck and Rehn's observation that Chi-phase only formed in their ionirradiated specimens when the irradiation temperature was 750°C or higher.

Erck and Rehn [22-24] have studied the segregation of Re to the front surface of ion-bombarded Mo-xRe alloys, where x = 13, 42 and 45 wt%. The ion irradiation was conducted over the temperature range of 550-1255°C. Their study was conducted at a higher displacement rate compared to that of neutron irradiation and did not involve transmutation. In addition, they were limited to doses of ~1 dpa due to blistering of the surface from the ion-implanted He atoms. They found that Chi-phase formation only occurred in Mo-Re alloys with 42 and 45 wt% Re, and then only in the temperature range (750-1075°C) where enough segregation occurred that the Re concentration near the foil surface exceeded the solid solubility of Re in Mo (~42 wt% Re). Irradiation of the Mo-13 wt% Re alloy produced Re levels of ~14wt% Re in the near-surface regions of the foils, far below the solid solubility limit, and consequently no Chi-phase was formed.

Erck and Rehn modeled the segregation in terms of preferential segregation of the heavier but "undersized" Re atoms (based on King's work on size factors [31]) by an interstitial mechanism. King reported in his tabulation of size factors that Re has a volume size factor 5.56% less than that of Mo, and a linear size factor 1.89% less than Mo. However, these values are for a maximum concentration of 15 wt% Re in solid solution, so their applicability to Mo-41Re is suspect since this exceeds the solubility of Re at temperatures less than 650°C. There was no corresponding data listed for Re with Mo added as solute.

The impact of the Os on precipitation is not known, however. Although Re and Os exhibit complete solid solubility in each other, they do have much different volume size factors in Mo (-9.62% for Os vs. -5.56% for Re). Based on the size factors alone, both Re and Os should segregate toward boundaries in Mo, though most likely at different rates. Additionally, the progressive transmutation of Re to Os should eventually lead to an increase in density with time, as was indeed observed in most specimens.

Nemoto and coworkers [17] noted that the ratio of Re/Os in the "sigma" phase in Mo-10 wt% Re was very similar to that of the matrix in irradiated Mo-Re alloys, 0.25 vs. 0.22 respectively at ~20 dpa, implying that the precipitates formed early and the majority of the transmutation occurred afterwards. In our study of Mo-41 wt% Re the ratios for the hcp and Chi phases were 0.23 at ~40 dpa and 0.33 at 53 dpa, respectively.

The authors of the current study are not convinced that Nemoto observed sigma phase at all Re levels, especially at 41 wt% Re. Nemoto drew on his parallels with his more-detailed work on W-Re alloys to identify the phases in Mo-Re alloys. He may have correctly identified sigma phase in the 2-13 wt% Re range, but it is not clear from his paper that sufficient attention was directed toward the Mo-41wt% Re alloy, whereas our study showed that the hcp Re-rich phase forms easily at all temperatures examined.

In comparison to the work of Erck and Rehn where only Chi-phase was observed at 41 wt% Re, our work indicates that the formation of the hcp precipitates during neutron irradiation is much more dominant. This difference may be related either to the lower displacement rate inherent in neutron irradiation and/or to the formation and participation of osmium in the precipitation process. Osmium may have segregated concurrently with rhenium, but probably also formed by transmutation in the Re precipitates after they formed. However, the morphology and size of the hcp precipitates suggests that the precipitates arise

primarily and very quickly due to very strong radiation-induced segregation to radiation-induced interstitial loops.

The initial density decreases or "apparent swelling" observed in Mo–41 wt% Re in this experiment did not arise as a consequence of void formation as was originally anticipated. Therefore, it must have arisen from formation of the non-equilibrium hcp phase and the removal of Re from solution. Since Mo-41 wt% Re has a density 134% that of pure Mo (10.22 g/cm³) according to our experimental measurements, and pure Re and Os both have densities of around 20 g/cm³, segregation of Re could easily produce overall volumetric dilations as large as several percent. Subsequent formation of Os would tend to densify the alloy and most likely accounts for the non-monotonic behavior of the density with dose.

The observed radiation-induced microstructural changes in this study are so overwhelming that they may preclude the application of Mo-Re alloys with high Re (>40%) content as structural materials in neutron environments, at least in the temperature range (430-730°C) of the current study. While Busby and coworkers [18] showed that tensile tests on Mo-41Re did not exhibit brittle failure when the alloy was irradiated above 800°C to ~1 dpa in HFIR, Hasegawa and coworkers demonstrated very brittle behavior after irradiation at 373-800°C in FFTF to doses comparable (7-34 dpa) to those of the current study[16,17]. While the doses attained in the two cited studies are quite different, the transmutation levels in the specimens of Busby and Hasegawa are more comparable. It is reasonable to wonder, however, if Busby's results would shift toward a more brittle behavior of Mo-41Re if the dpa levels were closer to the levels obtained in FFTF. Indeed Busby saw a drop in ductility in Mo-47.5Re relative to that of Mo-41Re in the same experiment, suggesting that a larger chemical driving force and perhaps a longer exposure might produce less ductility in Mo-41Re than observed in his relatively low dose study.

Conclusions

The combined influence of both strong neutron-induced segregation and transmutation of Re in Mo-41 wt% Re has strong consequences on its phase stability. Radiation in the range 420-730 °C induced complete instability of the alloy matrix involving the formation of a non-equilibrium Re-rich phase to form in lieu of the anticipated Chi-phase. Only at the highest temperature and highest dose explored was the equilibrium Chi-phase observed to form and compete with the hcp phase. The observed microstructural changes are so pronounced that they may preclude the application of Mo-Re alloys with high Re content as structural materials in neutron environments.

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6.0 AUSTENITIC STAINLESS STEELS

THE CONFLICTING ROLES OF BORON ON THE RADIATION RESPONSE OF PRECIPITATE-FORMING AUSTENITIC ALLOYS - T. Okita, N. Sekimura (Department of Quantum Engineering and Systems Science, University of Tokyo) and F. A. Garner (Pacific Northwest National Laboratory)[†]

OBJECTIVE

The object of this effort is to determine the interactive influence of material and environmental factors that influence void swelling of austenitic alloys

SUMMARY

The behavior of void swelling at 400°C of model f.c.c. alloy Fe-15Cr-16Ti-0.25Ti-0.05C doped with boron was examined in the FFTF-MOTA. Boron additions modify the neutron-induced swelling of Fe-15Cr-16Ni-0.25Ti-0.05C somewhat, but the changes appear to arise primarily from the influence of boron as a chemical species rather than as a source of helium. Boron additions initially depress swelling strongly, but the effect saturates by ≤ 100 appm. The reduction in swelling is thought to arise from boron's influence on distribution and precipitation of carbon.

As the boron level is raised to significantly larger levels swelling then swelling begins to increase, but at a slower rate per boron atom. This subsequent increase is thought to reflect the higher He/dpa ratio generated by the boron, overwhelming the helium produced by (n, α) reactions with nickel.

PROGESS AND STATUS

Introduction

In an earlier report it was shown that two simple, annealed austenitic alloys, ternary Fe-15Cr-16Ni and quaternary Fe-15Cr-16Ni-0.25Ti, when irradiated in FFTF-MOTA at ~400°C over a wide range of dpa rates, exhibited a very strong influence of dpa rate on void swelling [1]. While the steady state swelling rate of ~1%/dpa was unaffected by dpa rate, the transient regime was strongly affected, with a progressive shortening of the transient duration as the dpa rate decreased. A later paper showed that carbon additions to the quaternary alloy resulted not only in a reduction of swelling but also in a total loss of the influence on dpa rate [2].

It was also shown in the earlier study that the addition of 500 appm of natural boron to the ternary and quaternary alloys had very little effect on swelling [1]. However, this latter conclusion was not as confidently demonstrated at all irradiation conditions.

The ambiguity arose from the manner in which the specimens were stacked in the experimental packets which contained as many as 100 specimens each. All specimens were standard 0.3 mm thick microscopy disks stacked in stainless steel packets. In some packets, the boron-containing alloys were separated by ~1.5 cm distance from the boron-free alloys. In packets which were irradiated in-core with minimal gradient in dpa rate the conclusion was very clear in that there was no obvious influence of boron on the swelling. In packets lying across the core boundary or away from the core boundary, however, it appeared that swelling could be either increased or decreased by boron. However, not only was the effect of dpa rate gradients across the packet dominating the results but there was no record of how a given packet was oriented in the gradient, giving rise to both increases and decreases in swelling.

Also contained in the FFTF-MOTA experiment was Fe-15Cr-16Ti-0.25Ti-0.05C, also in the annealed condition. Boron-doped variants of Fe-15Cr-16Ni-0.25Ti-0.05C were also included in other packets. As shown in Figure 1, however, there was no significant separation of the boron-free and boron-containing

[†] Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830.

specimens, allowing a more confident determination of the role of boron on swelling, even in packets that exist in dpa gradients.



Figure 1. Sealed stainless steel packets containing ~100 microscopy disks. Note in the original study [1] that the boron-free and boron-containing specimens were separated by ~1.5 cm such that strong gradients in dpa rate out of core could lead to significant differences in dpa. However, in the experiments of the current paper, all boron contents including zero appm were in intimate contact.

Experimental Details

Relatively pure Fe-15Cr-16Ni-0.25Ti-0.05C (at %) with no added solute was prepared by arc melting from high purity Fe, Ni, Cr, Ti and C. The alloys was rolled to sheets of 0.25 mm thickness, cut into 3 mm disks and annealed for 30 minutes at 1050°C in high vacuum. Also included in some sets of specimens were Fe-15Cr-16Ni-500 appm natural boron, and/or Fe-15Cr-16Ni-0.25Ti-0.05C with boron levels of 100, 500 and 2500 appm boron, all prepared using the same procedure. The specimens were stacked in the same order in each nominally identical packet, but there was no control placed or record kept of which end of the packet was oriented toward the top or bottom.

Two sets of identical specimens are placed in sealed, helium-filled packets at each of seven different capsule positions of the Materials Open Test Assembly (MOTA), ranging from below the core to above the core of the Fast Flux Test Facility (FFTF). The packets in general contained four identical specimens of each of the two alloys. The various alloys were located side-by-side in the same packet. Two or more identically-loaded packets were placed in each capsule, with the dpa rate dependent on the axial location in MOTA.

With the exception of the below-core canister, the temperatures in MOTA capsules are actively controlled to $\pm 5^{\circ}$ C of the nominal target, although the nominal target temperatures varied a little from capsule to capsule. In the below-core capsule the temperatures are largely controlled by the inlet coolant temperature and the gamma heating level, and therefore can be calculated with rather small error.

The first irradiation sequence occurred in Cycle 11 of MOTA-2A for 2.58×10^7 sec, and a subset of specimen packets was then removed. Other identical specimen packets continued in Cycle 12 of MOTA-2B for 1.71×10^7 sec. The dose rates in the various capsules ranged from 8.9×10^{-9} to 1.7×10^{-6} dpa/sec. The dose levels attained by the specimens varied from 0.23 to 43.8 dpa in Cycle 11 and an additional 0.38 to 24.0 dpa in Cycle 12.

The starting and post-irradiation densities were measured using an immersion density technique known to be accurate to ± 0.2 % change in density. In some cases it was not possible to clearly identify and retrieve all four specimens, but in general there were at least two identical specimens measured in each capsule.

Results

As shown in Figure 2 by Sekimura and coworkers [2], the swelling of the carbon-doped alloy at ~400°C appears to show no obvious influence of the dpa rate. As was observed in the two simple undoped alloys, the range of swelling between identical specimens is relatively small, indicating the reproducibility of the swelling phenomenon. Surprisingly, the swelling of the twelve data ensemble of the carbon-doped alloy appears to be following a general, lower-swelling trend somewhat characteristic of the undoped alloys at the highest dpa rate.



Figure 2. Swelling of simple model f.c.c. Fe-15Cr-16Ni-0.25Ti-0.05C in FFTF-MOTA at ~ 400°C, showing that the swelling is relatively independent of dpa rate. The red data were obtained from irradiation in MOTA-2A only and the black data from irradiation in both MOTA-2A and 2B.

Figure 3 shows that addition of 500 appm boron to the carbon-doped alloy reduced the swelling level somewhat, but the alloy in general retained its insensitivity to dpa rate. Since this comparison was made only at 500 appm B, it is not possible from this comparison to determine the effect of smaller amounts or observe the effects of progressively larger additions of boron. Three packets containing a wider variety of boron levels were examined to address this issue.

Figure 4 shows that most of the decrease in swelling observed at 500 appm boron was already attained at the 100 appm level. Beyond 500 appm there was a tendency to increase swelling, with the amount of the increase dependent on the dpa rate.



Figure 3. Swelling of simple model f.c.c. Fe-15Cr-16Ni-0.25Ti-0.05C-500 appm B in FFTF-MOTA at ~400°C, showing that the swelling is reduced somewhat by boron addition but remains relatively independent of dpa rate. The red data were obtained from irradiation in MOTA-2A only and the black data from irradiation in both MOTA-2A and 2B



B Content (appm)

Figure 4. Swelling of simple model f.c.c. Fe-15Cr-16Ni-0.25Ti-0.05C with various levels of boron, as observed after irradiation in FFTF-MOTA at ~400°C at three different dose rates to reach three dose levels.

Discussion

It is clear that addition of boron at 500 appm decreases the swelling somewhat of Fe-15Cr-16Ni-0.25Ti-0.05C but does not appear to change the insensitivity to dpa rate that occurred when carbon was added. Boron is well-known to interact with the precipitation of carbides and therefore may exert its influence on void swelling both directly or indirectly through its influence on carbon [3]. With respect to boron's contribution it must be recognized that boron can play several roles, however, first as a chemical species and second as a source of transmutants helium and lithium produced by the ${}^{10}B(n, \alpha) {}^{7}Li$ reaction with thermal and epithermal neutrons.

Note, however, that ¹⁰B comprises only 20% of natural boron. As shown in reference [4] some helium in these specimens is produced by various (n, α) reactions, primarily with nickel in these alloys, such that the boron-generated helium is additive to that generated in the base alloy. Additionally, the burn-up of boron in a fast reactor is very sensitive to minor differences in the epithermal portion of the neutron spectra, with the He/dpa ratio due to boron increasing strongly below the core and decreasing above the core [4].

In the core center positions from which the data shown in Figure 4 were attained, the impact of 100 appm boron is only a 30-40% increase in the helium generation rate which is already rather large. For example, at 67.8 dpa the boron contribution increased the helium from 15.5 appm generated by the base alloy to only 20 appm arising from the 100 appm boron addition.

Since the primary impact of boron was attained by 100 appm boron and the boron-induced increase in helium was not large, it is concluded by the authors that the primary effect of boron is probably chemical in nature and most likely arises from its influence on the distribution of carbon and its precipitation in the alloy.

These results suggest that use of boron to simulate fusion-relevant helium generation rates in alloys prone to carbide precipitation may yield misleading results.

Conclusions

Boron additions depress the neutron-induced swelling of Fe-15Cr-16Ni-0.25Ti-0.05C somewhat at 400°C, but the changes appear to arise primarily from the influence of boron as a chemical species rather than as a source of helium. Boron additions initially depress swelling strongly but the effect saturates by <100 appm. The depression is thought to arise from boron's influence on distribution and precipitation of carbon.

As the boron level is raised to significantly larger levels, then swelling increases but at a slower rate per boron atom. This increase is thought to reflect the higher He/dpa ratio generated by the boron overwhelming the helium produced by (n, α) reactions with nickel.

Acknowledgements

This work was supported by MONBUSHO, the Japanese Ministry of Education, Science and Culture under the FFTF-MOTA collaboration and the JUPITER program (Japan-USA Program for Irradiation Testing for Fusion Research), and the US Department of Energy, Office of Fusion Energy under Contract DE-AC06-76RLO 1830 at Pacific Northwest National Laboratory.

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VERY HIGH SWELLING AND EMBRITTLEMENT OBSERVED IN A Fe-18Cr-10Ni-Ti HEXAGONAL FUEL WRAPPER IRRADIATED IN THE BOR-60 FAST REACTOR - V. S. Neustroev (Research Institute of Atomic Reactors, Dimitrovgrad, Russia) and F. A. Garner (Pacific Northwest National Laboratory, Richland WA USA)

OBJECTIVE

The object of this effort is to determine the generality of fundamental mechanisms of radiation damage to structural steels by examining experiments on Russian steels that are comparable to Western steels. Similarity of response in fission spectra will hopefully imply similarity in fusion spectra.

SUMMARY

The highest void swelling level ever observed in an operating fast reactor component has been found after irradiation in BOR-60 with swelling in Kh18H10T (Fe-18Cr-10Ni-Ti) austenitic steel exceeding 50%. At such high swelling levels the steel has reached a terminal swelling rate of ~1%/dpa after a transient that depends on both dpa rate and irradiation temperature. The transient duration at the higher irradiation temperatures is as small as 10-13 dpa depending on which face was examined. When irradiated in a fast reactor such as BOR-60 with a rather low inlet temperature, most of the swelling occurs above the core center-plane and produces a highly asymmetric swelling loop when plotted vs. dpa.

Voids initially harden the alloy but as the swelling level becomes significant the elastic moduli of the alloy decreases strongly with swelling, leading to the consequence that the steel actually softens with increasing swelling. This softening occurs even as the elongation decreases as a result of void linkage during deformation. Finally, the elongation decreases to zero with further increases of swelling. This very brittle failure is known to arise from segregation of nickel to void surfaces which induces a martensitic instability leading to a zero tearing modulus and zero deformation.

PROGRESS AND STATUS

Introduction

Currently there is a strong interest in the void swelling behavior of austenitic steels used for the core internals of Western pressurized water reactors (PWRs) and Russian water-cooled, water-moderated energy reactors (VVERs) [1-5]. The primary construction materials of the internals are AISI 304 stainless steel and Kh18H10T (Fe-18Cr-10Ni-Ti) stainless steel, respectively. Void swelling has been raised as a potentially life-limiting phenomenon with respect to license extension of these reactors. In addition to dimensional distortion arising from void swelling and irradiation creep, it is known that swelling at ≥10% induces a severe form of void-induced embrittlement which raises some safety concerns [6, 7].

Of particular interest is the swelling at low temperatures and low dpa rates characteristic of PWR and VVER internals. A number of papers by the authors of the current study have addressed this concern [8-20]. It has been clearly shown for both steels that lower dpa rates decrease the duration of the transient regime of swelling and therefore increase swelling at a given exposure level. It has also been convincingly shown that lower dpa rates cause swelling to occur at lower temperatures that encompass all temperatures of relevance to PWR and VVER internals. Similar irradiation conditions can occur in ITER and various proposed fusion energy devices.

Also of interest is the anticipated swelling behavior of the steels at high exposure levels and potentially higher swelling levels associated with life extension. Unfortunately, it is impossible to develop swelling data at very high exposures when irradiation proceeds at relatively low neutron fluxes and

^{*} Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830.

correspondingly lower displacement rates. However, it is possible to explore high neutron exposures at PWR and VVER-relevant temperatures using the BOR-60 fast reactor, which has an inlet temperature of 320°C.

In the current study it is desired to examine whether certain characteristics of swelling observed in AISI 304 stainless steel in the EBR-II fast reactor are also observed in Kh18H10T stainless steel. Of particular interest are the dependence of the transient duration of swelling on temperature and dpa rate, and whether the terminal swelling rate of ~1%/dpa is reached by this steel at high neutron exposures. An additional area of strong interest is the consequences of void swelling on the mechanical properties. This paper addresses these issues by examining a hexagonal wrapper irradiated to rather high swelling levels.

Experimental Procedure

A fuel assembly designated O-196 was irradiated without movement or rotation in cell D13 in the third row (11.9 mm from core center) of the BOR-60 fast reactor from December 1983 up to January 1987. All of its neighbors were fuel assemblies. The flux gradient across the assembly was rather small.

The hexagonal duct served as a wrapper surrounding the fuel assembly and was constructed from a titanium-stabilized Russian stainless steel designated Kh18H10T with nominal composition Fe-18Cr-10Ni-0.5Ti but with a small addition of scandium. This element has been shown in ion and neutron irradiation of pure nickel to strongly retard swelling [21]. The Kh18H10T steel is used in Russian reactors for nuclear applications where AISI 304 would be used in Western reactors. The closest Western analog of the Russian steel is AISI 321 stainless steel. The duct wall was 1 mm thick.

The chemical composition in wt. % was measured to be Fe-17.9Cr-10.1Ni-1.22Mn-0.46Ti-0.36Si-0.095C-0.009S-0.032P-0.012N-0.05Sc. The duct was fabricated and then annealed at 800°c for two hours, followed by annealing at 600°C for 1 hour.

The temperature and fluence profiles for this duct are shown in Figure 1. The duct reached a maximum exposure of $12.6 \times 10^{26} \text{ n/m}^2$ (E>0.1 MeV) corresponding to 56 dpa in the BOR-60 neutron spectrum and experienced life-averaged temperatures of 320 to 620°C.

When removed from reactor it was obvious from both observation and flat-to-flat measurements that significant volume changes had occurred in this duct. When cutting was employed to produce specimens for examination the duct was observed to be very brittle, with cracking and brittle failure often occurring.

Flat #2 was chosen for the most extensive examination but specimens were cut from all six flats. The duct was sectioned at various elevations to produce specimens of size $5 \times 50 \times 1$ mm on which to perform density measurements using hydrostatic weighing at room temperature in CCl₄ with an accuracy of ±0.2%. A second set of specimens were cut at $55 \times 15 \times 1$ mm to be used for production of tensile specimens. An electro-erosion technique was used to produce a gauge section that was 22.5 mm long, 5.5 mm wide and 1 mm thick. A third set of specimens of $4 \times 4 \times 1$ mm were cut for microscopy examination. Microscopy results were reported earlier by Borodin and coworkers [22].

Twenty-two flat tensile specimens were subjected to tensile tests at a strain rate of 1 mm/min. Tensile tests were conducted at room temperature, a temperature close to the radiation temperature and also at 800°C. Some of the tensile results have been presented previously in Russian [23, 24].



Figure 1. Calculated fluence and life-averaged temperature distributions along the axis of the wrapper. The temperature cited is the life-averaged value. The fluence quoted is the value above 0.1 MeV in units of 10^{26} n/m².

Results

Density change data are presented in Table 1 with all locations being measured from the core centerplane. The faces of the duct were arbitrarily but progressively numbered 1 through 6. The swelling peaked at ~100 mm above the core center-plane on all faces. Note that density changes ($\Delta\rho/\rho_0$) as large as 35.4 % were observed with some variations from face-to-face, especially in the high swelling portion of the duct.

However, swelling $(\Delta V/V_0)$ in % is defined as $(100 \Delta \rho/\rho_0)/(100 - \Delta \rho/\rho_0) = 100 \Delta \rho/\rho_{irr}$. Thus 35.4% density change represents a swelling level of 54.8%. Although relatively large errors are characteristic of microscopy measurements at such high swelling levels, the microscopy measurements by Borodin and coworkers largely confirm the swelling levels measured by density change [22].

Figure 2 shows the swelling distribution along Flat #2 which peaks at 44.3% at a position 100 mm above the core center-plane. Figure 3 shows the swelling observed along all six faces, with the peak swelling of 54.8% observed on Flat #1. Note, however, that Flat #1 swells somewhat less than Flat #2 at other elevations.

Looking at the density change data more closely in Figure 4, however, it appears that Flat #5 actually has the largest overall swelling, perhaps as large as ~60%, but a measurement at 100 mm was not made for this duct. The most significant feature of the swelling of the six faces is the face-to-adjacent face continuity of swelling at each elevation, as is also shown in Figure 4. It appears that face number 5 might be closest to the core centerline, but correlation of peak swelling of individual faces with respect to the core center line could not be made because no record was made of the initial orientation and no face was specifically marked.

Z, mm	350	300	250	200	150	100	50	0	-50	-100	-150	-400
fast fluence*	2.1	3	5	7.5	9.7	11	12	12.4	12.3	11.1	9.7	1.5
Temperature °C	600	600	590	585	560	530	500	465	430	395	360	320
dpa	11.3	16.2	27	40.5	52.4	59.4	64.8	67	66.4	59.9	52.4	8.1
flat 1	-	-	-	16.8	-	35.4	28.6	-	-	-	-	-
flat 2	4.8	3.6	10.6	20.4	29.2	30.7	28.2	21.2	9.2	2.3		1.2
flat 3	3.1	6.7	-	-	27.9	31.2	27.1	24.1	-	-	-	-
flat 4	1.7	-	-	-	29.2	33.4	26.5	-	6.8	1.5	1.8	-
flat 5	-	-	-	-	32.3	-	33.8	-	-	-	-	-
flat 6	-	-	13.2	-	28	-	31.2	-	-	-	-	-

Table 1. Density changes in % measured on various flats (fast fluence in units of 10²⁶ m/m² (E>0.1 MeV)

* Fast fluence in units of 10^{22} n/cm² E>0.1 MeV



Figure 2. Swelling observed along the length of flat #2 of the wrapper.



Figure 3. Swelling observed on all six faces of the wrapper.



Figure 4. Continuous swelling variation from face-to-adjacent face at a given elevation, plotting only density values for immediately adjacent faces and only density changes that are >15%. It is interesting to note in the lower-swelling portions of the core, both at lower temperature (0 mm) and higher temperatures (200 mm) the swelling increases from faces 1 to 3, a behavior opposite to that of the higher-swelling elevations.

Figure 5 presents the swelling data of Flat #2 vs. dpa where 10^{26} n/m² E>0.1 MeV produces 5.43 dpa. In this presentation the dependence on temperature and dpa rate is manifested as a "loop" determined by the interaction of the temperature and dpa rate to determine the duration of the transient swelling regime. It is known that the transient regime of swelling in this steel always decreases as the temperature increases from bottom to top of the duct, but increases as the flux increases as the flux falls above the core center-plane. Such loops have been observed previously in AISI 304 stainless steel [3].



Figure 5. Swelling plotted vs. dpa level for flat #2.



Figure 6. Swelling plotted vs. dpa level for all flats.

Each high-swelling data point on the flat 2 loop is thought to reside on a separate swelling curve with a swelling rate of $\sim 1\%$ /dpa where the transient duration is complete but was determined by a combination of the dpa rate and temperature. Note that on the high temperature side of the loop a

slope of ~1%/dpa is evident, indicating that all temperatures above ~530°C share the same transient duration of ~12 dpa. Figure 6 shows the swelling of all flats plotted together and reinforces the perception that 1%/dpa is indeed the terminal swelling rate, especially at the higher temperatures. It appears, however, that there may be a slight variation in the transient duration, being somewhat less than 12 dpa on the highest swelling face.

Mechanical Properties

Shown in Table 2 are the results of the tensile tests. Figure 7 presents the results for tests conducted at or near the irradiation temperature.

Note that in three of the test specimens designated numbers 26, 32 and 44, all with rather high swelling levels, failed with essentially zero elongation before the test was properly started, indicating a very high degree of embrittlement.

Rather than plot the tensile data vs. dpa level, irradiation temperature or test temperature it is instructive to plot the data vs. the swelling level only. Note that as the swelling level reaches and exceeds ~10%, the yield and ultimate strengths have converged. For swelling levels >20% the yield stress and frequently the ultimate stress plunge to zero. It is particularly noteworthy that the steel actually "softens" as the swelling increases.

Figure 8 appears to show that the strength and elongation measurements for tests conducted at 20 and 800°C. As expected, the strength at 20°C is somewhat higher than the strength observed at higher test temperatures, and the strength again decreases as swelling increases. In tests conducted at 800°C the steel is very "soft" with strengths of ~100 MPa for all swelling levels.



Figure 7. Mechanical properties of specimens tested at or near the irradiation temperature.

Specimen number	Elevation mm	Swelling %	Test temp. °C	Ultimate tensile strength, MPa	Yield strength, Mpa	Uniform elongation, %	Total elongation, %
14	+250	10.6	590	290	280	0.4	0.4
18	.200	13.2	20	740	610	1.1	1.1
19	+200	16.8	800	75	56	2.5	2.5
27		27.9	20	475	405	0.7	0.7
30		28.0	360	59	-	0	0
29	+150	32.3	500	140	-	0	0
26		29.2	560	0	-	0	0
28		29.2	800	125	110	1.9	3.4
31		35.4	20	138	-	0	0
34	+100	33.4	360	103	-	0	0
32	100	30.7	530	0	-	0	0
33		31.2	800	31	28	1.6	3.7
37		28.6	20	60	-	0	0
39		27.1	360	141	-	0	0
38	+50	28.2	500	172	-	0	0
40		26.5	590	245	225	1.2	1.2
44	0	21.2	470	0	-	0	0
45	0	24.1	320	482	-	0	0
50	-50	9.2	430	630	610	1.6	1.6
56	-100	2.3	400	765	605	2.0	2.5
62	-150	0	360	825	755	0.7	0.7
68	-400	1.2	800	100	75	11.7	48.6

Table 2. Mechanical properties of specimens.

26, 32, 44 -failed before testing





Discussion

Although neutron-induced swelling levels of 80-90% have been reached in experimental studies [2, 26] the highest swelling level ever reported for a stainless component irradiated in a U. S. fast reactor was ~37% at ~100 dpa in cold-worked D9 [27]. The swelling of 50 to perhaps 60% in the current study is therefore the largest reported swelling observed in any fast reactor component.

Based on a large number of earlier studies the higher swelling in Kh18H10T compared to that of D9 probably arises from the combined lack of cold-work, the lower nickel level and especially the pre-irradiation aging treatment employed [28]. It is well known that aging of most stainless steels at temperatures on the order of 600 to 800°C is the surest way to accelerate the onset of swelling [29-33].

It can be seen in Figures 5 and 6 that the incubation period at the higher irradiation temperatures was only 10-12 dpa, depending on what face was examined. Such aging promotes the early formation of carbide, intermetallic phases and non-equilibrium nickel-silicides such as G-phase, removing elements such as Ni, Si and Ti from solution that tend to resist the onset of swelling. Indeed, Borodin and coworkers found that in this duct large densities of both metal carbides and G-phase were formed with very high nickel (20-73%), silicon (3-25%) and titanium (5-99%) levels. Most interestingly, the scandium introduced into the steel to retard swelling was also concentrated into these precipitates.

The relative continuity of swelling on the various adjacent faces as seen in Figure 4 confirms that the variations in peak swelling probably arose from face-to-face variations in either temperature or dpa rate rather than as a result of purely random variations in swelling. It was initially assumed that there was not a very significant gradient in neutron flux across the fuel assembly, but this assumption might not be completely accurate to <5%.

In addition, here are always small variations in temperature distribution/history, especially since all neighbors of this assembly were fueled assemblies subject to burn-up and therefore experiencing temperature and flux histories of their own. The most likely origin of the face-to-face variations observed probably is related to minor variations in temperature especially.

Figure 5 demonstrates that all swelling values obtained above ~430°C lie on swelling curves where the terminal swelling rate of ~1%/dpa has already been reached. Eight of the twelve measurements lie on the above center-plane portion of the duct, where the dpa rate always falling as the temperature increases. The transient duration of swelling in this steel is known to decrease with falling dpa rate and/or increasing temperature [34, 35]. AISI 304 stainless steel exhibits the same behavior [36].

When plotted against dpa and ignoring temperature, swelling across components with sufficient swelling in simple steels such as Kh18H10T and AISI 304 stainless steel is seen to develop "loops" that demonstrate the competitive influence of flux and temperature gradient along the component axis. Figure 9 shows a previously published example of an annealed AISI 304 loop in an EBR-II hexagonal duct [3]. The EBR-II loop is more symmetric with both low and high temperature sides showing the 1%/dpa tangent.

The Kh18H10T loop is not as symmetric, however, primarily due to the much lower inlet temperature of BOR-60 (330 vs. 370°C) compared to EBR-II. As a consequence most of the swelling regime on this duct occurs above the core center-plane. Therefore swelling experiences a continuously declining dpa rate with increasing temperature and produces a rather asymmetric loop, while in EBR-II the swelling regime straddles both increasing and decreasing dpa rates.

When assessing the radiation-induced changes in mechanical properties it is important to realize that most of this duct is dominated by rather high swelling. Although voids initially serve to harden the microstructure [37], large swelling levels allow previously second-order void effects to become dominant [38]. The most consequential of these second-order effects is the strong decrease of elastic moduli at high swelling levels. All of the elastic moduli are well-known to decrease initially at ~2% per each percent of void swelling [39-43].

As a consequence the slope of the elastic region (Young's modulus) of the stress-strain curve decreases, and more even more importantly the barrier strengths of all sinks decrease as the shear modulus likewise decreases. Therefore the yield and ultimate strengths decrease with increasing swelling as seen in Figures 7 and 8, even though the strongly elongation decreases. This behavior has been observed in pure copper [44], but in stainless steel the apparent "softening" is enhanced by specimen failure in the elastic region of the stress-strain curve.



Figure 9. A swelling loop produced in annealed AISI 304 stainless steel employed as a hexagonal wrapper in EBR-II [3]. The fast fluence is specified in units of 10²² n/cm² E>0.1 MeV. The dotted line has a slope of 1%/dpa.

The failure mode is strongly influenced by void swelling in two ways. First, crack initiation arising from void-to-void linkage leads to a fracture surface showing extensive ductile dimpling arising from void interactions, a process covered in detail in other recent papers [45, 46]. Second, nickel segregation to voids, especially at higher swelling levels, leads to a martensitic instability in the matrix that produces a zero tearing modulus and a fracture surface covered with alpha ferrite [6, 47].

Three specimens in this test series failed while loading into the tensile holder and most specimens with >20% swelling appear to have failed by this mechanism. Other high swelling specimens that survived mounting also failed with zero elongation. However, in the current study the failure surface was not examined to confirm the action of the martensite instability.

Results

In this study is reported the highest void swelling level ever observed in an operating fast reactor component, exceeding 54 and perhaps ~60% swelling. At very high swelling levels the Kh18H10T steel approaches a terminal swelling rate of ~1%/dpa after a transient that depends on both dpa rate and irradiation temperature. When irradiated in a fast reactor such as BOR-60 with a rather low inlet temperature, most of the swelling occurs above the core center-plane and produces a very asymmetric swelling loop when plotted vs. dpa.

Voids initially harden the matrix, but as the swelling level becomes significant, the elastic moduli decrease strongly, with the consequence that the steel actually softens with increasing swelling, even as the elongation decreases as a result of void linkage during deformation. Finally, zero deformation levels occur at higher swelling levels, arising most likely from a segregation of nickel to void surfaces that induces a martensitic instability and produces a zero tearing modulus.

Acknowledgements

This work was supported by the Russian Science Program of Higher Education, grant # 2.1.2.7242. The participation of F. A. Garner was supported by the U.S. Department of Energy, Office of Fusion Energy Sciences under Contract DE-AC06-76RLO at Pacific Northwest National Laboratory.

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ANOMALOUSLY LARGE DEFORMATION OF 12Cr18Ni10Ti AUSTENITIC STEEL IRRADIATED TO 55 DPA AT 310°C IN THE BN-350 REACTOR - M. N. Gusev, O. P. Maksimkin, I. S. Osipov (Institute of Nuclear Physics, Kazakhstan) and F. A Garner (Pacific Northwest National Laboratory)*

OBJECTIVE

The objective of this effort is to determine the response to irradiation of austenitic steels at high neutron exposures.

SUMMARY

Whereas most previous irradiation studies conducted at lower neutron exposures in the range 100-400°C have consistently produced strengthening and strongly reduced ductility in stainless steels it now appears possible that higher exposures may lead to a reversal in ductility loss for some steels. A new radiation-induced phenomenon has been observed in 12Cr18Ni10Ti stainless steel irradiated to 55 dpa. It involves "a moving wave of plastic deformation" at 20°C that produces "anomalously" high values of engineering ductility, especially when compared to deformation occurring at lower neutron exposures. Using the technique of digital optical extensometry the "true stress σ –true strain ε " curves were obtained. It was shown that a moving wave of plastic deformation occurs as a result of an increase in the intensity of strain hardening, $d\sigma/d\epsilon(\varepsilon)$. The increase in strain hardening is thought to arise from an irradiation-induced increase in the propensity of the $\gamma \rightarrow \alpha$ martensitic transformation.

PROGRESS AND STATUS

Introduction

It is generally accepted that irradiation of stainless steels at temperatures of 100-400°C leads to a rapid increase in strength and a concurrent reduction in both uniform and total elongation during deformation, a behavior that is clearly seen in "engineering" stress-strain curves and that is almost always associated with early flow localization leading to necking.

Using a technique called "digital marker extensometry", however, we have shown recently that the stress-strain deformation characteristics (true stress-true deformation) continue unchanged in the necking region even though the remainder of the specimen no longer participates in the deformation process [1, 2]. Figures 1 and 2 demonstrate this behavior for stainless steels irradiated in two different reactors. These results signal that a distinction should be made between "true embrittlement" involving suppression of material capability for plastic deformation and "quasi-embrittlement" involving a reduction of uniform and total deformation as a result of development of a macroscopic neck.

Another well-accepted perception is that continued neutron exposure quickly leads to a saturation in mechanical properties that remains unchanged until significant void swelling is attained [3-7]. It now appears that this perception must be at least partially modified for relatively low irradiation temperature and very high fluence exposure, especially for steels prone to an austenite to martensite instability. In this paper we demonstrate that the trend toward reduced elongation with increasing exposure can be reversed at very high dose.

^{*} Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830.

Experimental Procedure

A hexagonal wrapper constructed from 12Cr18Ni10Ti steel was removed from a spent fuel assembly designated CC-19 after irradiation in the reflector region of the BN 350 fast reactor core. The wrapper walls were 2 mm thick with face-to-face distance of 96 mm. Prior to irradiation the wrapper was formed with a final cold deformation of 15 to 20%, followed by annealing at 800°C for an hour. During irradiation the wrapper reached a maximum dose and temperature of 55 dpa and 310°C. The inlet temperature of 280°C defines the lowest temperature of the wrapper.



Figure 1. Engineering curves (1, 2, 3) and " $\sigma_i - \varepsilon_i$ " relationships (1', 2', 3') for non-irradiated (1) and irradiated (2, 3) stainless steels tested at 20°C. 2 – 12Cr18Ni10Ti (WWR-K thermal reactor, 1.4x10¹⁹ n/cm² and 80°C), 3 – 08Cr16Ni11Mo3 (BN-350 fast reactor, 15.6 dpa and 340°C).



Figure 2. 12Cr18Ni10Ti irradiated to $1.4 \times 10^{19} \text{ n/cm}^2$ (E>0.1) in the WWR-K reactor at 80°C and tested at 20°C. Comparison of engineering (black) and true strain curves (designated by colors) for three areas, showing that all three areas follow the same true curve initially, but as necking develops the other areas drop out of the deformation process.

Hexagonal cross sections of 10 mm height were cut at various elevations between +160 mm and – 160 mm measured relative to the core center-plane. From these sections flat rectangular specimens of size $20 \times 2 \times 0.3$ mm were mechanically produced. Subsequently, mini-tensile specimens with gauge length of 10x2x0.3 mm were produced by mechanical grinding and electrolytic polishing to achieve the desired dimensions and surface quality.

Pneumatic grips were used for holding the specimen in an Instron-1195 tensile machine. Uniaxial tensile tests on both unirradiated and irradiated specimens were performed at 20°C at a strain rate of 8.3×10^{-4} sec⁻¹.

A technique called "digital marker extensometry" was used which incorporates digital video recording of the specimen during deformation. The surface of the specimen was marked with small (~0.3 mm) dots of dye in order to track the deformation on a local level. This technique was described in an earlier report and is especially useful in observing highly-irradiated miniature specimens subject to intense flow-localization [1, 2]. Application of this technique makes it possible to obtain the "true stress–true strain" behavior for a miniature specimen, as well as to identify the localized deformation region and to trace its evolving geometry during continuous deformation.

Results

In Figure 3 the engineering diagrams of both irradiated and unirradiated specimens are shown. As expected the unirradiated steel is characterized by high ductility and high ability to strain harden. Following irradiation to ~15 dpa at 340°C the yield strength of a similar steel strongly increases and a neck develops just after reaching the yield point. The uniform elongation is very small and total ductility falls to 3.7%.



Figure 3. Engineering diagrams (curves 1, 2, 3) at 20°C for 12Cr18Ni10Ti (1 and 2) and 08Cr16Ni11Mo3 irradiated in BN-350 (3) along with the corresponding "true" curves (1' and 3'): 1 – unirradiated steel; 2 –irradiated to 55 dpa; 3 –irradiated to 15.6. Curve 2 is shifted to the right to make visualization easier.

Based on current perceptions of saturation, one would expect that steel irradiated up to 55 dpa would achieve deformations <3.7%, even in the absence of void swelling. However, a ductility of 35 to 40% was achieved in this specimen. This result was confirmed by other tests to be typical and not an anomaly. Note that after a small decrease in strength after yielding there is an extended plateau without significant increase in load.

As shown in Figure 4, a series of freeze-frame video images taken during tensile testing shows that localized deformation initially forms near the upper gripp position, most likely due to stress concentration by the gripp. However, in contrast to irradiation to lower doses, a neck did not develop at 55 dpa. The localized deformation band instead progressively extended its lower boundary, producing a moving deformation front or deformation wave that moved down the specimen. The wave moved along ~2/3 of the specimen length. All of the deformation at a given instant appeared to occur at the wave front with material behind or in front of the wave being very weak or nonexistent.



Figure 4. Freeze frames taken during deformation at 20°c of the specimen irradiated to 55 dpa. Photographs have been digitally processed to increase the contrast. The boundary between the lighter distorted and darker undistorted areas moves downward with time. Distorted dots behind the boundary also show the local distortion. Arrows on photos 4 through 7 show the second later-developing and immobile neck.

Figure 5 shows the distribution of local deformation over the specimen length as the test progresses. An abrupt increase in local deformation from zero up to 30 to 35 % is observed at the moment the front passes that point. Failure with local deformation exceeding 60% occurred very near to the original place where the deformation wave appeared. It appears that the original wave might have continued its downward progress if failure had not occurred near the top of the specimen. Otherwise, formation of this second front had no effect on the progress of the original wave.

Failure arose via development of a second late-developing deformation band that was immobile. This band is marked by arrows on frames 4 through 7 in Figure 4. The immobility of the second deformation band was probably a result of the constraints imposed on the band by both the upper gripper and the upper boundary of the original wave. This suggests that deformation within the

deformed band is terminal and will not allow the second band to propagate through already deformed material.



Figure 5. Distribution of local deformation along the length of the specimen irradiated to 55 dpa at various stages of the experiment. Figures 1 through 7 correspond to numbers of photographs in Figure 4.

Discussion

The condition for occurrence and development of localized deformation of the neck is [8, 9]

$$d\sigma/d\varepsilon \leq \sigma$$
,

(1)

which can be rewritten in more convenient form:

$$d\sigma/d\varepsilon - \sigma \le 0 \tag{2}$$

One may show that localization of deformation in compliance with a given condition starts at the moment when local strain hardening can no longer compensate for geometrical "softening" which occurs as a result of a decrease in the specimen cross section.

It's clear that for stopping of local neck formation and displacement of the deformation into neighboring, less deformed space, the law which governs hardening must be changed, i.e., it is necessary that relation (2), on achieving a certain extent of deformation, becomes invalid. As a rule this does not happen in either unirradiated or neutron-irradiated pure metals, where $d\sigma/d\epsilon$ always decreases as ϵ grows (see for example curve 1 on Figure 6).

Figure 6 presents "stress-deformation" curves obtained using the marker extensionetry technique. One may observe (see curve 3' Figure1 and curve 2 Figure6) that in 12Cr18Ni10Ti at 55 dpa the initial stage of deformation is close to that of 08Cr16Ni11Mo3 at ~15 dpa. Almost immediately on reaching the yield point, $d\sigma/d\epsilon$ - σ reduces to negative values, and the neck develops. However, in contrast to other materials we have studied, at local deformations of ~25 to 30% a smooth upward trend is observed in the " σ - ϵ " curve. As $d\sigma/d\epsilon$ increases and the value of " $d\sigma/d\epsilon$ - σ " becomes positive, indicating that strain hardening is increasing strongly.



Figure 6. Curves of "true stress–true strain" for unirradiated 12Cr8Ni10Ti specimen (1) and 55 dpa specimen (2). The dependence of $(d\sigma/d\epsilon - \sigma)$ versus ϵ (for 55dpa-sample) is shown in curve(3).

Apparently it is the increase in $d\sigma/d\epsilon$ that leads to suppression of development of a local neck, thereby displacing the deformation source to neighboring, undeformed space, thus generating the deformation wave. We consider it to be very significant that the second late-forming deformation band could not move through the previously deformed region.

One potential source of the wave phenomenon is the $\gamma \rightarrow \alpha$ martensitic transformation. This lownickel steel is known to be very sensitive to martensite formation, especially during low temperature deformation, and to increase in propensity toward martensite with radiation-induced hardening and radiation-induced segregation [10]. The fact that this behavior occurs at higher exposures but not at lower doses where saturation of strength had already occurred was at first thought to reflect some second-order effect such as the progressive transmutation-induced loss of Mn, one of the γ stabilizing elements. A significant loss of the Mn due to transmutation has now been ruled out, with calculations showing only 2-3% maximum loss. Therefore some other mechanism is being sought, perhaps one related to radiation-induced segregation.

Similar deformation behavior involving an increase in intensity of strain hardening has been observed in this same steel in the unirradiated condition during deformation at cryogenic temperatures [11]. Intense martensitic transformation was cited as the cause, but the marker extensometry technique wasn't used in this experiment so it is not certain whether a deformation wave was associated with this behavior.

Conclusions

A new radiation-induced phenomenon has been observed in steel 12Cr18Ni10Ti irradiated to 55 dpa. It involves "a moving wave of plastic deformation" at 20°C that produces "anomalously" high values of engineering ductility, especially when compared to deformation occurring at lower neutron exposures or for more stable steels. Using the technique of digital optical extensometry the "true stress σ –true strain ε " curves were obtained. It was shown that a moving wave of plastic deformation occurs as a result of an increase in the strain hardening, $d\sigma/d\varepsilon(\varepsilon)$. The increase in strain hardening is thought to arise from an irradiation-induced increase in the propensity of the $\gamma \rightarrow \alpha$ martensitic transformation

Acknowledgements

The Kazakh portion of this work was supported by the Ministry of Energy and Mineral Resources of the Republic of Kazakhstan. The US portion was sponsored by the Office of Fusion Energy, US Department of Energy.

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ANISOTROPIC SWELLING OBSERVED DURING STRESS-FREE REIRRADIATION OF AISI 304 TUBES PREVIOUSLY IRRADIATED UNDER STRESS - F. A. Garner (Pacific Northwest National Laboratory)^{*}, J. E. Flinn, (Argonne National Laboratory, EBR-II Project, [Retired]) and M. M. Hall, (Bechtel Bettis Company)

OBJECTIVE

The objective of this effort is to determine the distribution of strains that arise from irradiation creep and void swelling in response to stress state and stress history.

SUMMARY

A "history effects" experiment was conducted in EBR-II that involved the reirradiation of AISI 304 cladding and capsule tubes. It is shown that when irradiated tubes had not previously experienced stress, subsequent irradiation led to additional swelling strains that were isotropically distributed. However, when tubes previously irradiated under a 2:1 biaxial stress were reirradiated without stress the additional swelling strains were not isotropically distributed. The tubes retained a memory of the previous stress state that appears to be attempting to distribute strains in the directions dictated by the previous stress state. It is clear, however, that the memory of that stress state is fading as the anisotropic dislocation microstructure developed during irradiation under stress is replaced by an isotropic dislocation microstructure during subsequent exposure in the absence of stress.

It is also shown that once the transient regime of swelling nears completion, further changes in stress state or irradiation temperature have no influence on the swelling rate thereafter.

PROGRESS AND STATUS

Introduction

Structural steels anticipated for fission and fusion applications will experience time-dependent changes in the radiation environment, i.e. stress level, stress state, irradiation temperature and dpa rate. All of these variables are known to affect void swelling when maintained at constant values [1]. There are insufficient data available, however, to allow confident prediction of the effects of changes in these variables on subsequent behavior of swelling during continued irradiation. Data on the effect of changes in stress state or irradiation temperature are especially lacking.

In this paper are presented the results of a reirradiation experiment conducted in EBR-II that addresses the effect of an abrupt loss of the stress and/or an increase in the irradiation temperature once swelling is already in progress. This "history effect" experiment was designed to determine whether there is some memory of previous conditions that persists after a change has occurred. The experiment was conducted in the mid-1970s but has only recently been examined for relevance to current design needs. It involved the reirradiation of concentric tube segments where the inner tube was originally irradiated under stress but the outer tube was stress-free.

Experimental Procedure

Materials

Annealed Type 304L stainless steel was obtained from a surveillance program conducted to qualify EBR-II Mark-II metal driver fuel pins. With the exception of a few unirradiated archive specimens, the specimens used in this study were taken from an fuel pin experiment consisting of encapsulated driver

^{*} Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830.

fuel in which the fuel elements, clad with Type 304L stainless steel, were sodium-bonded and sealed in Type 304L stainless steel capsules. The cladding and the capsule tubes were manufactured from different heats of Type 304L stainless steel. Sections of the unirradiated, as-fabricated cladding and capsule tubing materials were analyzed by wet chemistry techniques, and the results are given in Table 1, showing some differences in elemental composition that are not thought to impact the interpretation of the derived data.

	Mn	Р	S	Si	Ni	Cr	Ti	Cu	Мо	Со	С
cladding	1.66	0.016	0.014	0.59	10.6	18.3	<0.01		0.02		0.03
capsule	1.37	0.010	0.007	0.62	9.26	18.3	0.02	0.074	0.02	0.05	0.03

Table 1. Composition, wt %

Specimen Preparation and Measurements

Cladding-capsule specimen pairs were obtained by sectioning through cladding and capsule tubing at the same elevation. The cladding-capsule pairs experienced essentially the same flux-spectral exposures, but the capsules were stress-free and operating at ~50°C lower temperatures. Some specimen sets were extracted above the fuel column at lower fluence levels while others were extracted from the fueled regions at higher fluences.

Fuel was removed from the cladding sections by chemical dissolution of the fuel. Cladding and capsule sections had nominal outer diameters of 4.42 and 7.37 mm, respectively, and were cut to be approximately 25.4 mm long. Each tube had its ends ground and polished to ensure suitable surfaces for length measurements before and after reirradiation.

Specimen	Fluence, 10 ²⁶	Time averaged	Total diametral	Swelling,	Peak hoop
no.	nm ⁻² (E>0.1	temperature, °C	change, %	%	stress, MPa
	MeV)				
27	5.92	528	9.42	18.33	116
28	4.10	557	2.97	6.10	116
31	6.02	532	8.56	15.81	118
32	4.18	552	4.09	7.92	118
35	5.62	548	9.29	15.87	100
36	4.19	577	2.77	5.19	100
41	0		0	0	0
23	4.34	498	2.28	4.74	40
24	2.85	556	0.88	0.90	40
29	5.92	480	2.03	6.66	0
30	4.10	513	0.39	1.53	0
33	6.02	477	2.21	7.03	0
34	4.18	509	0.50	1.93	0
37	6.02	493	2.11	7.38	0
38	4.19	527	0.37	1.77	0
43	0		0	0	0

Table 2. Initial conditions of previously irradiated cladding and capsule tubes

Specimen length, diameters, and densities were measured before and after reirradiation. Length and diameter measurements were obtained from an optical-reading dial gauge, having a precision of \pm 0.005mm. Densities were determined by immersion techniques having an accuracy of approximately \pm 0.0005 of the measured values.

The specimens selected for this study are described in Table 2 which presents the initial irradiation temperature, neutron exposure (E >0.1 MeV), and peak hoop stress level. The initial irradiation temperatures are calculated time-averaged mid-wall values, and the stresses are based on the plenum pressures measured on the fuel elements prior to sectioning into specimens for reirradiation. There was initially some uncertainty concerning the stress state, however.

During the initial irradiation cladding stresses steadily increased for two reasons. First, the fuel swells and contacts the cladding near burn-up levels of ~2.0 at % [2-4], and second, fission-product-gas pressure increases linearly with fuel burnup above 2.0 at % [4]. In the absence of fuel-clad mechanical interaction, the ratio of hoop stress to axial stress is expected to be 2/1 arising from gas loading. The deviation from the 2/1 value depends on the contribution from mechanical interaction. If fuel swelling is the only source of stress and the shear strength of the fuel is large, the stress state approaches 1/1.

The nature of the stress state can be determined from a comparison of the integrated length changes with the integrated diametral strains. If the total length change measured for the fuel element corresponds to the integrated average of the total diameter profile, the strain state and therefore the stress would be 1/1. If, however, the measured total length change corresponds to the integrated average of the diameter-swelling profile, the stress state would be 2/1, since creep, which is volume conservative, is not expected to contribute to length change for this stress state.

Results of the dimensional analysis for four fuel elements are shown in Table 3. It was concluded that the stress state that best describes behavior of the fuel elements is nearer to 2/1 biaxial than 1/1 biaxial, since the measured length changes of the element correspond closely to the average swelling strain. The observation of a 2/1 biaxial stress state is important for analysis of the subsequent deformation state, because we can assume that the stress on the cladding is a function only of the plenum gas pressure, which is known as a function of time. The hoop stresses ascribed to the cladding specimens in Table 2 were calculated using the gas-pressurized thin-wall approximation.

Pin number	1/3 of integrated average of swelling, mm	Integrated average of total diameter change, mm	total length change, mm
265	21.3	35.8	19.7
267	15.6	26.3	14.5
284	16.0	30.1	15.8
200	17.3	28.1	17.3

Table 3. Analysis of length change of four fuel elements to determine the biaxial stress ratio, showing that the stress state was determined primarily by gas loading and not by fuel-clad mechanical interaction

Reirradiation Conditions

The reirradiation vehicle was a NaK-filled sub-capsule centered inside a Mark B-7 capsule. The specimens were placed in four tiers inside the sub-capsule. All specimens were axially located within 66 mm of the reactor core center-plane. Within this region, the neutron flux profile was relatively flat, and
therefore all specimens attained nearly the same additional fluence of 2.0×10^{26} n/m² (E>0.1 MeV) or ~10 dpa.

The thickness of the helium insulation gap and the gamma heating generated in the subcapsule and its contents determined the temperature which was measured using two passive thermal-expansion– difference (TED) monitors with an accuracy of $\pm 5^{\circ}$ C. The two monitors indicated 540° C in the top-tier and 546 °C on the bottom tier after corrections were made for irradiation-induced swelling of the TEDs.

Results

Cladding and capsule strains were determined from the length, diameter, and immersion density measurements taken before and after each irradiation period. Length and diameter strains were taken as the ratio of the change in length and diameter to the initial length and diameter of each specimen. Table 4 presents a summary of the strain data obtained from the second irradiation segment.

	Peak hoop	Swelling after				
	stress in first	second	Incremental	Incremental		
Specimen	irradiation	irradiation	diameter	length	Incremental	Anisotropic
no.	segment, MPa	segment, %	change, %	change, %	swelling, %	strain, % **
27	116	27.26	3.28	2.81	8.93	0.303
28	116	15.86	4.29	3.13	9.76	1.037
31	118	25.17	3.37	2.88	9.36	0.250
32	118	17.72	3.53	3.24	9.8	0.264
35	100	25.91	3.82	2.71	10.04	0.474
36	100	13.17	3.05	2.74	7.98	0.390
23	40	11.6	2.33	2.01	6.86	0.0436
24	40	8.54	2.53	2.33	7.64	-0.016
41	0	0.01	-0.07	0.07	0.01	-0.073
		0				
29	0	10.33	1.30	1.23	3.67	0.08
30	0	5.31	1.25	1.10	3.78	-0.01
33	0	11.24	1.32	1.33	4.21	-0.08
34	0	5.86	1.36	1.26	3.93	0.05
37	0	11.68	1.58	1.32	4.30	0.15
38	0	5.52	1.37	1.30	3.75	0.12
43	0	0.32	0.09	0.10	0.32	-0.02

Table 4. Summary of strain data after second irradiation segment at zero stress.

** Anisotropic strain was calculated by using the incremental diameter change minus one third of the incremental swelling value.

The total swelling strain for the cladding and capsule specimens before and after the reirradiation experiment is shown in Figures 1 and 2 as a function of neutron exposure. If differences in prior temperature are ignored, the cladding, even after the fuel has been removed, continues to swell at a rate that is significantly greater than that for the capsule tubing. Contrary to expectations prevalent when this experiment was conducted in the late 1970s, the swelling rate did not fall upon removal of the applied stress.



Figure 1. Swelling observed in reirradiation of previously stressed cladding specimens

Note that once swelling in excess of several percent is attained the average swelling rate of the cladding at 540°C in the second irradiation segment is ~1%/dpa as is known to occur in AISI 304 and other 300 series steels [1, 5, 6]. While the average incubation intercept is on the order of 2-3 x 10^{22} n/cm² (E>0.1 MeV) in the cladding, it is somewhat larger in the capsule material which was irradiated initially at lower temperatures, and the average swelling rates are lower, indicating that transient swelling regime is probably still in progress in the second segment.



Figure 2. Swelling observed in unstressed capsule specimens.

The spatial distribution of dimensional changes in the cladding and capsule specimens after reirradiation show the most interesting effects, as can be seen in Figure 3. In this figure, the diameter and length

changes that occurred during reirradiation are plotted against one-third of the volume swelling strain. This figure shows that while the capsule specimens essentially swelled isotropically during the reirradiation, the cladding appears to have swelled anisotropically. In all cases the diameter strain for the cladding is significantly larger than the length strain, as would be expected if the cladding retained some memory of the original 2:1 biaxial stress state.

The anisotropic components of the diameter strain in the cladding after reirradiation are shown in Figure 4. The slope of the solid line drawn through the initial anisotropic strain values is the anisotropic strain rate expected for cladding driven by gas loading. For each reirradiated cladding specimen, the dashed lines connect the initial and final strain values. Figure 4 shows that during the second irradiation segment, the average rate of anisotropic growth is substantially less than during the initial irradiation, but is nevertheless significant. It therefore appears that memory of the stress state was fading over the second segment. One would expect that the degree of anisotropy would increase with the hoop stress and roughly this is the behavior observed in Figure 5, indicating qualitatively that the retained anisotropy is most likely stress-related.

Discussion

The results clearly show that there is a retained but probably diminishing memory in the microstructure of the previous stress state and that the memory is strongest for higher stress levels. This memory is probably expressed in the stress-induced anisotropic distribution of Burgers vectors of Frank loops and line dislocations that is known to develop during irradiation under stress [7-9]. Continued irradiation in the absence of stress is expected to erase this anisotropy eventually, but averaged over the lifetime of the dislocation array there is a net anisotropic growth attained. We can not from these data alone determine whether complete relaxation of dislocation anisotropy has occurred at or before 10 dpa, or whether relaxation might still be in progress, since we are seeing only the integrated effect of the anisotropy. Another radiation segment would be required to determine if the anisotropy is still growing or not.



Figure 3. Isotropic swelling in the second irradiation segment observed in capsule specimens in contrast to highly anisotropic swelling observed in previously stressed cladding specimens.



Figure 4. Anisotropic strain components observed in previously stressed cladding specimens. The solid line represents the expected behavior if the 2:1 biaxial stress state was maintained in the second irradiation segment.



Figure 5. Anisotropic growth strain observed as a function of final hoop stress level.

It is now well-known but it was not recognized at the time this experiment was conducted that stress only accelerates the transient regime of swelling [1]. The expectation that the swelling rate would increase until it reached the terminal swelling rate of ~1%/dpa, and would not fall for any reason thereafter was also not known when this experiment was conducted. There was some speculation at that time, however, that the steady-state swelling rate might depend on the stress level and possibly the stress state. We know now

that stress affects only the transient duration and not the steady-state swelling, as was confirmed in this experiment.

This experiment also involved substantial increases in the irradiation temperature for the unstressed capsule specimens while most of the cladding specimens were not subjected to large changes. From this study alone, we cannot with confidence determine the effect that temperature changes may have had on swelling. In an earlier study by Yang and Garner [10] on AISI 316 stainless steel it was shown that if the transient regime was nearly complete when temperatures were changed, neither increases or decreases in temperature had any effect on the subsequent swelling rate, especially if it was already approaching 1%/dpa.

Bloom and Wolfer performed a reverse version of this experiment [11]. They made flat tensile specimens from the unstressed walls of an irradiated EBR-II safety rod thimble and then subjected them to applied stresses arising from differential swelling that was driven by a much higher-swelling steel. While their objective was to study in-reactor stress rupture, we can use their data to observe the influence of late-term increases in stress state on subsequent swelling.

In the Bloom-Wolfer experiment the specimens in the first segment were irradiated over a wide range of fluences and at temperatures of 400, 450 and 550°C, while the second irradiation segment proceeded only at 450°C. Thus the experiment not only explored increases in stress state but also isothermal and non-isothermal (increases and decreases) temperature histories. Figure 6 shows that all swelling curves proceed as expected, increasing toward 1%/dpa with increasing fluence, although it appears that the low fluence specimens may have experienced a somewhat shorter transient regime as a result of stress application when compared to the higher fluence specimens that were beyond the transient regime before the second irradiation segment started.



Figure 6. Swelling observed by Bloom and Wolfer in a reirradiation experiment conducted on AISI 304 stainless steel where previously non-stressed specimens were subjected to stress in the second irradiation segment. Temperature changes were also involved in this experiment.

Conclusions

If AISI 304 stainless steel was already swelling at a significant rate while under neutron irradiation and stress, removal of the stress will not change the subsequent swelling rate. However, a memory of the previous stress state is retained and produces an anisotropic distribution of strains consistent with the strain distribution behavior operating when the stress was present. It is clear however, that this is a transient behavior with the memory fading during continued irradiation. When there was no stress previously operating on the specimen the strains during subsequent irradiation are isotropically distributed as would be expected in stress-free swelling [1].

Once the transient regime of swelling is nearing completion, changes in stress state or temperature appear to have no effect on the subsequent swelling rate.

Acknowledgements

The experimental portion of this work was conducted in the late 1970s under the auspices of the U.S. Liquid Metal Reactor Program of USDOE. The recent analytical participation of F. A. Garner was sponsored by the Office of Fusion Energy, USDOE under Contract DE-AC06-76RLO 1830 at Pacific Northwest National Laboratory.

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7.0 MHD INSULATORS, COATINGS, INSULATING CERAMICS AND OPTICAL MATERIALS

FURTHER CHARACTERIZATION OF THE TRANSFORMATION OF Al₂O₃ TO LiAIO₂ IN Pb-17Li AT 800°C – B. A. Pint and K. L. More (Oak Ridge National Laboratory, USA)

OBJECTIVE

One proposed U.S. test blanket module (TBM) for ITER uses ferritic-martensitic alloys with both eutectic Pb-Li and He coolants at ~475°C. In order for this blanket concept to operate at higher temperatures (~750°C) for a DEMO-type reactor, several Pb-Li compatibility issues need to be addressed. One issue is functional coatings such as alumina for corrosion resistance and a tritium permeation barrier.

SUMMARY

In order to study the compatibility of $-Al_2O_3$ with Pb-17Li, a FeCrAl substrate was pre-oxidized at 1000°C to thermally grow an external alumina scale. The specimen was then isothermally exposed to Pb-Li for 1000h at 800°C in a Mo capsule. The alumina layer prevented dissolution of the metallic substrate but was found to transform to LiAlO₂. The current report includes additional XRD and TEM characterization of the external oxide layer before and after exposure to Pb-Li.

PROGRESS AND STATUS

Introduction

A recent focus of the U.S. fusion energy program has been on developing a proposal for a test blanket module (TBM) for ITER. The dual coolant Pb-Li (DCLL) TBM concept has both He and eutectic Pb-Li coolants and uses ferritic steel as the structural material and a SiC/SiC composite flow channel insert (FCI).[1] The interest in this concept has focused compatibility-related research on Pb-Li. Many materials have poor compatibility with liquid Li,[2] but the activity of Li is much lower in Pb-17Li,[3] and this allows a wider range of materials to be considered. However, Pb-Li still readily dissolves many conventional alloys. While the TBM maximum operating temperature will be <500°C, this blanket concept would be more attractive for a commercial reactor with a higher maximum operating temperature, perhaps >700°C if oxide dispersion strengthened (ODS) ferritic steels [4] were used. However, at these higher temperatures, compatibility is even more of a concern. Therefore, static capsule testing has been conducted on materials at 700° and 800°C.[5,6] In order to study the Pb-Li compatibility and potential for corrosion protection of -Al₂O₃, one FeCrAl substrate was pre-oxidized at 1000°C to thermally grow an external alumina scale. The specimen was then isothermally exposed to Pb-Li for 1000h at 800°C in a Mo capsule.[6] A previous report characterized the external oxide layer before and after exposure to Pb-Li and found that the -Al 2O3 layer transformed to LiAlO2.[7,8] The current report includes additional characterization of the oxide layer before and after exposure to Pb-Li at 800°C.[8]

Experimental Procedure

Specimens of ODS FeCrAl (Plansee alloy PM2000, Fe-20at.%Cr-10.6Al-0.7O-0.4Ti-0.2Y) with dimensions of ~15 x 18 x 1-1.5mm were polished to a 0.3µm finish. Pre-oxidation of both specimens was conducted with a rapid insert to a pre-heated furnace at 1000°C in dry, flowing O_2 for 2h. One specimen was then held with Mo wire in a Mo capsule containing 125g high purity (99.9999%) Pb shot (chemical composition in Table 2) and 0.86g Li to make Pb-17at.%Li. The Mo capsule was loaded in an argon-filled glove box and it was then welded shut to prevent interstitial contamination during the test. The Mo capsule was then sealed inside a type 304 stainless steel capsule and was heated inside a resistively-heated box furnace in air to 800°C for ~1h to allow the Pb and Li to melt. The capsule was then inverted to submerge the specimen in Pb-Li. After 1,000h at 800°C, the system again was inverted to allow the liquid metal to drain away from the specimen. To remove residual Pb-Li on the specimen, it was soaked in a 1:1:1 mixture

of acetic acid, hydrogen peroxide and ethanol for up to 72 h. Both specimens were characterized including x-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) equipped with an energy dispersive spectrometer (EDS). Cross-sectional TEM specimens were prepared using focused ion beam thinning. A W layer was applied to the specimen surface to protect the outer surface of the reaction product.

Results and Discussion

Prior reports described the specimen mass change and oxide morphologies and metallographic crosssections.[5-8] To further clarify the transformation of the external oxide layer from $-Al_2O_3$ to LiAlO₂, Figure 1 shows the XRD results with and without exposure to Pb-Li. The XRD spectra for the unexposed -Al $_2O_3$ scale is shown in Figure 1a with peaks matching JCPDS card #83-2080. The peaks are relatively weak for the thin (<0.5µm) oxide layer compared to the strong ferritic substrate peak. In Figure 1b, all of the major peaks on the Pb-Li exposed specimen matched with JCPDS card #38-1464 for tetragonal LiAlO₂. The peaks are stronger in this case because the oxide layer increased in thickness after exposure to Pb-Li.[7]

Because the pre-oxidized $-AI_2O_3$ layer was so thin, a TEM cross-section was necessary to examine the microstructure of the reaction product. Figure 2 shows a STEM cross-section along with EDS maps of several minor elements. The STEM annular dark field image shows a thin outer layer and an inner layer with a columnar grain structure, typical of the scale formed on Y-doped FeCrAI.[9] Fine voids (dark in this image) could be observed in the oxide, but generally the layer was dense and adherent. The thin (~100µm) outer layer was rich in Cr and Fe, Figures 2b and 2c, typical of the first-formed transient oxide on FeCrAI.[10] However, very little Cr and Fe was detected below this outer layer. Within the -AI $_2O_3$ inner layer, some second phase oxide precipitates were observed, rich in Y and/or Ti, Figures 2d and 2e. These elements also were observed to be segregated to the -AI $_2O_3$ grain boundaries in the maps.[11-13] Arrows point to the Y- and Ti-rich oxides and grain boundaries, Figures 2d and 2e.

For the oxide layer after exposure to Pb-Li, selected area diffraction (by TEM) was consistent with the lattice spacings of the tetragonal structure of $LiAlO_2$. Unfortunately, the $LiAlO_2$ TEM section was easily damaged by the electron beam. Therefore, more extensive chemical analysis (such as Figure 2 for the $-Al_2O_3$ section) was not possible.

Because the temperature of this exposure is higher than expected in most blanket concepts, additional experiments are being planned to study this reaction at lower temperatures. A capsule is currently being assembled to expose a similarly pre-oxidized ODS FeCrAl specimen for 1,000h at 700°C in Pb-Li.

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Figure 1. X-ray diffraction from ODS FeCrAI (a) after pre-oxidation for 2h at 1000°C and (b) after pre-oxidation and subsequent exposure for 1000h at 800°C in Pb-Li.

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8.0 BREEDING MATERIALS

No. contributions.

9.0 RADIATION EFFECTS, MECHANISTIC STUDIES, AND EXPERIMENTAL METHODS

MULTISCALE MODELING OF POINT DEFECT INTERACTIONS IN BCC FE-CR ALLOYS -

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OBJECTIVE

The objective of this work is to investigate the interaction of Cr with point defects in BCC Fe-Cr alloys within a hierarchical multiscale framework and to evaluate the diffusivity of Cr and Fe by vacancy and interstitial migration mechanisms within the context of Cr segregation behavior at grain boundaries.

SUMMARY

Predictive performance models of ferritic/martensitic alloys in fusion neutron irradiation environments require knowledge of point defect interactions with Cr, which can be investigated by a multiscale modeling approach. Molecular dynamics simulations, using Finnis-Sinclair-type potentials, have been used to investigate interstitial diffusion, and the resulting atomic transport of Cr and Fe using interatomic potentials that predict Cr as either an under - or over-sized solute with otherwise constant materials properties. *Ab initio* calculations on vacancy–Cr interactions reveal complex electronic and magnetic interactions between Cr and Fe. These values have been used to calculate the ratio of Cr-to-Fe diffusion by a vacancy mechanism using the LeClaire multi-frequency model and a kinetic lattice Monte Carlo model, both of which indicate that Cr diffuses faster than Fe by a vacancy mechanism. The results are discussed in the context of the radiation-induced segregation of Cr at grain boundaries in BCC Fe-Cr alloys.

PROGRESS AND STATUS

Introduction

Ferritic/martensitic Fe-Cr alloys are candidate first wall and breeder blanket materials for future Fusion reactors, in addition to candidate fuel dadding, pressure vessel and structural materials for Generation IV reactors [1]. Fundamental understanding of microstructural evolution in these alloys under conditions of fission and fusion neutron irradiation is important, since microstructural changes control mechanical behavior and ultimately, performance.

The observed microstructural evolution of irradiated Fe-Cr alloys include a number of observations that indicate the importance of Cr – point defect interactions, most notably the non-monotonic dependence of Cr on irradiation-induced swelling [2,3], complex shifts in the stage I defect recovery processes [4] and short-range ordering at low (<10%) Cr concentrations [5]. Furthermore, there is an indication that Cr segregation behavior under irradiation is more complex than in irradiated austenitic FCC alloys, where Cr depletes at grain boundaries [1,6]. As indicated in Figure 1, the observed radiation-induced segregation behavior of Cr in ferritic/martensitic Fe-Cr based alloys and steels involves both enrichment and depletion at grain boundaries, with no clear trend as a function of dose, temperature or Cr content [6]. Enrichment of Cr at grain boundaries can lead to precipitation of secondary phase particles, and negatively affect the mechanical behavior and fracture toughness [1]. Although Cr has been shown to have minimal effect on point defect creation in displacement cascades [7,8], the subsequent diffusion of point defects and their interactions with solutes, impurities, and transmutants ultimately dictates the microstructural evolution and changes in mechanical properties [9-14].

The objective of the present report is to investigate the interaction of Cr with point defects in BCC Fe-Cr alloys within a hierarchical multiscale framework and to evaluate the diffusivity of Cr and Fe by vacancy and interstitial migration mechanisms. The modeling results will be discussed within the context of the segregation behavior of Cr at grain boundaries.



	? ₀	? 2	? ₃	? 4	? ₃	, ? 4	? ₃ "	?"	? 5	?6
(2x2x2) 0.61	0.56	0.68	0.57	0.65	0.55	0.47	0.63			
(3x3x3) 0.66	0.52	0.66	0.62	0.65	0.59	0.60	0.57	0.74	0.69	

Table 1. Migration energy barrier (eV) corresponding to the vacancy – atom exchanges for a vacancy in proximity to a Cr solute atom in the BCC lattice, following Le Claire's definition [27].

Results

Fe and Cr diffusivity by an interstitial migration mechanism

Wong and co-workers have previously shown, using either the Fe-Cr I or Fe-Cr II potential, the effect of Cr solute atoms is to decrease the diffusivity of single interstitials and small clusters of interstitials [21]. Terentyev and co-workers have obtained similar results [22]. The addition of oversized Cr causes the interstitial dumbbells to rotate more frequently to avoid mixed dumbbell formation; in contrast, the positive binding of mixed dumbbells traps interstitials at the undersized Cr and hinders long translational jumps. Here, we have extended the previous work by calculating the ratio of Cr-to-Fe diffusion by an interstitial mechanism. Figure 2 plots the ratio of the Cr and Fe diffusivities in an Fe-10%Cr alloy obtained with a single, di- and tri-interstitial for the Fe -Cr I and Fe-Cr II potentials. The results are consistent with the binding energies, namely that the Fe-Cr I potential predicts that Cr is a slower diffuser than Fe when Cr is oversized (repulsive interaction with the interstitial). In contrast, when Cr is undersized/attractive in FeCr II, Cr diffuses 10-30% faster than Fe as a consequence of mixed dumbbell formation and the Cr-interstitial dumbbell binding energy. The Fe-Cr II potential is consistent with the size effects and interstitial binding energies for Cr atoms in BCC Fe-Cr alloys predicted by ab-initio calculations [23], and thus the preliminary conclusion of these MD simulations is that Cr diffuses faster than Fe by an interstitial mechanism. Faster diffusivity of Cr by an interstitial mechanism is consistent with an inverse Kirkendall-based model [13] whereby Cr is dragged in the same direction as the interstitial flux, which would produce Cr enrichment at the dominant interstitial sinks in the microstructure. However, quantifying the predicted levels of Cr enrichment will require more precise values of the Cr and Fe diffusivities by interstitial and interstitial cluster mechanisms, including the use of more recent potentials developed for Fe [24] in addition to determining the partitioning of interstitial-type defect fluxes to dislocation and grain boundary sinks.



Figure 2. The ratio of Cr to Fe diffusion by an interstitial mechanism obtained from MD simulations in an Fe -10%Cr alloy using different interatomic potentials. The diffusivity ratio has been evaluated for single, di- and tri-interstitials.

Vacancy – Cr interactions in BCC Fe – Cr alloys

The VASP ab-initio calculations predict a reference state of pure Fe that is ferromagnetic BCC with a lattice parameter of 0.283 nm and a magnetic moment of 2.19?_B, while the Cr ground state is an anti ferromagnetic BCC structure with a lattice parameter of 0.285 nm and a magnetic moment of ±1.09? B. which are consistent with both experimental observations [25] and previous ab-initio calculations by Olsson [23,26]. In the Fe-Cr alloys, the magnetic moment and atomic size of the Cr atoms depend strongly on the alloy Cr content. At Cr concentrations below 16.7%, Cr is strongly anti-ferromagnetic, and the excess atomic volume of the system is positive for Cr concentrations up to 25%, suggesting that Cr is oversized in Fe matrix. However, careful examination of the 1st nearest neighbor (NN) Fe atoms indicates relaxation toward the Cr atom, indicating that Cr is undersized. This apparent difference in the observed Cr atomic volume can be rationalized by comparing with the relaxation near a vacancy, in which oscillating expansion and contraction of NN shells occurs. In this case, the total relaxation over all NN shells produces an increase in the system volume even for an undersized species. Thus, our calculations indicate that Cr is an undersized solute with a surrounding tensile field and therefore should not be expected to bind with a vacancy. However, the further ab -initio results show that the binding energy of a vacancy and a first NN Cr atom is about 0.05 eV, which is likely caused by electronic and magnetic interactions. For example, when Cr is paired with a vacancy in a Fe-1.8%Cr alloy, the magnetic moment on the Cr decreases from -1.88 to -2.12 ? B, while the magnetic moment on the 1st NN Fe atoms increases from 2.2 to 2.4? _B.

The activation energy from our VASP calculations for vacancy exchange with Fe in pure BCC Fe is 0.66 eV, whereas it is 0.52 eV for the direct exchange with a Cr atom in an Fe-1.9%Cr alloy. This suggests a faster diffusivity for Cr relative to Fe due to both vacancy binding and preferential vacancy exchange. However, since solute diffusion in BCC alloys is controlled by more than just the direct vacancy exchange, we have followed the multi-frequency models developed by LeClaire [27,28] to calculate the activation energies of vacancy-atom exchanges for a vacancy in close proximity to Cr. The resulting vacancy migration energies are presented in Table 1 for simulation cells containing 2x2x2 (Fe -6%Cr) and 3x3x3 (Fe-1.9%Cr) unit cells.

Self-diffusivity of Fe and Cr from vacancy migration

The self-diffusivity of Fe in BCC Fe was calculated using the LeClaire model [27,28], based on the values presented in Table 1 and values for the vacancy formation and migration energy ($E^{v,m}$ =0.65 eV, $E^{v,f}$ = 2.18 eV) obtained from *ab-initio* calculations. This results in a predicted Fe self-diffusivity given by Eq (1),

$$D_{BCC?\,Fe}^{Fe} ? \ 2.051 \ ?10^{?5} \ ? \ exp(\ ? \frac{2.84}{k_{_{\rm B}}T}) \qquad \mbox{[m}^2\mbox{/sec]} \eqno(1). \eqno(1).$$

This value for the Fe self-diffusivity is consistent with the range of values previously obtained by Becquart and Domain [29,30].

Similarly, the Cr diffusivity has been calculated from the LeClaire model [27,28] using the values presented in Table 1. For this calculation, it is assumed that the various jump frequencies are determined by the activation free enthalpies with an invariant pre-exponential factor (? $_{o}$), given the similar atomic size and mass of Cr and Fe, although there may be effects of Cr on the vacancy migration entropy and the vibrational density of states at the saddle point that are not included in this assumption. Thus, in the dilute limit, the Cr diffusion coefficient is:

$$D_{BCC?Fe}^{Cr} ? a^2 w_2 f_2 \frac{w_4}{w_3} c_v^{eq},$$
(2),

where
$$f_2 ? \frac{1?t_1}{1?t_1}$$
, $t_1 ? ? \frac{w_2}{w_2 ? 3w_3 ? 3w_3 ? w_3 ? \frac{w_3w_4}{w_4 ? Fw_5} ? \frac{2w_3w_4}{w_4 ? 3Fw_0} ? \frac{w_3w_4}{w_4 ? 7Fw_0}}$ (3),

and F = 0.512. For concentrated alloys, the Fe self-diffusivity will be modified by the presence of Cr atoms, which has been determined [27,28] to follow:

$$D_{BCC?Fe}^{Fe}(c_{Cr}) ? D_{BCC?Fe}^{Fe}(c_{Cr} ? 0)(1 ? bc_{Cr}),$$
(4),

where b is a solute enhancement factor. Assuming the effect of the solute is not sufficiently strong to alter the solvent correlation factor f appreciably from the value f_0 in pure solvent,

$$b??20?\frac{1}{w_0}[(3w_3'?w''?3w_3)\frac{w_4}{w_3'}?(3w_4?3w_5)\frac{w_6}{w_5}?3w_4'?w_4''?3w_6]$$
(5).

From the above equations, the ratio between the Cr and Fe diffusivity is obtained as:

$$\frac{D_{BCC?Fe}^{Cr}}{D_{BCC?Fe}^{Fe}(c_{Cr})}?\frac{w_2}{w_0}\frac{f_2}{f_0}\frac{w_4}{w_3}\frac{1}{(1?bc_{Cr})}$$
(6).

The ratio between Cr and Fe diffusivities in BCC Fe-Cr alloys obtained from Eq (6) are plotted in Figure 3 as a function of temperature. The results predict that Cr is a much faster diffuser than Fe, both in the dilute limit (solid line) and when including the solute enhancement of solvent diffusion in a concentrated Fe-10%Cr alloy (dashed line). KLMC simulations have also been performed to evaluate the ratio of Cr to Fe diffusivity. In these simulations, the values of vacancy jump migration energies modified when near a Cr solute atom presented in Table 1 have been used to determine the specific vacancy – atom exchanges, assuming an invariant jump frequency pre-factor. The KLMC simulation results, plotted as filled symbols in Figure 3, also predict that Cr diffuses much faster than Fe and in fact, with much larger ratios than predicted by the LeClaire model, but with a similar temperature dependence. The clear conclusion from this analysis is that Cr will diffuse faster (~2 to 150 times larger) than Fe by a vacancy mechanism, and that it appears that the relative ratio of Cr to Fe diffusion is much larger for a vacancy than an interstitial mediated diffusion mechanism. Within an inverse Kirkendall model of radiation-induced segregation [13], the faster diffusivity of Cr by a vacancy mechanism would deplete Cr at the grain boundaries.



Figure 3. The ratio of Cr to Fe diffusivity by a vacancy mechanism, as calculated based on *ab-initio* simulations of the vacancy – atom exchange energies implemented into the multiple frequency LeClaire model [27,28] in the dilute limit (solid line), as compared to KLMC simulations (data points). As well, the effect of solute enhancement of Fe self-diffusion in the LeClaire model in an Fe-10%Cr alloy is shown with the dotted line.

Conclusions

A hierarchical multiscale modeling approach has been used to evaluate Cr interactions with point defect clusters in BCC Fe-Cr alloys. Ab-initio calculations of vacancy-Cr binding energy and the activation energy for vacancy - atom exchanges in the proximity of Cr have been used to calculate the diffusivities of Fe and Cr by a vacancy mechanism in the LeClaire multiple frequency model and kinetic lattice Monte Carlo simulations. This analysis leads to the conclusion that Cr diffuses much faster (~2 to 150 times larger) than Fe by a vacancy mechanism. The relative diffusivity of Cr to Fe by an interstitial mechanism has been investigated using molecular dynamics simulations, with two different Fe-Cr potentials that predict either an attractive or repulsive interaction between Cr and the interstitial defects. The potential predicting an attractive interaction of Cr with interstitials (Fe-Cr II) is more consistent with ab-initio predictions, and for this case, the Cr diffusivity by an interstitial mechanism is between 10 and 30% larger than Fe diffusivity. Thus, it seems apparent that either Cr enrichment or depletion at grain boundaries could be expected under irradiation, depending on the relative fluxes of interstitial versus vacancy defects. Future efforts will focus on developing atomicscale models of Cr transport based on vacancy and interstitial-type diffusion mechanisms and on evaluating the relative point defect fluxes to various microstructural sinks to better understand the apparently contradictory experimental observations of Cr segregation in irradiated ferritic/martensitic alloys.

Acknowledgements

This work has been supported by the Office of Fusion Energy Sciences, U.S. Department of Energy, under Grant DE-FG02-04ER54750.

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Footnote: This paper has been published in the proceedings to the Thirteenth International Conference on Fusion Reactor Materials (ICFRM-13).

MOLECULAR DYNAMICS SIMULATION OF MIXED DISLOCATION INTERACTION WITH STACKING FAULT TETRAHEDRON—H.-J. Lee and B. D. Wirth (University of California, Berkeley)

OBJECTIVE

The objective of this work is to understand the interaction mechanisms between a mixed dislocation and a commonly observed irradiation defect in face center cubic (FCC) materials, which is a stacking fault tetrahedron (SFT), with an ultimate aim of gaining insights into clear channel formation in irradiated materials.

SUMMARY

The interaction between a 60 degree mixed dislocation and a stacking fault tetrahedron (SFT) is investigated using molecular dynamics (MD) simulation. The interaction strongly depends on the sense of the dislocation Burgers vector, with un-faulting and stable shear ledge formation occurring in one case, while simple bypass and immediate reconstruction of the SFT is observed for the opposite Burgers vector direction. SFT un-faulting by a mixed dislocation occurs following the constriction of a mixed dislocation on the SFT, which produces a Shockley partial that can glide on the SFT face(s). In particular, when the dislocation intersects the SFT edge side, the SFT base is absorbed into the dislocation core as a superjog pair. After dislocation bypass, a smaller SFT and vacancy clusters remain behind. When the dislocation glides on the base plane of the SFT, the strong repulsion between the mixed dislocation and the SFT induced SFT collapse.

PROGRESS AND STATUS

Introduction

An extensive research effort has investigated the interaction between dislocations and radiation induced defects (RIDs) to provide a theoretical framework to understand, and ultimately predict, the changes of mechanical properties of structural materials due to high-energy particle irradiation [1-3]. In face centered cubic (FCC) Copper (Cu), about 90% of the radiation defects observed in the transmission electron microscope (TEM) are stacking fault tetrahedra (SFTs) [4]. The SFTs act as obstacles to dislocation motion, thus changing the local deformation behavior of the materials, which are observed in tensile tests as increases in yield and ultimate tensile stress and decreases in the uniform ductility [5]. A common feature of the microstructure of irradiated and deformed materials (including Cu) observed by TEM is the formation of defect free channels, in which the as-irradiated defect has been removed in a localized region by the dislocation motion [6]. Such localized deformation is believed to be related to the ductility loss in irradiated materials. The micro-structural characterization of defect free channels, including their approximate width (~ 200 nm) and spacing (~ 1 µm), and the conditions of strain rate, temperature and irradiation dose (RID density) necessary for the defect free channel formation are relatively well established by TEM experiments [6]. However, the atomistic interactions between a dislocation and an SFT, and in particular a mechanism for the complete removal of an SFT, that leads to the defect free channel formation remain an open question.

Molecular dynamics (MD) simulations have been widely used to understand the atomistic interactions of edge and screw dislocations with an SFT [7-14]. When intersected by an edge dislocation, the SFT is often sheared, but absorption of the SFT base also occurs when the extra-half plane of an edge dislocation is oriented toward the base of the SFT [12]. When intersected by a screw dislocation, the SFT can either be partially absorbed or simply sheared, depending on the interaction geometry, the applied shear stress and temperature [11-14]. Thus, the resulting SFT structure consists of either a perfect SFT or two SFTs, or an SFT with defects such as ledges, vacancy clusters, or truncated base. A notable feature is that the screw dislocation. Early and more recent in-situ TEM observations show that screw dislocations are more efficient than edge dislocations at removing radiation induced defects [15-18]. In particular, Matsukawa et al. reported collapse of an SFT into a smaller SFT and the annihilation of the base portion in a quenched gold by a moving screw dislocation [18].

Regarding the interaction between an SFT and a mixed dislocation, there are no known available MD simulations results, but SFT collapse into a Frank loop has been proposed by Kimura and Maddin [19]. More recently Robertson et al have observed destruction of an SFT in quenched gold by a mixed dislocation, although the mechanism has not been fully established [20].

In this report, we present the results of MD simulations of a 60 degree mixed dislocation intersecting an SFT to elucidate the interaction mechanisms. The results presented here investigate four possible interaction geometries between a mixed dislocation and an SFT, as shown in Figure 1. We found that the interaction results strongly depend on the dislocation Burgers vector direction, in which one type (b=CA) leads to partial un-faulting of the SFT and shear ledge formation while the other type (b=AC) involves simple bypass and immediate reconstruction of the SFT. For the dislocation b=CA intersecting an SFT, where the un-faulting of the SFT occurs, we found that the mixed dislocation dissociates to two Shockley partial and a stair-rod partial dislocations upon constriction on the SFT. One particular case that shows absorption of the SFT base and super-jog formation is discussed in detail and the corresponding dislocation reaction mechanism is analyzed. However, the predicted collapse mechanism by Kimura and Maddin was not observed.



Figure 1. Schematic representation of the four possible interaction geometries between a mixed dislocation and an SFT: (a) b=CA and SFT face (b) b=CA and SFT edge (c) b=AC and SFT face (d) b=AC and SFT edge. The grey arrow indicates the dislocation gliding direction.

Simulation Methods

The MDCASK code [21] with an embedded atom method (EAM) potential by Mishin et al [22] was used to simulate an atomistic process in face centered cubic (FCC) Cu. A simulation cell with FCC crystalline structure and orientations of $x=[\overline{1}11]$, y=1/2[110] and $z=1/2[1\overline{1}2]$ is used. The size of the system used in this work is 31.4 nm in x, 22.5 nm in y, 44.3 nm in z direction, which is (50x88x100) in unit cells and contains 2,640,000 atoms. To generate an SFT, a triangular vacancy platelet of 153 vacancies is inserted in the system, which corresponds to an SFT edge length of 4.6 nm. The mixed dislocation with

b=CA is generated by introducing an edge dislocation core of b=-1/4 [$1\overline{1}2$] and screw dislocation core of b=-1/4[110] at the same location. The dislocation reaction between these two dislocations produces a perfect mixed dislocation of b=1/2[$0\overline{1}1$] by $-1/4[110]+1/4[1\overline{1}2] \rightarrow 1/2[0\overline{1}1]$. The mixed dislocation with an opposite Burgers vector (b=AC) is generated by inserting an opposite sign of screw and edge dislocation cores at the same location.

Periodic boundary conditions are used in the y and z directions, while the x direction is a free surface, subject to an applied shear surface force. The periodic boundary condition in the z direction is modified by shifting atomic positions in the y direction to ensure the continuity of the [110] plane across the periodic boundary in the z direction, as performed in the work of Rodney [23]. To reduce the distortion of the elastic field due to the modified periodic boundary condition, we used a longer simulation cell length in the z direction (44.3 nm) compared to the x direction (31.4 nm).

The simulation cell was equilibrated for 10 ps at T = 100 K using a micro-canonical (NVE) ensemble. Following equilibration, a constant shear stress of 100 MPa is applied to the system by adding constant forces in the Burgers vector direction to the atoms on the free x surface. When the direction of the applied shear stress is reversed, the dislocation glides in the opposite direction as shown in Fig. 1(a) vs. (b) and Fig. 1(c) vs. (d).

The defect and dislocations were identified by the common neighbor method [24]. In the figures, the light colored (yellow) atoms are atoms in HCP structure, thus corresponding to stacking faults, and the dark colored (blue) atoms are neither FCC nor HCP, corresponding to a Shockley partial dislocation, a stair-rod partial dislocation, or other defect structures.

Results

Mixed dislocation (b=CA) intersecting SFT face

When the mixed dislocation glides toward the ABD face of the SFT at an applied shear stress of 100MPa, the two Shockley partials, C δ and δA , first constrict on the SFT face as shown in Fig. 2(a). Then, a stairrod dislocation ($\delta\gamma$) is formed at the constriction line as shown in Fig. 2(b). The C δ leading partial continues to glide by cutting through the SFT, while the δA partial cross-slips to become γA that glides on the (c)-plane. Thus, the dislocation reaction is: $C\delta+\delta A\rightarrow C\delta+\delta\gamma+\gamma A$. The γA reacts with the AB and AC edge of the SFT as shown in Fig. 2(b). The leading partial C δ detaches from the SFT by cutting through the SFT and detaching around the CD edge of the SFT, while the trailing partial δA detaches from the SFT by an Orowan mechanism (Fig. 2(b)-(d)). Immediately after the detachment of both partials, the remaining structure consists of a smaller SFT and a truncated base, which is identical to the previously reported structure of a screw dislocation intersecting an SFT face [14]. Subsequently, the remaining Shockley partial δA on the BCD face of the SFT (Fig. 2(d)) moves back to the smaller SFT and the truncated base. This initiates a series of dislocation reactions that produce an SFT with shear ledges as shown in Fig. 2(e). Again, the reactions for the shear ledge formation are similar to those observed and analyzed when a screw dislocation intersects an SFT face [14]. The ledge on the ABD face is vacancy type (V) and the ledge on BCD face is interstitial type (I). Initially the I-ledge was connected to the Vledge and parallel to the BC edge of the SFT but about half of it changes its orientation parallel to DB edge of the SFT as shown in Fig. 2(e). The detailed step-by-step dislocation analysis of this interaction and the comparison to the corresponding interaction between an SFT and screw or edge dislocation are previously reported by Lee et al. [25].

Mixed dislocation (b=CA) intersecting SFT edge

When the mixed dislocation glides toward the CD edge of the SFT, the constriction of two Shockley partials (δA and C δ) occurs in the short segment around the CD edge. The following two reactions are observed simultaneously on the SFT faces near the constriction line around the CD edge.

 $\delta A + C\delta \rightarrow \delta A + C\beta + \beta\delta$ on the ACD face ((b)-plane) of the SFT

 $\delta A + C\delta \rightarrow \delta A + C\alpha + \alpha\delta$ on the BCD face ((a)-plane) of the SFT

Then, the leading partial δA glides forward by cutting through the SFT cross section while the C β and C α Shockley partials glide on the ACD and BCD face of the SFT, respectively, toward the base and un-fault the SFT. When the C β and C α Shockley partials reach the base of the SFT, they form the C δ Shockley partial via reaction with the stair-rod partials at the SFT edges. The C δ glides on and un-faults the ABC face ((d)-plane) of the SFT, which removes the C apex of the SFT as shown Fig. 3(b). As the dislocation glides further to bypass the SFT, a super-jog appears near the A apex (Fig. 3(c)). The leading partial detaches from the SFT as the two arms of the dislocation bow and recombine around the super-jog, which then is pushed back to the SFT (Fig. 3(d)). As the trailing partial detaches from the SFT, the shear ledges starts to form (Fig. 3(e)). The I-ledge is formed on the ABD face and the V-ledge is formed on BCD face of the SFT as shown in Fig. 3(f). The shear ledges remain stable and no further reaction is observed until the second dislocation bypass. The second bypass reaction is essentially identical to the results shown in Figure 3, except that the SFT is now sheared by 2 Burgers vectors.



Figure 2. MD snapshots of the mixed dislocation, b=CA, intersecting SFT face:

- (a) Constriction on the SFT face (32ps)
- (b) Un-faulting of the c-plane (35ps)
- (c) Leading partial leaves the SFT by recombining around the SFT (41ps)
- (d) Trailing partial leaves the SFT by an Orowan mechanism, leaving a smaller SFT and a truncated base (59ps)
- (e) Smaller SFT and the truncated base forms a sheared SFT (64ps)

Mixed dislocation (b=AC) intersecting SFT face

While the leading partial (A δ) is pinned by the SFT, the trailing partial (δ C) does not glide to constrict with the leading partial but remains at a stand-off distance of about 2.2 nm from the SFT, and begins to bow. Note that this is a considerably different interaction from the dislocation of b=CA case, where the leading and the trailing partial constrict upon the SFT face (Section 3.1). The leading partial A δ continues to glide forward and detaches from the SFT by cutting through the SFT (Fig. 4(a)), which leaves dislocation segments on the SFT faces. Then, the trailing partial (δ C) glides towards the SFT. It combines with the dislocation segments on the SFT faces and forms I- and V-ledges on the ABD and BCD face of the SFT, respectively. The shear ledges glide towards the D apex of the SFT as the trailing partial cuts through and detaches from the SFT (Fig. 4(b)-(c)). Immediately after the mixed dislocation (b=AC) bypasses, the SFT is fully reconstructed to a perfect SFT.

Mixed dislocation (b=AC) intersecting SFT edge

The leading partial (δ C) intersects the CD edge of the SFT and bends around the SFT initially (Fig. 5(a)). As the trailing partial ($A\delta$) approaches, the leading partial cuts through the SFT and the trailing partial follows (Fig. 5(b)-(d)). During the bypass, shear ledges form on the BCD and ABD faces of the SFT. Both shear ledges move almost simultaneously toward the D apex of the SFT as the two partial dislocations detach by a shear mechanism. As in the case of the mixed dislocation of b=AC intersecting the SFT face, the SFT is fully reconstructed to a perfect SFT immediately after dislocation (b=AC) bypass.



Figure 3. Interaction results of the mixed dislocation, b=CA, intersecting SFT edge:

- (a) Constriction on the SFT edge (36ps)
- (b) Un-faulting of the a and b-plane (38ps)
- (c) Un-faulting of the c-plane (47ps)
- (d) Recombination and detachment of the leading partial (50ps)
- (e) Reaction between the smaller top SFT and the truncated base during the detachment of the trailing partial (67ps)
- (f) Formation of an SFT with shear ledges on a and c-plane (70ps)



Figure 4. Interaction results of the mixed dislocation, b=AC, intersecting SFT face:

- (a) Recombination of the leading partial around the CD edge of the SFT (35ps)
- (b) Formation of the I-ledge segment on the c-plane (37ps)
- (c) Gliding of shear ledges toward the D apex (38ps)
- (d) Complete reconstruction of the SFT (39ps)

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Discussions

The partial absorption followed by stable shear ledge of the SFT was observed when b=CA, while a simple dislocation cutting and shear ledge formation that results in complete reconstruction of the SFT was observed in b=AC case. The SFTs with shear ledges (b=CA case) were stable for more than 40 ps at which point, a 2nd dislocation intersection occurs. After the 2nd dislocation intersection, which involved a similar mechanism to the first interaction, the SFT has V- and I- shear ledges, which are sheared by 2b. The effect of applied shear stress (dislocation velocity) was examined by applying a higher shear stress of 300 MPa, but the interaction results were essentially identical. We further analyzed cases that involve (partial) SFT un-faulting (b=CA) as shown below.



Figure 5. Interaction results of the mixed dislocation, b=AC, intersecting SFT edge:

- (a) Intersection on the SFT edge side (36ps)
- (b) Constriction on the ACD plane (37ps)
- (c) Bypass through the ACD plane (38ps)
- (d) I-ledge formation on BCD plane (39ps)
- (e) Gliding of shear ledges toward the D apex (40ps)
- (f) Complete reconstruction of the SFT (41ps)

Interaction mechanism of dislocation (b=CA) intersecting an SFT edge

The interaction of b=CA intersecting an SFT edge initially shows an un-faulting of the c-plane (Figure 3(c)), which later reconstructed by the dislocation reaction associated with detachment of the leading partial via recombination around the SFT. However, when recombination does not occur, the un-faulting of the c-plane continues and ultimately leads to the absorption of the SFT base. This absorption of the SFT base was observed when the thickness of the simulation cell (x-direction) is reduced to 12.5 nm (20 unit cells). In this case, the same shear stress (100 MPa) was applied to the system but the dislocation velocity was about 2.5 times larger than with the larger cell. Increasing the dislocation velocity at a constant thickness generally produces a larger local bowing of the dislocation around the obstacle. However, in this case, there appears to be less curvature of the dislocation in the thinner sample, which prohibits the subsequent recombination cell thickness reduces the screw dislocation line curvature around an obstacle [11]. This interesting observation is in apparent agreement with our results of SFT base absorption (no recombination of the bowing leading partial dislocation) due to reduced dislocation line curvature. As a result, the dislocation detaches from the SFT with a super-jog pair that has a height corresponding to the distance between the dislocation gliding plane and the SFT base plane.

The initial interaction mechanism is identical to that depicted in Fig. 3(a) to (c). When the dissociated δA and $C\delta$ partial dislocations glide on the (d) plane towards the CD edge of the SFT, constriction occurs on the CD edge and the (a) and (b) faces of SFT. Upon constriction, the dislocation has a screw character on the (b) face of the SFT while it has a 60 degree mixed dislocation character on the (a) face of the SFT. Therefore, it is reasonable to assume that the dislocation on the (b) face crossslips to βA and C β partial dislocations ($\delta A + C\delta \rightarrow CA \rightarrow \beta A + C\beta$) while δA and C δ on the

(c) face becomes δA , $\alpha \delta$, and $C\alpha$ ($\delta A + C\delta \rightarrow \delta A + \alpha \delta + C\alpha$) based on the previous observations. However, the constriction and cross-slip occurs very quickly. It is difficult to confirm the individual reactions on both (a) and (b) faces of the SFT.

The δA partial dislocation on the (a) face continues to glide on the (d) plane and reacts with the cross-slipped βA dislocation on the (b) face of the SFT, forming a $\beta \alpha$ stair-rod partial on the ACD face of the SFT. And the C β and C α Shockley partials glide on the (b)- and (a)-plane of the SFT, respectively, toward the base while removing stacking faults and stair-rod edges around the SFT apex C, as shown in Fig. 6(b). The corresponding dislocation representation is shown in Fig. 6(e).

As shown in Fig. 6 (b) and (e), the δA partial is now constricted on the AD and BD edges and the (c) face of the SFT. Due to the applied shear stress, the C β intersects the AD edge ($\gamma\beta$) and $C\beta + \beta\gamma \rightarrow C\beta + \beta A + A\gamma$ occurs. The A γ removes the stacking fault on the (c)-plane of the SFT as shown in Fig. 6(f). As the dislocation moves away from the SFT, three dislocations around the apex B (γA , $\alpha\gamma$, and C α intersect to form the dislocation CA ($C\alpha + \alpha\gamma + \gamma A \rightarrow CA$). Since the dislocation CA cannot dissociate into Shockley partials on the adjacent (a) or (c) planes, it rearranges its configuration to lie on the (b) plane. In the process, some vacancies are emitted as shown in Fig. 6 (d). The original mixed dislocation now glides with a super-jog pair, which lies on the (b) and (d) planes.



Figure 6. Interaction between a mixed dislocation (b=CA) and an SFT observed in a thinner simulation cell. The MD simulation snapshots are shown in (a)-(d) and the dislocation analysis results are shown in (e) and (f).

(a) Initial configuration. The dislocation glides toward the SFT edge side.

- (b) Unfalting of SFT faces.
- (c) Super-jog formation.
- (d) Final configuration. The smaller SFT and vacancies are left behind.
- (e) The dislocation analysis of MD snapshot (b)
- (f) The dislocation analysis of MD snapshot (c)

The effect of the applied stress direction

When the shear stress is applied in the y direction (τ_{yx}), the direction of stress is 60 degrees with respect to the direction of the Burgers vector (b=CA). Therefore, the effective stress in the Burgers vector direction is $\tau_{yx} \times \cos(60)$, with an orthogonal component of $\tau_{yx} \times \sin(30)$.

Under this applied stress condition, the interaction between an SFT and a mixed dislocation is different than those previously described. In particular, when the dislocation intersects the SFT face as shown in Fig. 7, the SFT is decomposed into two small perfect SFTs. When the dislocation intersects the SFT edge as shown in Fig. 6, the results are the same as when the applied shear stress is the same direction as the Burgers vector direction.



Figure 7. The effect of the applied shear stress direction

Inverse Silcox-Hirsch mechanism

When a mixed dislocation of b=CA glides on the SFT base plane and intersects the SFT face (Fig. 1(a)), the leading C δ Shockley partial is repelled by the $\delta\gamma$ stair-rod dislocation of SFT as shown in Fig. 8(a). This is due to the interaction of two dislocations (C δ and $\delta\gamma$) that produce a C γ Frank dislocation upon reaction, which is energetically unfavorable. However, with increasing applied shear stress, the dislocation further glides towards the SFT and the SFT becomes unstable by unzipping from the A apex. The destruction process involves the reverse Silcox-Hirsch mechanism, except the final formation of the Frank loop predicted by Kimura and Maddin is not observed [26], as shown in Figure 8(b)-(d). This behavior is more pronounced for larger SFT, possibly due to the longer edge length of the SFT, and correspondingly longer C γ Frank partial upon intersection which is energetically less favorable, in addition to the decreased stability of larger SFT with respect to the Frank loop. Thus, complete collapse of the

SFT to a Frank loop by a dislocation may occur for SFT sizes in which the SFT is meta-stable or unstable versus the Frank loop. However, for Cu with a stacking fault energy of 45 mJ/m², the size of meta-stable SFTs are about an order of magnitude larger than used in this study. It is also tempting to speculate that this reaction might be responsible for the SFT collapse observed in the in-situ TEM experiments of dislocation interacting with quenched-in SFTs in gold, where the SFTs are of a size corresponding to the meta-stable or unstable size range. In the small (stable) SFTs used in the MD simulations, the partially destructed SFTs reconstructs to a perfect SFT immediately after the dislocation bypass.



Figure 8. The dislocation gliding on the base plane of the SFT with the interaction geometry of b=CA and SFT face (Fig. 1(a)). The grey arrows indicate the dislocation gliding direction. (a) 4.6 nm size SFT with a projection from the D apex side. (b)-(d) 8.7 nm size SFT with a projection from the SFT base side.

- (a) The leading partial (C δ) is repelled by the AB edge of the SFT ($\delta\gamma$) to avoid the formation of a Frank partial (C δ + $\delta\gamma$ →C γ).
- (b)-(d) The SFT is destructed starting from the A apex of the SFT following the inverse Silcox-Hirsch mechanism.

Conclusions

We have investigated four possible interaction geometries between a 60 degree mixed dislocation and an SFT when the dislocation is gliding about mid-plane between an apex and the SFT base. Depending on the Burgers vector, one case (b=CA) leads to partial absorption, but subsequent stable shear ledge formation is observed on the SFT upon dislocation detachment, while the other case (b=AC) involves simple shear and reconstruction to a perfect SFT. These results were independent of the dislocation intersection geometry, either on the SFT face or the SFT edge.

In case of a dislocation with b=CA, constriction of the mixed dislocation occurs upon contact with the SFT. The trailing Shockley partial cross-slips to glide on the SFT face(s), and leaves a stair-rod partial at the constriction site. When the simulation cell thickness is decreased, absorption of the SFT base into the dislocation core was observed, presumably due to the reduced bowing of the leading partial which limited recombination and detachment around the SFT. The majority of the absorbed vacancies appear as a super-jog pair on the dislocation line, while a couple of vacancies are emitted from the super-jog during the subsequent dislocation glide. In case of b=AC, the individual partials of the dislocation detaches from the SFT separately without constriction. As the trailing partial dislocation detaches from the SFT, the SFT is reconstructed to a perfect SFT by shear ledge glide toward an SFT apex.

Acknowledgements

We gratefully acknowledge the financial support of the Office of Fusion Energy Sciences, U.S. Department of Energy, under Grant DE-FG02-04ER54750, and the DOE-Nuclear Engineering Education Research (NEER) program under Contract No. DE-FG07-04ID14594.

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MOLECULAR DYNAMICS SIMULATION OF DISLOCATION-VOID INTERACTIONS IN BCC MO-

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OBJECTIVE

The objective of this work is to study the interaction behavior between a screw dislocation and commonly observed radiation induced obstacles such as void in body centered cubic (BCC) molybdenum (Mo) to understand the plastic deformation process in a BCC metal under irradiation.

SUMMARY

Molecular dynamics (MD) and molecular statics (MS) simulations have been performed to simulate the plastic deformation processes in irradiated body centered cubic (BCC) Mo. Considering the unique nonplanar core structures of the screw dislocation in BCC metals, the behavior of screw dislocation motion as a function of temperature and applied shear stress is first discussed. A transition from smooth to rough motion of the screw dislocation is observed with increasing shear stress, as well as a change of dislocation glide plane from {110} to {112} with increasing temperature. The interaction of a screw dislocation with nanometer-sized voids observed in both dynamic and static conditions is then reported. The obstacle strength calculated from MS calculations shows a large increase in critical resolved shear stress for void diameter larger than about 3 nm. However, the MD results indicate that the screw dislocation interaction with void occurs via a simple shear mechanism.

PROGRESS AND STATUS

Introduction

The irradiation of structural materials in nuclear environments can produce radiation induced defects and significant mechanical property changes, including yield stress increases and ductility decreases. Depending on material and irradiation conditions, the defect population varies from small point defect clusters to dislocation loops, voids, helium bubbles, and radiation-induced precipitates. Transmission electron microscopy (TEM) characterization following deformation of irradiated materials showed that these defects act as obstacles to dislocation motion, thus changing the local deformation behavior. However, detailed knowledge of the interaction mechanisms between a dislocation and radiation induced obstacles is difficult to obtain by post situ and even in situ TEM methods.

In BCC metals, TEM studies indicate that screw dislocations control plasticity. While atomistic simulation methods can provide the sequence-of-events controlling the interaction between a dislocation and an obstacle, the screw dislocation interaction with radiation obstacles in BCC metals has not been extensively studied using MD methods, presumably because of the more complex motion of screw dislocations in BCC metals by kink pair formation, which shows a smooth to rough transition [1]. Typical defects in BCC Mo are mostly dislocation loops and small voids at lower irradiation temperature, whereas only voids are observed at higher temperatures [2]. Previous analytical work on void strength indicates that the void is a very strong obstacle and the bypassing stress can approach the Orowan stress for impenetrable obstacles [3]. Thus a clear understanding and reliable estimate of their strengthening effect is important for evaluating performance of BCC Mo under irradiation conditions.

In this report, we present atomistic simulation results that investigate the interaction between screw dislocations and voids in BCC Mo. Considering the unique non-plannar core structure of the screw dislocation, we first present the deformation behavior of a screw dislocation in BCC Mo. Conjugate gradient MS simulation results are then presented to quantify the energetics of void shearing. Finally, the dynamic detachment behavior is studied using MD simulations.

Simulation Methods

The MD simulations have been performed using a modified version of the MDCASK code [4], implemented with the Finnis-Sinclair N-body potential to describe the atomic interactions in Mo [5]. The simulation cell consists of a body centered cubic lattice, bounded by $(1\overline{1}0)$, (111), and $(\overline{1}\overline{1}2)$ faces in $X = a_0[1\overline{1}0]$, $Y = a_0/2[111]$, and $Z = a_0[\overline{1}\overline{1}2]$ directions, respectively.

*This report has been submitted to Journal of Nuclear Materials for publication.

The size of the BCC Mo simulation cell is 60x100x60 unit cells, approximately 27 x 27 x 46 nm (*X*, *Y* and *Z* directions), and contains about 2.2 million atoms. Periodic boundary conditions are applied in the Y and *Z* directions. The *X* surface is initially free, but is subject to a shear stress ranging from 0.7~4 GPa following equilibration. A screw dislocation with *b*=1/2[111] is introduced using the elastic isotropic displacement field. The void is introduced into the simulation cell by removing atoms of spherical region.

The conjugate gradient MS simulations with a screw dislocation and a void of diameter from 1.5 to 5 nm have been performed to calculate the critical resolved shear stress and obstacle strengths as a function of a void size. A simulation cell size from 20x50x20 to 20x150x20 and 60x100x60 unit cells has been used to determine the effects of cell size and void spacing.

Results and Discussions

Screw dislocation motion

The observed screw dislocation core structure in BCC Mo is degenerate (N and P type), with core spreading into three {110} planes along <112> directions as anticipated with a Finnis-Sinclair potential [6]. At T=100K and an applied shear stress of 1 GPa, screw dislocation motion occurs through the double kink nucleation and propagation mechanism, which agrees with previous observation in BCC Fe at low temperature and low stress [1,7]. The motion is relatively smooth but does involve cross-slip, thus the dislocation trajectories appear wavy and non-crystallographic. Close examination of dislocation displacement (DD) map suggests that such cross-slip is favored after the dislocation core flip between N and P type. At a higher applied stress of 1.5 GPa, the dislocation again moves by a double kink nucleation and propagation mechanism, although the higher applied stress results in a larger rate of double kink nucleation. This leads to interactions amongst kinks, which are formed on different glide planes, that necessitate the formation of Frenkel pairs to resolve the topological constraint, as previously observed in BCC Fe [1,7]. The vacancies are immediately emitted from the dislocation as individual point defects, whereas the self-interstitial atoms are dragged along the dislocation core and form clusters of <111>-oriented self-interstitials (crowdions). The self-interstitial clusters are later emitted from the moving screw dislocation with a distribution of cluster sizes in the form of <111> crowdion interstitial clusters and dislocation loops. Thus, the motion of the screw dislocation at high applied shear stresses results in the formation of a self-debris field marking the path of dislocation motion. When the applied shear stress is



Figure 1. Dislocation multiplication via loop generation. The MD snapshots of a dynamic sequence in which self-pinning leads to dislocation loop generation, growth, coalescence, and dislocation multiplication. The simulation temperature is 100 K and the applied shear stress is 4 GPa.

further increased to 4 GPa at, the dislocation loops generated by the rough motion rapidly expand on {110} planes and coalesce with other dislocation loops, or itself through the periodic boundary, as shown in Fig. 1. As a result, dislocation multiplication occurs in the smulation cell.

As well, a strong temperature dependence of screw dislocation motion is observed. As summarized in Fig. 2, the MD simulation results show that the screw dislocation glides in the <112> direction on {110} planes at T < 250K, but switches to glide in the <110> direction on {112} planes at T > 250K. At above T = 250K, the screw dislocation moves on {112} planes in the twinning direction. When the applied stress is low, smooth motion is observed. When the applied stress is increased, rough motion is observed. When the applied stress is increased, rough motion is observed. When the applied stress is increased, rough motion is observed in BCC Fe [1,7]. However, Marian et al. report no temperature dependence of the screw dislocation glide plane in BCC Fe [1], while Chassidon et al. reports only BCC Fe with non-degenerate core glides on {110} plane at low temperature [7]. It should be noted that the core type of BCC Mo in this study is degenerate and thus different from the previous observation in BCC Fe.



Figure 2. Deformation map of BCC Mo as a function of temperature and applied shear stress. At T < 250 K, the dislocation glides on the {110} plane while it glides on the {112} plane at T > 250 K. A smooth to rough transition occurs with increasing the applied shear stress increases. Upon further increase of the stress, dislocation multiplication is observed at T < 250 K, while twinning on {112} planes is observed at T > 250 K.

Molecular Statics (MS) study of screw dislocation interaction with void

Conjugate gradient MS simulations have been performed to obtain the equilibrium configurations, energetics and forces associated with the dislocation – void interaction. These quantities provide the critical resolved shear stress and obstacle strengths required in constitutive models and provide a means of validating the interaction results obtained from high strain rate MD simulations.

The excess potential energy as a function of dislocation position relative to the void has been obtained from the conjugate gradient MS calculations as shown in Fig. 3(a). From this data, the critical resolved shear stress (_{CRSS}) of a regular array of voids is calculated for void diameters between 1.5 and 5.0 nm, and void spacing of 50, 100 and 150b using the following equation:

$$\tau_{CRSS} = \frac{F_{\max}}{b(L-D)} \approx \frac{\Delta E_{\max}}{\Delta x} \cdot \frac{1}{b(L-D)}$$
(1)

where F_{max} is the maximum force exerted by the void against dislocation shear, as numerically evaluated from the potential energy vs distance calculations, b is the dislocation Burgers vector amount, L is the inter-particle (void) spacing along the dislocation line and D is the void diameter [8]. Notably, a significant

increase in the predicted critical resolved shear stress occurs for void sizes larger than about 3 nm diameter, as shown in Fig. 3(b). Interestingly, MD simulations in Cu by Hatano and Matsui show similar behavior for dislocation – nanovoid pinning, showing an abrupt increase of the critical stress of the leading partial when the void diameter is larger than 2 nm [9].



Figure 3. Static simulation results: (a) Excess potential energy as a function of screw dislocation position relative to a 3 nm void centered at the center of the <112> axis. The asymmetry in the curve at the periodic boundary conditions (Distance = \pm 80 Å) results from introducing a sheared surface step of one Burgers vector on the void following dislocation passage (b) Critical resolved shear stress (τ_{CRSS}) for a screw dislocation interacting with a regular array of voids, as calculated by Eq. (1) from the conjugate gradient MS calculation results for void diameters between 1.5 and 5.0 nm and inter-particle spacings between 50 and 150b. A significant increase in the τ_{CRSS} occurs for void sizes larger than about 3 nm in diameter.



Figure 4. The critical resolved shear stress (τ_{CRSS}) as a function of the void diameter (D). The calculated τ_{CRSS} from the MS results increases abruptly at D = 3 nm. The calculated Orowan stress is lower than the MS results at D > 3nm, suggesting a possible change in the interaction and detachment mechanism at D ~ 3 nm.

MD study of screw dislocation interaction with void

To determine the dynamic critical resolved shear stress as a function of the void size and the detachment mechanism of a screw dislocation from a void, MD simulations are performed. At low temperature (T = 100K), the dislocation glides on {110} plane with frequent cross-slip. Thus, in general, the specific {110} glide plane as the dislocation enters the void is not identical to the glide plane following detachment. The dislocation bends towards to the void as it approaches due to the attractive interaction, and it start to annihilate upon contact with the void. During detachment, the annihilated dislocation segments renucleate on the exit surface of the void, while the other dislocation segments continue to glide. The detachment angle appears to be larger than 90 degrees in all cases, suggesting that the void is not a very strong obstacle against screw dislocation motion. The similar interaction behavior between a void and a screw dislocation is observed even at higher temperature (T = 1000K), where the dislocation glides on {112} plane. In summary, the screw dislocation interaction and detachment with void occurs via a shear mechanism and the void is sheared by one Burgers vector as a result of each passage of the dislocation in MD simulations.

Thus, the preliminary MD simulation results have not demonstrated a change in the dislocation – void interaction mechanism from shear to Orowan looping for voids larger than 3 nm diameter, contrary to the predictions of the MS results. The large increase in critical resolved shear stress for void diameters above about 3 nm are not fully understood at this time, and will be further investigated by atomistic simulations.

Conclusions

Using large-scale MD simulations, we have found that the gliding plane of a screw dislocation in BCC Mo changes from {110} to {112} at T ~ 250 K as the temperature increases. As well, a smooth to rough transition is observed with increasing applied shear stress, independent of the temperature. When the applied shear stress is further increased, dislocation multiplication is observed in the lower temperature, {110} glide regime, while nano-twin formation is observed in the higher temperature, {112} glide regime. The MD results indicate that the screw dislocation interaction with voids of diameter from 1.5 to 5 nm occurred via a simple shear mechanism independent of void size. However, the obstacle strength calculated from MS calculations shows a large increase in critical resolved shear stress for void diameter larger than about 3 nm, indicating a possible change in the interaction mechanism. Currently, detailed dynamic studies on the interaction mechanism between a screw dislocation and void as a function of the void size are in progress. Other ongoing research activities include MD and MS simulations of screw dislocation interaction with vacancy and self-interstitial type dislocation loops, as a function of loop Burgers vector and interaction geometry.

Acknowledgements

We gratefully acknowledge the financial support of the Office of Fusion Energy Sciences, U.S. Department of Energy, under Grant DE-FG02-04ER54750, and the DOE-Nuclear Engineering Education Research (NEER) program under Contract No. DE-FG07-04ID14594.

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POST-IMPLANTATION THERMAL DESORPTION OF HELIUM FROM POLY- AND SINGLE-CRYSTALLINE IRON – Donghua Xu and Brian D. Wirth (Department of Nuclear Engineering, University of California, Berkeley, CA 94720-1730)

OBJECTIVE

The objective of this work is to experimentally measure the thermal desorption spectra of helium implanted in poly- and single-crystalline iron to determine the He trapping and diffusion kinetics. These energetic parameters are important parameters for modeling the transport and fate of He and its effect on microstructural evolution in ferritic alloy components in future fusion energy environments.

SUMMARY

The results of He desorption measurements are presented for both poly- (PC) and single-crystalline (SC) iron (>99.99%) using constant rate (1 K/s) heating following room temperature ⁴He implantations at energies of 5 and 10 keV, and fluences of 10¹⁴ and 10¹⁵ He/cm². A sharp desorption peak due to BCC-FCC phase transformation is observed for both PC and SC specimens, which provides precise temperature calibration. Within the BCC structural range, three groups (I: below 300 °C; II: 300-600 °C; III: 600-900 °C) of desorption signal are identified for PC specimens while only two groups (I: below 300 °C; III: 550-900 °C) are identified for SC specimens. The low T group appears broader for PC specimens than for SC specimens. PC and SC desorption spectra show similar dependence on implantation energy and fluence, namely that the relative intensity at low and intermediate temperatures decreases with increasing implantation energy or fluence, while the fluence effect is much more pronounced than the energy effect. Simple first order dissociation kinetics are used to estimate the average activation energies associated with all the desorption groups, and these energies range from about 1.1 to 3.4 eV. However, precise identification of the mechanisms controlling each desorption event requires further study by complementary characerization and modeling techniques. The present SC iron data are expected to provide an appropriate experimental reference for future rate-theory or kinetic Monte-Carlo modeling of helium defect evolution in BCC iron.

PROGRESS AND STATUS

Introduction

Helium effects on the microstructure and mechanical properties are among the most important subjects in fusion materials research. It has been shown that the high level of implanted or transmutationally produced (by high energy neutron flux) helium under fusion conditions can cause nucleation and growth of helium bubbles in structural materials and subsequently result in significant mechanical property degradation [1-4]. The key to understanding helium effects is to determine the mechanisms by which helium atoms migrate and interact with various microstructural features in irradiated materials. This is an inherently multi-scale problem spanning from atomistic to macroscopic dimensions in both time and space.

At the atomistic level, computer simulations using ab initio and Molecular Statics/Dynamics approaches have been performed to investigate the kinetics, energetics and thermal stabilities of He and small Hecontaining clusters, as well as He interactions with dislocations and grain boundaries in BCC iron [5-12]. On the nano-, micro- or macro-scopic level, experiments using optical or electron microscopy, nuclear reaction depth profiling, positron annihilation spectroscopy, coincidence Doppler broadening, thermal desorption and other techniques have been conducted to analyze He behavior and the coupled He and defect evolution in BCC iron and ferritic alloys [13-18]. More recently, continuum rate-theory modeling [19] has been compared to isothermal He desorption from BCC iron to validate ab initio results.

All previous thermal desorption experiments on iron appear to have only used poly-crystalline (PC) specimens. It is thus not clear whether the grain boundary has made any contribution to the resulting desorption signals. For the purpose of validating fundamental parameters such as migration or binding energies of He and He-V clusters, single crystalline specimens are more appropriate. In this paper we report results from thermal desorption experiments on high purity (>99.99%) specimens, which consisted of both polycrystalline (PC) and single crystal (SC) iron, following room temperature ⁴He ion implantations at He energies of 5 and 10 keV and fluences of 10¹⁴ and 10¹⁵ He/cm². Similarities and distinctions

between the Helium desorption spectra for the PC and SC specimens, along with their dependence on implantation energy and fluence are presented. The desorption spectra have been analyzed using simple first order dissociation kinetics to obtain the activation energies associated with the observed desorption signals.

Experimental Procedure

High purity PC iron plates were purchased from Alfa Aesar. High purity SC iron disks were provided by Dr. S.A. Maloy at Los Alamos National Laboratory. Small specimens (~0.5-1 X 2.5 X 3.5 mm) were cut from the plates or disks, mechanically polished to 1 μ m grade smoothness, and then commercially implanted at room temperature with ⁴He ions at 5 or 10 keV to fluences of 10¹⁴ or 10¹⁵ He/cm². The He implantation flux was ~7-10 X 10¹⁰ He/cm²s.

Partial He current was measured in our ultrahigh vacuum thermal desorption system (TDS) as a function of temperature during constant rate (1 K/s) ramping on each of these He-implanted specimens from room temperature up to 1300 °C. The He current was then converted to the instantaneous desorption rate by multiplying with a proportionality coefficient, determined separately with a calibration procedure. More details regarding our TDS system are available in Reference [20].

Results and Discussion

TRIM/SRIM calculations

Probabilistic depth distributions of generated Frenkel pairs and the stopped ⁴He ions during implantation in iron were evaluated using SRIM 2003 software [21]. For 5 and 10 keV implantation energies, the maximum production of Frenkel pairs occurs at ~12 and 26 nm below the implantation surface, while the maximum in the distribution of He occurs at 25 and 50 nm, respectively. On the average, 20 and 33 Frenkel pairs are generated per He ion for the two energies, respectively. These values correspond to a peak displacement damage of ~85 and 75 mdpa, and a peak He concentration of 2830 and 1760 appm for the two energies, respectively, at a fluence of 10¹⁵ He/cm².

Background signal

In an earlier publication [20], we noted the possibility of spurious background signal interfering with real desorption spectra and causing problems in data analysis. It is thus very critical to have a clean background in order to obtain reliable desorption data. By enhancing the cooling of the chamber walls, the problem of spurious background signal has been solved. The background He current from non-implanted control specimens now remains almost constant at a low value of ~6 X 10^{-13} A from room temperature up to 1300 °C. In addition, the total pressure of our system is now also very low (~1X10⁻⁹ Torr) and stable over the entire temperature range.

General features of PC spectra and effects of implantation energy and fluence

The He desorption spectra obtained in PC specimens for the four combinations of implantation energies and fluences used in this work are presented in Fig. 1 (a)-(d). Two general features of the desorption spectra can be noticed from Fig. 1. First, there exists a sharp peak for each of the spectra around 900 °C which is not consistent with a first order dissociation model generally adopted in classical rate theory, due to its excessive sharpness. Such a sharp peak has also been observed for PC iron and ferritic alloys under other implantation conditions [17, 20]. In Ref. [20], we discussed the strong evidence leading to the conclusion that this peak is primarily due to the alpha-gamma (BCC-FCC) phase transformation [22]. Therefore, in this work, we have used this peak to calibrate our thermocouple temperature readings by setting the peak position to 912 °C (the well known value for alpha-gamma transformation in iron) and using a linear-correction to the other temperature values. It should be pointed out that the exact mechanism of the sharp He release peak at the alpha-gamma phase transformation is not entirely clear. Sugano et al. [17] interpreted this sharp peak as evidence for the lower stability of He-vacancy clusters in FCC iron than in BCC iron. This argument, nevertheless, can not explain the re-appearance of the peak during cooling as reported in Ref. [20], since in that case the specimen transforms back from FCC to BCC structure. Here we tend to consider this peak as a result of the transient structural instability during the proceeding phase transformation (in either direction), and that it may not represent the relative stability of



Fig. 1. Desorption spectra of high purity polycrystalline iron implanted with ⁴He at: (a). 5 keV, 10¹⁴ He/cm²; (b). 5 keV, 10¹⁵ He/cm²; (c). 10 keV, 10¹⁴ He/cm²; (d). 10 keV, 10¹⁵ He/cm².

He-vacancy clusters in BCC and FCC structures.

The second general feature of the observed He desorption in PC specimens is that the release signal can be divided into three groups within the BCC structural range (prior to alpha-gamma phase transformation), as shown in Fig. 1 (a)-(d). Group I lies on the low T side, spanning from room temperature up to around 300 °C, Group II in the intermediate T range, from 300 °C to 600 °C, and Group III in the high T range, from 600 °C to ~900 °C ending with the sharp peak induced by the alpha-gamma phase transformation. Above 912 °C, i.e., in the FCC structural range, there is another group of release signal which will be called FCC Group in the subsequent context. Here the word 'Group' is used instead of 'Peak' because each 'group' requires more than a single (defined by a definite activation energy) dissociation event to reasonably reproduce the peak width and thus, may involve multiple dissociation mechanisms [23].

By comparing the four release spectra from the PC specimens, the effect of varying implantation energy and fluence can be extracted. For example, at a fixed energy of 5 keV, as the He fluence increases from 10^{14} (Fig. 1 (a)) to 10^{15} (Fig. 1 (b)) He/cm², the relative strengths (intensities) of Group I and Group II at low and intermediate T with respect to the entire spectrum apparently decrease while that of the release

in the FCC phase at very high T apparently increases. Similar trends can be recognized when spectra corresponding to a common He fluence, but with increasing implantation energies are compared. However, it is evident from Fig. 1 (a)-(d) that the effect of varying He fluence is much more significant than that of varying He energy, at least within the range of fluence and energy in the present study.



General features of SC spectra - similarities and distinctions with respect to PC spectra



As shown in Fig. 2 (a)-(d), the He desorption spectra from the SC specimens display certain similarities and distinctions when compared with the PC spectra shown in Fig. 1 (a)-(d). Similar to the PC spectra, the SC spectra also exhibit the sharp, alpha-gamma phase transformation peak, and again this peak has been used to calibrate the temperature readings. The second similarity involves the existence of multiple He release groups in well separated temperature ranges, although there are differences in the details of such grouping. Third, the SC spectra exhibit similar effects of implantation energy and fluence as the PC spectra.

The SC spectra are distinct from the PC spectra in the following three aspects. First, the SC spectra only comprise two groups of signal within the BCC structural range, Group I from room temperature to 300 °C, Group II from ~550 °C to 900 °C, with no obvious signal between 300 °C and 550 to 600°C as in the PC spectra (Group II, PC). Second, Group I at low T and the release within the FCC phase at very high T are both narrower in SC than in PC. Third, the major desorption group (Group III for PC, Group II for SC) appears to have more splitting, or fine-scale structure in the SC specimens than in PC. The above three aspects, when viewed together, are actually consistent in that they reflect a common distinction between SC and PC spectra: SC spectra are less diffuse than PC spectra.

It is tempting to ascribe the less diffuse character of SC spectra to the absence of grain boundaries, considering the wide range of He trapping strength (binding energies) that can be provided by grain boundaries of different structures, associated with the trapping of He with excess volume in the boundary [12]. To uncover the exact reason behind the observed distinction(s) between SC and PC desorption spectra requires further investigations perhaps incorporating more systematic modification of grain boundary density. Yet, the present result evidently shows that the desorption behavior of iron is indeed influenced by the presence or absence of grain boundaries and thus that caution should be taken when comparing rate-theory or kinetic Monte-Carlo modeling results with experimental data collected from PC specimens. As a matter of fact, the present SC spectra are expected to provide additional, and perhaps more appropriate experimental reference for future modeling work.

Activation energies

In both Fig. 1 and Fig. 2, we have included an energy scale as the top axis, in correlation with the bottom temperature scale. The displayed energy values were calculated based on simple first-order dissociation

kinetics, i.e., $\frac{d}{dt}N = -Nf \exp\left(-\frac{E}{k_BT}\right)$, where *N* is the remaining number of He atoms not yet desorbed

in a specific trap, *f* is the jumping frequency (assumed to be 10^{13} /s), *E* is the activation energy for the trap, and $k_{B}T$ has its normal meaning. Within this model, it is straightforward to derive the relationship among

peak temperature T_p , heating rate R, and activation energy E, i.e., $\ln(R/T_p^2) = -E/k_BT_p + \ln(f k_B/E)$

[20], which provides a one to one correlation between peak temperature and activation energy at chosen R (here 1 K/s) and f values. It should be noted that this simple model has assumed that there are no mutual transformations among traps with different E values, which is certainly not the real case since evolution among different traps/defect-clusters with distinct E values is unavoidable. However, this simple model can provide an estimate for the average E values of a group of traps which have mutual transformation among themselves and yet sufficiently separated from other groups with respect to E values.

CONCLUSIONS

In this report, we present the results of He desorption in polycrystalline and single-crystalline iron (99.99%) using constant rate (1 K/s) heating following ⁴He implantations at energies of 5 or 10 keV and fluences of 10¹⁴ or 10¹⁵ He/cm². The results reveal both similarities and distinctions between the He desorption of the PC and SC specimens. The similarities include the appearance of a sharp release peak induced by alpha-gamma phase transformation, the existence of multiple desorption groups, and the influence of varying implantation energy and fluence on desorption behavior. The primary distinction is that SC spectra are less diffuse than PC spectra, which is reflected in three details: 1. within BCC structural range, SC spectra comprise only two groups of signal (Group I, room temperature to 300 °C; Group II 550-900 °C) as opposed to three observed in PC spectra (Group I, room temperature to 300 °C; Group II, 300-600 °C; Group III 600-900 °C); 2. Group I appears narrower for SC than for PC; 3. Group II of SC display more fine-scale structure than Group III of PC. The average activation energies associated with the observed desorption groups have been estimated based on simple first order dissociation kinetics. While the underlying microscopic mechanisms are not entirely clear at this stage, our result suggests that it may not be advisable to compare rate-theory or kinetic Monte-Carlo modeling which does not include grain boundaries with desorption experiments conducted on PC specimens. The present

desorption data from SC iron are expected to provide additional, and perhaps a more appropriate experimental reference for future modeling.

ACKNOWLEDGEMENTS

The authors thank Dr. Stuart A. Maloy (LANL) for providing the single crystal Fe specimens, and Drs. Maria Jose Caturla (University of Alicante), Cu-Chun Fu (CEA-Saclay), Rick Kurtz (Pacific Northwest National Laboratory), Bob Odette (University of California, Santa Barbara), Christophe Ortiz (University of Alicante), and Kazunori Morishita (University of Kyoto) for helpful discussions. This work has been supported by the Office of Fusion Energy Sciences, U.S. Department of Energy, under Grant DE-FG02-04ER54750.

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INTERACTION OF He_nV_m CLUSTERS WITH COHERENT AND SEMI-COHERENT Fe/Cu

INTERFACES - R. J. Kurtz, H. L. Heinisch, and F. Gao (Pacific Northwest National Laboratory)*

OBJECTIVE

To use molecular dynamics computer simulations to compare the trapping of He_nV_m clusters at coherent and semi-coherent bcc Fe/bcc Cu interfaces. The semi-coherent interfaces contain an array of misfit dislocations.

SUMMARY

Previous computational modeling has shown that interstitial and substitutional He as well as Hedivacancy clusters are strongly bound to extended defects in Fe such as dislocations, grain boundaries and particle-matrix interfaces. One aspect of the earlier work was the interaction of He with nanometerscale, coherent particles embedded in an Fe matrix. Our earlier research also established that the core of an edge dislocation strongly traps He. Thus we hypothesized that a semi-coherent interface might be a stronger trap for He than a coherent interface due to the array of misfit dislocations needed to accommodate the lattice parameter mismatch between the particle and the matrix in the semi-coherent case. In the present study we employ atomisitic simulations to compare the binding of He_nV_m complexes to coherent and semi-coherent bcc Fe/ bcc Cu interfaces. The simulations show that the binding energy of He_nV_m complexes to a coherent Fe/Cu interface range from 0.35 eV for a single vacancy up to 0.70 eV for a He₁V₂ complex. A semi-coherent interface was found to be a much stronger trap for He near the core of a misfit dislocation. Binding energies varied from 0.86 eV for a substitutional He atom up to 2.38 eV for a He₁V₂ complex. These binding energies were found to be significantly larger than the values obtained for simple edge dislocations in Fe. The trend in binding energies can be rationalized in terms of the spatial dependence of excess atomic volume for each interface.

PROGRESS AND STATUS

Introduction

The work reported here is part of a comprehensive effort to develop a multi-scale model of He transport and fate in ferritic/martensitic alloys [1]. The model will be used to predict the performance of irradiated ferritic/martensitic steels, both conventional and oxide dispersion strengthened. In previous studies we employed atomistic simulations to explore the binding and migration of He at extended defects in Fe such as dislocations, grain boundaries (GB), and particle-matrix interfaces [2-5]. The results showed that interstitial He is strongly bound to both dislocations and GBs with maximum binding energies ranging from 0.55-2.66 eV. Substitutional He is also bound to dislocations and GBs, but much more weakly than for interstitial He, with maximum binding energies between 0.17-0.78 eV. Point defect complexes are also bound to coherent, positive misfit, 2 nm Cu particles embedded in an Fe matrix with binding energies ranging from 0.50-0.58 eV for single vacancies and substitutional He atoms. Divacancies and He/divacancy complexes are more strongly bound with binding energies of ~0.85 eV. Point defects are not as strongly bound to particles elastically softer than Fe when compared to particles elastically stiffer than Fe.

A key result from this research is that binding energies strongly correlate with defect excess volume. Consequently edge dislocations are stronger He traps than screw dislocations because of the much larger excess volume available in an edge dislocation compared with a screw dislocation. However, jogs on edge dislocations are even stronger traps for He. Helium trapping at GBs is somewhat greater to somewhat less than for dislocations depending on the type of GB. Coherent, positive misfit, Cu nanoparticles also efficiently trap He, but it is apparent that semi-coherent particles may be more efficient traps because of the excess volume associated with the array of misfit dislocations needed to accommodate the lattice parameter mismatch between the particle and matrix. Consequently our interest

^{*}Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830.

here is to compare the relative efficiency for trapping He_nV_m complexes at a coherent interface between bcc Fe and bcc Cu to a semi-coherent interface between the same two materials.

Computational Methods

Details of the computational methods for studying the interaction of He_nV_m complexes with various defects in an Fe matrix have been described previously [5]. Here we present only the salient features of the calculations pertaining to the question of He trapping at coherent versus semi-coherent interfaces. The model consists of a two-part rectangular computational cell, periodic in x and z. One part, Region 1, contains movable atoms embedded in a semi-rigid part, Region 2. The interface approximately bisects the model as shown in Figure 1. Equilibrium structures at T ~ 0K are obtained via relaxation using a conjugate gradient scheme. The two crystals on either side of the interface are free to move and undergo homogenous strain in all three directions. This movement occurs during the relaxation via a viscous drag algorithm, i.e., the velocities and strain rates associated with such motions are proportional to the net forces acting on each of the two crystals within Region 1.



Figure 1. Schematic of the model. The interface is parallel to the x-z plane.

Coherent Interface

A cube-on-cube oriented Fe/Cu interface was studied with the interface parallel to (010). This interface was selected for investigation so that the results could be compared to a previous study of coherent Cu nanoparticles in Fe [5]. With the Fe and Cu interatomic potentials employed here [5] the lattice parameter for Fe is 0.28665 nm and for bcc Cu is 0.29607 nm, which corresponds to a mismatch of ~3.2%. Completely coherent interfaces in thick Fe/Cu bilayers likely never occur because they are energetically unfavorable compared to semi-coherent interfaces, but it is instructive to examine a coherent system because it is the favored configuration for thin layers and for nano-scale particles constrained by the crystal structure of the matrix phase. In order to construct a coherent interface that is in mechanical equilibrium the procedure described by Hoagland et al. [6] was followed. Triaxial strains were applied to each layer so that the Fe layer was in a state of biaxial tension and the Cu layer biaxial compression. The computational cell was then relaxed. To determine defect formation energies, various He_nV_m (n=0,1; m=1,2) complexes were placed at specific locations within the relaxed computational cell and the atoms in the cell were relaxed again. The binding energy of the He_nV_m complex to the coherent interface is the difference between the formation energy of the He_nV_m complex in the interface model and its formation energy in either a perfect crystal of bcc Fe or bcc Cu depending on which side of the interface the defect was located.

Semi-coherent Interface

Misfit dislocations are spontaneously created when two semi-infinite perfect crystals with different lattice parameters are joined together. The long-range elastic portion of the dislocation is not present in Region 2, and consequently Region 1 contains an image field. However, the stress and displacement fields of a periodic array of such dislocations with spacing, d, have relatively short range, vanishing with increasing distance from the interface. Thus, in bilayers where the misfit spacing is less than the height of the model, it is not necessary to adjust the positions of the atoms in Region 2. Near the interface, between misfit dislocations, coherency stresses are high. Binding energies of He_nV_m complexes were determined in the same manner as for the coherent interface. The structure of the coherent Fe/Cu interface compared to the semi-coherent Fe/Cu interface is illustrated in Figure 2. Note only one layer of atoms normal to the page is shown in Figure 2.



Figure 2. Structure of a coherent Fe/Cu interface on left and a semi-coherent Fe/Cu interface on right. Only one layer of atoms normal to the page is shown.

Results

Coherent Interface

Excess volume within and near interfaces strongly influences the disposition of He in crystalline materials. The atomic volume is defined as the locus of all points in space surrounding an atom that are closer to that atom than to any other atom. Excess volume at a location near an interface is defined in terms of the deviation of the atomic volume at that location from the atomic volume at a similar location in a perfect lattice. Here we calculate excess atomic volume centered on lattice sites. The distribution of excess atomic volume for the coherent Fe/Cu interface is shown in Figure 3. Note there is positive excess atomic volume everywhere in the Fe layer, and negative excess volume everywhere in the Cu layer. This is because the Fe layer is dilated relative to a perfect Fe lattice and the Cu layer is compressed relative to a perfect bcc Cu lattice. Near the interface in the first two layers of Fe and Cu the excess volume is either larger or smaller than the values far from the interface.

The binding energies of various He_nV_m complexes to a coherent Fe/Cu interface are presented in Figure 4. Single vacancies and substitutional He atoms are bound to the coherent interface on the Fe side of the bilayer with maximum binding energies of 0.35 and 0.41 eV, respectively. Divacancies and a He_1V_2 complex, with maximum binding energies of 0.66 and 0.70 eV, respectively, are more strongly bound to

the Fe side of the bilayer than are single vacancies or substitutional He atoms. The Cu layer adjacent to the interface is a relatively unfavorable site for substitutional He and the He_1V_2 complex. However, the same layer was not observed to be unfavorable for either vacancy-type defect. From these results we can conclude that the trend of binding energies to the interface for point defects containing He follows the distribution of excess atomic volume given in Figure 3.

Semi-coherent Interface

The distribution of excess atomic volume for the semi-coherent Fe/Cu interface is illustrated in Figure 5. The plot shows the excess volume for only the first two layers or rows of Fe atoms adjacent to the interface as a function of distance from the origin of the misfit dislocation. Midway between misfit dislocations the interface is coherent, so the excess volume should correspond to the value found for a purely coherent interface. From Figure 3 the excess volume for the first and second Fe layers is about 0.4 and 0.2 Å³, respectively. Approximately the same values for excess volume are found in the semicoherent model at distances far from the origin of the misfit dislocation. From Figure 5 the excess volume at ~40 Å from the misfit dislocation is 0.41 and 0.22 Å³ for the first and second Fe layers, respectively. Consequently we would expect that the binding of point defects remote from misfit dislocations in the semi-coherent model will exhibit behavior similar to that found for the purely coherent case. Near the misfit dislocation there is a sharp increase in excess volume in the first Fe layer. The increase in excess volume dies away quickly with distance from the misfit dislocation and is almost the same as the purely coherent case excess volume at 6 Å away. In contrast, there is a sharp decrease in excess volume for atoms in the second Fe layer near the misfit origin. This is not surprising since the extra half plane of atoms associated with the misfit dislocation resides on the Fe side of the interface so a local state of compression exists in this region.

Figure 6 shows the dependence of binding energies for single vacancies or substitutional He atoms located in either the first or second layer of Fe atoms adjacent to the interface as a function of distance from the misfit dislocation origin. The largest binding energies for these point defect types occur in the first layer of Fe atoms where the peak positive excess volume is found. Single vacancies are bound somewhat more strongly (0.95 eV) to the misfit dislocation than substitutional He atoms (0.85 eV). The binding energy of substitutional He to the misfit dislocation is larger than the value found for the same point defect to an edge dislocation in pure Fe (0.51 eV) [3]. This may be due to the dilated state of the Fe in the Fe/Cu interface relative to an edge dislocation in pure Fe, although the calculated excess volume for the edge dislocation was about 1.2 $Å^3$ [3] compared to an excess volume for the misfit dislocation of 0.75 Å³. In the second Fe layer we find single vacancies are bound to the misfit dislocation core with an energy of about 0.32 eV. This is expected since the compressive stress field of the misfit is a region where vacancies should segregate. On the other hand, substitutional He atoms are not attracted to this region due to an unfavorable excess volume. The situation for binding of divacancies and a He_1V_2 complex to the semi-coherent interface is shown in Figure 7. In the first Fe layer these defects are very strongly bound to the misfit dislocation with the binding energy for a divacancy of 1.47 eV and for the He₁V₂ complex 2.38 eV. We have also investigated the binding of a He₁V₂ complex to an edge dislocation in pure Fe and determined the binding energy to be 1.26 eV. Clearly the He₁V₂ complex is much more strongly bound to the misfit dislocation than it is to a simple edge dislocation in pure Fe. For the second Fe layer both divacancies and the He₁V₂ complex are less strongly bound to the misfit dislocation than for the first Fe layer. The divacancy is the most strongly bound in this region (0.64 eV) compared to the He_1V_2 complex (0.42 eV). Evidently, segregation of divacancies to the compressive side of the misfit dislocation should facilitate binding of He-vacancy clusters in this region.



Figure 3. Distribution of excess atomic volume in a coherent Fe/Cu interface.



Figure 4. Binding energy of vacancies and He_nV_m complexes to a coherent Fe/Cu interface.



Figure 5. Dependence of excess atomic volume parallel to a semi-coherent Fe/Cu interface for the first two layers of Fe atoms adjacent to the interface as a function of distance from a misfit dislocation.



Figure 6. Binding energies of single vacancies and substitutional He atoms to semi-coherent Fe/Cu interface for the first two layers of Fe atoms adjacent to the interface.



Figure 7. Binding energies of divacancies and He_1V_2 complexes to a semi-coherent Fe/Cu interface for the first two layers of Fe atoms adjacent to the interface.

Summary

 He_nV_m complexes are bound to a coherent bcc Fe/bcc Cu interface with binding energies ranging from 0.35 eV for a single vacancy up to 0.70 eV for a He_1V_2 complex. He_nV_m complexes are more strongly bound to a semi-coherent Fe/Cu interface in the vicinity of the misfit dislocation with maximum binding energies ranging from 0.86 eV for a substitutional He atom up to 2.38 eV for a He_1V_2 complex. The binding energy trend for point defects containing He atoms follows the spatial dependence of excess atomic volume for each interface.

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INTERACTION OF VACANCIES AND HELIUM ATOMS WITH a/2 <111> **SCREW DISLOCATIONS IN** α -Fe - H. L. Heinisch, F. Gao, R. J. Kurtz (Pacific Northwest National Laboratory)¹

OBJECTIVE

The objective of this research is to understand the fate of lattice defects and He atoms produced in metals and alloys by fusion neutron-induced transmutation reactions. In the present work the migration energies and diffusion mechanisms of vacancies and He atoms in and near screw dislocations in α -Fe are studied using atomic-scale simulations.

SUMMARY

Migration energies of vacancies and He atoms in and near the core of an a/2<111> screw dislocation in α -Fe were determined in atomistic simulations using conjugate gradient relaxation and the Dimer method for determining saddle point energies. Results for defects in initial positions in and near the screw dislocation core were obtained for migration toward and away from the dislocation line, as well as along the dislocation line direction. For both vacancies and individual interstitial helium atoms migration is favored toward and along the screw dislocation. Vacancies trapped in the dislocation core migrate along the dislocation with a migration energy of about 0.4 eV, which is about half the migration energy of vacancies in the perfect crystal.

PROGRESS AND STATUS

Introduction

A detailed study of how He interacts with dislocations and other microstructural features is needed to develop improved kinetic Monte Carlo and rate theory models for prediction of long-time material behavior in the high helium environment of fusion reactor materials. A key element of He effects is the role that vacancies play in these interactions. In the present work molecular statics, molecular dynamics and the dimer method of potential surface mapping are being used to study vacancy-dislocation interactions within the core and in the vicinity of dislocations in alpha-iron, which we consider to be a first-order model for ferritic steels. We report here on the calculations of migration energies of vacancies in the vicinity of a screw dislocation, including migration of vacancies within the dislocation core.

Computer Simulations

An a/2<111> screw dislocation was created along the axis of a cylindrical cell of body-centered cubic Fe, oriented as in Fig. 1(a). The dislocation was introduced by displacing the atoms according to the anisotropic elastic displacement field of the dislocation, then relaxing the entire model with fixed boundary conditions. The model is periodic along the dislocation line. In previous studies [1] conjugate gradient relaxations were performed to determine binding energies for single He atoms placed at various substitutional and interstitial positions in the dislocation-distorted lattice and at various distances from the dislocation line. Also in those studies the Dimer method [2] was used to determine saddle point energies for possible transitions of interstitial He atoms to other locations, starting from a number of relaxed He atom positions about the dislocation. Within about 1 nm from the dislocation core center, single He atoms were found to be attracted to the screw dislocation and to preferentially migrate along it, Fig. 1(b).

The Dimer results give the migration energies and saddle point atom configurations for defects as they migrate from one equilibrium position to another. In a single run the Dimer method can find saddle points for more than one transition from a given starting configuration, not just the transition having the lowest energy. Thus, it is useful for locating unexpected and competing transitions, which can be especially

¹ Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830.

important in exploring a complicated potential energy landscape such as near a dislocation or a grain boundary.



Figure 1. a) The orientation of the computational cell for the a/2<111> screw dislocation in α -Fe. The dislocation line and Burgers vector lie along [111] (the z-direction, out of the page), b) Regions of attraction of interstitial He atoms toward the center of the screw dislocation and migration along it.

In the present study Dimer calculations were performed to determine saddle point energies for the migration of single vacancies in and near the screw dislocation. In these calculations a single vacancy was introduced at various locations within the regions near the dislocation illustrated in Fig. 1(b), and at each location saddle point energies for transitions corresponding to migration toward, away from or along the dislocation line were identified. In addition, at many of the same locations, similar calculations were also performed for divacancies of various orientations relative to the dislocation line. Initial studies of He-divacancy stability within the screw dislocation were also performed.

In all cases the set of interatomic potentials due to Ackland [3], Wilson and Johnson [4], and Beck [5] were used for the Fe-Fe, Fe-He and He-He interactions, respectively. These potentials were used primarily because they have been used extensively by us and others investigating He disposition in α -Fe. We have tested other potentials, especially the more recently developed Fe-Fe potential by Mendelev et al. [6], in similar calculations, and we find it gives somewhat smaller values for the formation and migration energies. However, the energies calculated using the Mendelev potential tend to scale with those determined using the Ackland potential. Thus, we expect that the phenomena observed in these simulations will be the same with either potential, but the energies will be somewhat smaller proportionally using the Mendelev potential.

Results

In the earlier work [1] single interstitial He atoms placed at various locations in the vicinity of a <111> screw dislocation were found to migrate preferentially toward the dislocation core with a migration energy of $E_m = 0.2 - 0.4$ eV within a region of about 1 nm radius. He atoms are trapped in the core region with a binding energy of $E_b \sim 1$ eV relative to their energy in a perfect Fe lattice. He atoms trapped within the core region were found to migrate along the dislocation core with a migration energy of $E_m \sim 0.4$ eV. Migration energies of He and vacancy defects in the perfect crystal and along the dislocation are summarized in Table 1.

Vacancies. In the present simulations vacancy migration trajectories were determined starting well outside the core of the screw dislocation and continuing until the "trapped" vacancy migrates along the dislocation line. Two views of such a trajectory are displayed in Fig. 2. The differences in the energies for hopping forward and back between the same atom locations are show in Fig 2a, illustrating that the vacancy's path is "downhill" (i.e. the vacancy in the matrix is attracted to the dislocation) until it approaches the region in the dislocation at which it is most strongly trapped. Once trapped in the core region, the vacancy migrates back and forth along the dislocation with migration energy of 0.43 eV, which is about half the migration energy required for vacancy migration in the perfect crystal.



Figure 2 Two views of one possible path for a single vacancy migrating from nearly perfect crystal to become trapped in a <111> screw dislocation and subsequently migrating along the dislocation line. (a) The X-Z plot on the left shows the transition energies for hopping from one atomic location to another in both directions. (b) The Y-Z plot on the right shows the same path rotated by 90 degrees about the dislocation line.

Divacancies. In the perfect Fe crystal divacancies that consist of second nearest neighbor (2nn) sites are slightly more stable (by ~ 0.05 eV) than first nearest neighbor (1nn) divacancies. Divacancies migrate in the perfect crystal by hopping alternately between 2nn and 1nn configurations with an overall migration energy of $E_m = 0.89$ eV.

For divacancy migration near and within the screw dislocation there are a number of possible transition state pathways, including intermediate metastable states, for divacancy migration and dissociation, depending on location and orientation of the divacancy relative to the dislocation. The following conclusions are based on a sampling of the possibilities: Within the screw dislocation the 2nn divacancy is overall more stable than the 1nn divacancy by up to 0.21 eV. However, the 1nn divacancy stability depends on the orientation of the two vacancies relative to the dislocation line. Overall, the most stable divacancy configuration within the dislocation is as 1nn along the direction of the divacancy is greater within the screw dislocation than in the perfect crystal. Migration of a divacancy within a screw dislocation is similar to migration in the perfect crystal, i.e. hopping alternately between 1nn and 2nn configurations, but with a slightly smaller migration energy of $E_m = 0.82 \text{ eV}$ in the dislocation.

<u>Helium-Divacancy Complex</u>. In the perfect crystal the He-divacancy complex is much more stable (by 0.27 eV) in the 1nn configuration where the vacancies are first nearest neighbors and the He atom sits in a stable position between the lattice site and the midpoint of the two 1nn sites, compared to the 2nn configuration, where the He becomes a substitutional He in one of the vacancies. In the perfect crystal the migration energy of the He-divacancy, from the initial 1nn configuration via an intermediate 2nn configuration to another 1nn configuration, is $E_m = 1.13 \text{ eV}$.

Near the core of a screw dislocation the He-divacancy complex is also more stable in the 1nn configuration, and the migration energy of the complex is about the same as in the perfect crystal, $E_m = 1.11 \text{ eV}$, for hopping from the 1nn configuration into a 2nn configuration. However, for at least one case within the dislocation, a He-divacancy complex in the higher energy 2nn configuration can more easily decompose to an immobile substitutional He plus a migrating vacancy (activation energy = 0.56 eV) than to continue (or return) to a stable1nn He-divacancy complex (activation energy = 0.69 eV).

Defect Type	Migration Energy in Perfect Crystal, eV	Migration Energy in Screw Dislocation, eV
Interstitial He atom	0.08	0.40*
Vacancy	0.78	0.43
Divacancy	0.89	0.82
He-Divacancy	1.13	1.11

*Minimum, along dislocation line.

Table 1. Defect migration energies in α -Fe for migration in the perfect crystal as well as within <111> screw sislocations calculated using the Dimer method for determining transition state saddle point energies.

Conclusions

The results of these simulations indicate that single vacancies are attracted to and trapped at <111> screw dislocations in α -Fe. Within the dislocation core, vacancies migrate along the core with $E_m = 0.43$ eV, about half the migration energy within the perfect crystal. Single He atoms, migrating as octahedral interstitials, are also attracted to the screw dislocation and can migrate along the dislocation with a migration energy of 0.4 – 0.5 eV. Thus, with both single vacancies and interstitial He atoms easily trapped at the screw dislocation and highly mobile along it, the probability of forming substitutional He in the dislocation is high. Understanding how or whether these trapped He atoms are involved in He bubble formation may be more clearly revealed by our continuing studies of the stability, mobility and interaction of small He and vacancy clusters.

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MIGRATION OF VACANCIES, HE INTERSTITIALS AND HE-VACANCY CLUSTERS AT GRAIN BOUNDARIES IN ALPHA-FE – F. Gao, H. L. Heinisch and R. J. Kurtz (Pacific Northwest National Laboratory)*

OBJECTIVE

The objective of this work is to fundamentally understand the migration mechanisms of vacancies, He interstitials and small He-vacancy clusters at grain boundaries in α -Fe using the dimer method and long-time molecular dynamics.

SUMMARY

The dimer method for searching transition states has been used to systematically study possible migration paths of vacancies, He interstitials and He-vacancy (He/V) clusters at $\Sigma 11 < 110 > \{323\}$ and $\Sigma 3 < 110 > \{111\}$ grain boundaries (GBs) in α -Fe. Vacancies trapped at the GBs diffuse along the GBs with migration energies much less than that within the perfect crystal. Long-time dynamics simulations of diffusion pathways reveal that vacancies migrate one-dimensionally along the close-packed rows in the $\Sigma 3$ GB, and one-dimensionally in zigzag paths within the $\Sigma 11$ GB. Also, dimer saddle point searches show that He interstitials can diffuse along the GBs with migration energies of 0.4-0.5 eV, similar to those of individual vacancies at the GBs, and the corresponding mechanisms are determined. The rate-controlling activation energy for migration of a He-divacancy cluster in the GBs determined using the dimer method is about 0.9 eV, which is comparable to the migration energy for a He-divacancy cluster in bulk α -Fe.

PROGRESS AND STATUS

Introduction

The interactions of He impurities with microstructural features, such as dislocations and grain boundaries (GBs), can result in adverse effects on mechanical properties of metals and alloys. Thus, the formation of He bubbles both in bulk and at GBs remains one of the most important aspects in nuclear fusion technology. A detailed knowledge of He diffusion in both the bulk and at GBs, including the mobility of small helium-vacancy clusters and the nucleation of helium bubbles, is extremely important to quantitatively understand the fate of He atoms with respect to the microstructural features with which they interact.

Previously, molecular statics, molecular dynamics and the dimer method have been combined to study the fate of He atoms in the vicinity of dislocations [1, 2] and GBs [3, 4] in α -Fe. These results have demonstrated that both substitutional and interstitial He atoms are trapped at GBs, with binding energies ranging from 0.2 to 0.8 eV and from 0.5 to 2.7 eV, respectively. Molecular dynamics simulations have shown that the diffusion coefficient for He diffusion along an extended defect is expected to depend significantly on the type of extended sink (dislocation or GB). Also, the diffusion mechanisms strongly depend on the atomic structures of GBs as well as the temperatures [4]. In the present study, the detailed diffusion mechanisms and energy barriers of He interstitials and small He-vacancy clusters in two representative GBs are studied using the dimer method. In parallel, the migrations of vacancies in these GBs are studied using both the dimer method and long-time dynamics simulations to understand their possible contributions to the formation of helium bubbles.

^{*}Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830.

Computational Approach

The details of the methodology used in the calculations of the atomic arrangement of GBs have been previously described elsewhere [3, 4]. The two symmetric tilt GBs studied in the present work are Σ 3{112} Θ =70.53° and Σ 11{323} Θ =50.48°, and their corresponding ground-state structures are shown in [5]. Periodic boundary conditions are applied in the directions parallel to the GB plane, whereas a semi-rigid boundary condition is applied in the direction normal to the GB. The dimension of the simulation cell is 33.3 Å x 36 Å x 32.4 Å, consisting of 3120 and 3247 atoms for the Σ 3 GB and Σ 11 GB, respectively.

The lowest energy configurations of a single He interstitial and a He_1V_2 cluster in each GB were determined by raising the lattice temperature to 1000 K, with simulation time up to about 10 ps, and then slowly cooling down to 0 K. The possible transitions starting from these stable configurations were systematically searched using the dimer method [6]. In all cases 100 dimer searches were carried out starting from each initial state. The end configuration that corresponds to the lowest energy barrier was used for the next set of dimer searches. This approach repeats until the He interstitial and He_1V_2 cluster migrate to positions which are equivalent to their original positions. In addition, long-time dynamics based on the dimer method [7] was employed to investigate the long-time behavior of a single vacancy in the GBs. The interatomic potentials describing the Fe-Fe, Fe-He and He-He interactions are the same as those used previously [4]. In the simulations of vacancy migration, the recently developed Fe-Fe potential by Mendelev et al. [8] was also used to check the potential-sensitivity of its migration energy and path in both the bulk and GBs.

Results

The transition states of He interstitials, vacancies and HeV₂ clusters are searched in both the GBs using the dimer method, and the highest energy barrier along the lowest energy path is determined to be the corresponding activation energy for migration of a defect or a cluster. Table 1 summarizes the possible migration energies for He interstitials, vacancies and HeV₂ clusters in the Σ 3 and Σ 11 GBs, along with those in the bulk for comparison.

E _m (eV)				
	Не	V	He_1V_2	
Σ3	0.46	0.48 (0.38)	0.9	
Σ11	0.47	0.74 (0.61)	0.92	
Bulk	0.08	0.78 (0.64)	1.13	

Table 1 Migration energies of defects in both bulk and GBs, along with those of vacancies. Values in parenthesis were obtained using the new Mendelev potential [8] for comparison.

He interstitial. The possible migration mechanisms for a He interstitial in the Σ 3 GB are shown in Figure 1(a). Initially, the He atom can migrate from one octahedral position below the GB plane to a similar position above the GB plane along the $[\overline{1}\ \overline{1}1]$ direction, as indicated by one of the arrows, overcoming an energy barrier of 0.46 eV. Then, the He atom can further migrate to an equivalent position below the GB plane with the same energy along the $[1\overline{1}\ \overline{1}]$ direction, but in a different atomic row, which results in the

net diffusion of the He atom along the $[1\overline{1}1]$ direction, denoted as path A. If the He migrates to a row above the GB plane along the $[\overline{1}11]$ direction, and then migrates to a different location in its initial row along the $[\overline{1}\overline{1}\overline{1}]$ direction, the migration of the He atom leads to its net diffusion along the [110] direction, which is denoted as path B. These two paths have the same migration energy and are equivalent, which may be associated with the typical atomic structure of the $\Sigma 3$ GB, and results in two-dimensional migration of He within the GB plane. Previously, molecular dynamics simulations revealed that the He atom migrates two-dimensionally at low temperature and three-dimensionally at higher temperatures in the $\Sigma 3$ GB [4]. The present dimer results are in excellent agreement with the previous MD simulations, and they now provide a physical explanation for the observed phenomena.



Figure 1. Possible migration paths of a He interstitial in (a) the Σ 3 GB and (b) the Σ 11 GB, where a small sphere represents the He atom and arrows indicate possible paths.

Figure 1(b) shows the possible migration paths of a He interstitial in the Σ 11 GB. Dimer searches indicate that the He atom can migrate from a tetrahedral position below the GB plane to a similar position above the GB plane, and this movement leads to the He atom diffusion along the [$\overline{1}$ 13] direction, as indicated by the arrows. This path is the lowest energy path, with an activation energy of 0.47 eV. Also, dimer searches reveal other possible transition states, but with much higher energies. These results suggest that the He atom migrates one-dimensionally along the [$\overline{1}$ 13] direction, but its path is zigzag along the interface in the same plane. The present dimer results are in good agreement with the previous MD studies [4]. The MD simulations suggest that the He interstitial is strongly bound to the middle plane on which the initial starting position of the He interstitial is located, and it can only move in the spaces between the three planes.

Vacancy: One of the components controlling He bubble nucleation and growth is the mobility of vacancies in both bulk and GBs. Both He atoms and vacancies can be deeply trapped by dislocations and GBs, and the fundamental understanding of their migrations within dislocations and GBs is important for multi-scale computer simulation of microstructural evolution under radiation conditions. The dimer searches find the lowest vacancy migration energy to be 0.48 eV in the $\Sigma 3$ GB, which is much smaller than that in the bulk (see Table 1). The surprising result is that the vacancy migrates one-dimensionally along the Σ 3 GB, as demonstrated in Figure 2(a), where the arrows indicate possible paths. A long-time dynamics simulation has also been carried out to study the vacancy migration, and it is found that the vacancy moves forwards and backwards along the $[1\overline{1}1]$ direction. This confirms that the vacancy migrates only one-dimensionally with a similar energy to that of a He interstitial in the $\Sigma 3$ GB. Figure 2(b) shows the possible mechanisms for a vacancy to migrate in the Σ 11 GB, and its path is a zigzag path along the interface, with strong bonding to the interface. One of the interesting results is that the vacancy migrates within a plane perpendicular to the interface, and the migration out of the plane requires much higher energy (~0.77 and 0.9 eV within the Σ 3 and Σ 11 GBs, respectively). These results suggest that the vacancies may migrate one-dimensionally at low temperatures and two-dimensionally at higher temperatures.

We have also used the new Fe potential recently developed by Mendelev at al. [8] to study the vacancy migration in both GBs (included in Table 1), as included in the parenthesis. The migration mechanisms of the vacancies are very similar to those observed in the Ackland potential, i.e. the vacancy migrates onedimensionally along the $[1\overline{1}1]$ direction in the $\Sigma 3$ GB, whereas its path is a zigzag path in the $\Sigma 11$ GB, with one-dimensional behavior along the $[\overline{1}13]$ direction, but with slightly smaller migration energies.



Figure 2. Possible paths of a trapped vacancy in (a) the Σ 3 GB and the Σ 11 GB, where the white squares represent vacancies and arrows indicate their movements along the GBs.

 He_1V_2 cluster: The most stable configuration for a He_1V_2 complex in the GBs is found to be two first neighbor vacancies, with a He atom located between them, as shown in Figure 3(a). This configuration is slightly different from the most stable configuration of the He_1V_2 cluster in the bulk, where the He atom is substitutional He, but slightly displaced from one vacancy along the line between the two vacancies. To understand the migration of a He_1V_2 cluster within GBs, the dimer searches of transition states were first carried out to study its migration in the bulk. The results show that there exist a number of possible transition states. The lowest transition state corresponds to the He jumping from one vacancy to the other with an activation energy of 0.02 eV for first neighbor vacancies, but this energy increases to 0.66 eV for second neighbor vacancies. The migration of the He₁V₂ cluster is dominated by the vacancy migration, rather than by the He atom, i.e. it is a vacancy mechanism. The migration energy is determined to be about 1.13 eV. Fu and Willaime [9] studied the migration of a He₁V₂ cluster in the bulk using *ab initio* methods, and they found that the He₁V₂ cluster can migrate as a unit over appreciable distance via substitutional He-vacancy mechanisms, with an activation energy of 1.17 eV. The mechanisms and migration energy obtained in the present study are in excellent agreement with their results.

Figure 3 shows the migration mechanisms of a He₁V₂ cluster in the Σ 3 GB, and its path is a rotational path within the interface. Starting with the stable configuration, the He atom diffuses into the nearest vacancy site above the GB plane, and becomes a substitutional He. At the same time, an Fe atom close to one of the two vacancies below the GB plane diffuses into this vacancy site, resulting in a configuration where the He atom and the vacancy are in second neighbor positions, as exhibited in Figure 3(b). The arrows in Figure 3(a) indicate the movements of the He atoms and vacancies, and it should be noted that the migration behavior of the He_1V_2 cluster follows a collective motion. However, these defects are strongly bound to the interface, and the possible dissociation from the interface requires much higher energy. The further diffusion of an Fe atom above the GB plane to the vacancy and of the He atom to a nearest-neighbor site lead to the formation of a configuration similar to the initial configuration, but with different direction. This collective motion is indicated by the arrows in Figure 3(b). There are two possible migration paths for the configuration in Figure 3(c), one back to its original position in Figure 3(a) and another resulting in its migration along the $[\overline{1}1\overline{1}]$ direction. Similar to the migration of a vacancy, these collective motions eventually lead to one-dimensional migration along the interface, with a corresponding migration energy of 0.9 eV. It should be emphasized that these collective motions occur within a plane perpendicular to the interface, and out-of-plane migration of the He_1V_2 cluster is not observed, or it may require much higher energy. Similar behavior of the He₁V₂ cluster in the Σ 11 GB is observed, and its migration energy is about 0.92 eV. It is noted that the migration energy of a He₁V₂ in the GBs is similar to that in the bulk, but the migration mechanisms are completely different. In the bulk, the He₁V₂ cluster can migrate three dimensionally, while it migrates only one-dimensionally via the substitutional He-vacancy migration mechanism within the GBs.



Figure 3. Migration mechanism of a HeV₂ cluster, where the arrows indicate the collective motion of Fe and He atoms, resulting in its one-dimensional migration along the Σ 3 GB.

Summary

The possible migration paths and mechanisms of vacancies, He interstitials and He-vacancy (He/V) clusters at $\Sigma 11$ and $\Sigma 3$ GBs are studied by combining dimer saddle point searches and long-time dynamics in alpha-Fe. In contrast to the three-dimensional migration behavior of vacancies in the perfect crystal, they migrate one-dimensionally along close-packed rows in the $\Sigma 3$ GB and one-dimensionally in zigzag paths within the $\Sigma 11$ GB. He interstitials can diffuse along the GBs with migration energies of 0.4-0.5 eV, similar to those of individual vacancies at the GBs. There are two equivalent paths for a He interstitial within the $\Sigma 3$ GB plane, leading to its two-dimensional migration, but there is only one possible path in the $\Sigma 11$ GB. The migration energy of a He-divacancy cluster in the GBs using the dimer method is determined to be about 0.9 eV, and the corresponding migration mechanism shows that its path is a rotational path within the GBs, but its collective motion exhibits one-dimensional migration parallel to the GB plane.

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MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION -A. Caro, P. Erhart, M. Serrano de Caro, B. Sadigh (Lawrence Livermore National Laboratory), E. Lopasso (Centro Atomico Bariloche, Argentine), D. Farkas (Virginia Polytechnical Institute), S.G. Srinivasan, and C. Jiang (LANL).

OBJECTIVE

This research has two main objectives:

• The development of computational tools to evaluate alloy properties, using the information contained in thermodynamic functions. We aim at improving the ability of classical potentials to account for complex alloy behavior, and

• The application of these tools to predict properties of alloys under irradiation, in particular the FeCr system.

SUMMARY

Computer simulations of processes related to radiation damage have provided deep insight into atomistic processes at the origin of all changes that irradiation produces on mechanical properties of materials. However, as progress continues and more and more complex materials are developed, like the nanostructured Oxide Disperse Strengthened (ODS) ferritic steels, the simulations are confronted with the necessity to capture intricate thermodynamic and kinetic effects. The work reported here is an attempt to bring simulation capabilities to new domains where such effects are accurately described. In this report we present our recent results on the nature of the phase diagram of FeCr in the low Cr region, where finite solubility together with the existence of new intermetallic phases may be at the origin of the explanation of embrittlement and swelling under irradiation, with their intricate dependence on Cr composition.

Our work in the last few years has followed a systematic approach to model this alloy that started with a methodology to generalize many-body classic potentials to incorporate complex formation energy curves. Application to Fe-Cr allowed us to predict the implications of the *ab initio* results of formation energy on the phase diagram of this alloy and to get a detailed insight into the processes leading to precipitation of α ' phase under irradiation. In this period we report on the consequences of the negative heat of formation at low Cr composition on the formation of new phases at low T, in particular ordered intermetallic phases, whose existence have been the subject of speculation in recent years.

PROGRESS AND STATUS

Short-range order (SRO) in Fe-rich Fe-Cr alloys is an anomaly originated in the negative heat of formation of this alloy for Cr content below about 5at%. In this region of composition, the mixture is expected to have ordered phases.

To describe the energetic origin of the order in FeCr we notice first that the heat of solution of a single Cr impurity in Fe is large and negative; i. e. the mixture is exothermic with a strong tendency to form compounds. However, as the Cr composition increases, a strong Cr-Cr repulsion, originated in magnetic effects and explained in detail by the work of P. Klaver in Belfast, prevents further incorporation of Cr turning the mixture into an endothermic, or positive heat of formation, i. e. an alloy with tendency to segregate into heterogeneous solid solutions, rich in Fe and rich in Cr. The question that arises then is whether this repulsion is able to stabilize long range ordered structures.



Cr-Cr separation

Figure 1: (left) Scheme of the effective Cr-Cr interaction in dilute FrCr alloys. (right) With an effective interaction potential repulsive at all distances, the system exhibits short range order. If the potential has a negative value at some distances, then possibly new long range order, or intermetallic phases, may exist.

Figure 1 (left) schematizes this topic: for the purpose of the argument, Cr-Cr interaction can be thought of as an effective interaction in a medium represented by the Fe matrix. If this interaction is purely repulsive, then short range order, SRO, appears as a consequence of the tendency of the effective interaction to maximize Cr-Cr separation. This issue has been extensively studied by us and has been reported in the July 2007 Semiannual Report. The corresponding publication is in press in Phys. Rev. B. However, if the effective interaction has a range of distances where it becomes negative, as schematized in Fig. 1 (right), then in addition to SRO, long range order, i. e. true new crystallographic phases may exist. This has been the subject studied in the period covered by this report, and the corresponding publication in under review in Appl. Phys. Lett.



Figure 2: Schematic representation of the energetics of FeCr as a function of composition. For a purely repulsive potential, all possible configurations of Cr atoms must lay below the energy at infinite dilution.

The search for intermetallic phases is equivalent to the search for long range ordered structures whose energy is below the embedding energy at infinite dilution, as shown in Figure 2. For a purely repulsive Cr-Cr interaction, the energy per Cr atom of a given LRO structure can only be larger or equal to the energy at infinite dilution, region marked yellow in Fig. 2. However, for an attractive interaction, some compositions commensurate with long range order, points blue in the figure, must lay below the energy at infinite dilution.

The *ab initio* data by P. Klaver et al., Figure 3, unequivocally shows that no such structures have been found so far, since for every composition, the energy per Cr atom is above the value at the lowest composition (infinite dilution limit). It is important to point out that the structures explored where not the result of a systematic search of possible minimum energy configurations.



Figure 3: Energy per Cr atom of several long range order compounds in the FeCr system reported by Klaver (2006).

In our work we used the results of short range order described in the previous semiannual report to guide the search of ordered structures by distributing Cr atoms along particular crystallographic directions which minimize or maximize the number of Cr-Cr pairs. Since we have calculated the SRO layer by layer up to 4th neighboring shells, we can reverse-engineering the structures in search of those configurations more akin to produce long range order.



Figure 4: Energy per Cr atom of several long range order compounds in the FeCr system reported found by us (red dots) and those by Klaver (2006) (green swuares). Clearly seen are

configurations with energy below the infinite dilution limit, reflecting the existence of a positive Cr-Cr interaction and therefore new intermetallic phases.

The *ab initio* calculations were done using VASP; details can be found in the corresponding publication. The results of our calculations are presented in Figure 4. Clearly seen are numerous long range ordered structures with energies below the dilute limit. These are candidates to be stable intermetallic compounds. One of them, marked S1 in the figure has the absolute minimum energy, at a composition of x_{Cr} = 0.0385 or Fe₂₆Cr. Figure 5 shows the superstructure, with Cr atoms located in a bcc lattice with $a_{supercell}$ = 3 a_{bcc} . Cr's are located in the 10th shell of another Cr atom, filling it at 1⁄4 with Cr and 3⁄4 Fr. The crystallography is shown in figure 5.



Figure 5: Lowest energy structure (S1 in Fig. 4).Red atoms are Cr, blue atoms are Fe. Cr atoms sit on a bcc super lattice with $a_{super lattice} = 3 a_0$

If data in Figure 4 are presented in the conventional energy per atom plot, we can use common tangent construction to trace the phase diagram at 0 K. Figure 6 shows those results. The line connecting points S1 and S2 with x=0 and x=1 represents the lowest energy configurations and therefore identify the stable phases, namely: the Fe rich solid solution (bcc), the intermetallic Fe₂₆Cr (bcc superlattice), the intermetallic Fe₁₅Cr(base centered monoclinic), and the Cr rich solid solution (bcc). Additionally we know that the Cr rich solid solution has a miscibility gap and therefore the Cr rich solution may be heterogeneous.

These results represent the most detailed study of the energetics of FeCr in the region of interest for nuclear applications. Even if the ordering energies of these intermetallic phases are probably very low and therefore they are not expected to be observed or to be developed under irradiations, they are the true equilibrium at low T; the remnant order measured experimentally can be considered as originated in them.

The study of order that we have performed during 2007 is the basis for the next step in our work that is the study of dislocation mobility in presence of order. As it is well know, order hinders dislocation motion since dislocation glide disrupts order across the glide plain, generating

a source of hardening. Our next objective is therefore to quantify the influence of order on the mobility functions of screw dislocations in FeCr alloys.



Figure 5: Mixing enthalpy per atom of several long range order compounds in the FeCr system reported found by us (red dots) and those by Klaver (2006) (green squares). The blue line connecting points labeled S1 and S2, being lower in energy that any other configuration, identifies the phases existing at 0 K in FeCr.

Conclusions:

In the period reported here, We have concluded the study or order in FeCr with the discovery of two intermetallic phase that represent the ground state of this system at low T. The compounds $Fe_{26}Cr$ and $Fe_{15}Cr$ with bcc and bc monoclinic structures respectively represent the lowest energy structures for this system and their existence confirms the presence of an attractive effective Cr-Cr interaction, whose origin is still to be determined.

Publications

P. Erhart, B. Sadigh, A. Caro, M. Serrano de Caro, "Intermetallic phase in FeCr alloys". Submitted Appl. Phys. Lett.

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L. Malerba, A. Caro, and J. Wallenius. "Multiscale modeling of radiation damage and phase transformations: the challenge of FeCr alloys". Submitted to Jr. Nucl. Mat. 2007.

Conference Presentations

<u>Paul Erhart</u>, Alfredo Caro, Babak Sadigh, Magdalena Caro "Short-Range Order, Precipitation, and Intermetallic Phases In Fe-rich Fe-Cr Alloys". **Invited Talk**, MRS Fall meeting Boston Nov 2007.

<u>M. Caro, A. Caro, P. Erhart.</u> "Precipitation, Segregation, and the Origin of Corrosion Resistance of FeCr Alloys". MRS Fall meeting, Boston Nov 2007

Alfredo Caro. "The Computational Modeling of Alloys: From *ab initio* and Thermodynamics to Precipitation in Fe-Cr. **Invited talk**, Materials for Generation IV Rectors. NATO Advanced Study Institute Cargese, Corsica, Sept 24 – Oct 6 2007.

APPLICATION OF DIGITAL MARKER EXTENSOMETRY TO DETERMINE THE TRUE STRESS-STRAIN BEHAVIOR OF IRRADIATED METALS AND ALLOYS - M. N. Gusev, O. P. Maksimkin, I. S. Osipov (Institute of Nuclear Physics, Almaty, Kazakhstan) and F. A. Garner (Pacific Northwest National Laboratory, Richland WA USA)

OBJECTIVE

The object of this effort is to develop experimental tools to better understand the origin and parametric dependencies of radiation-induced changes in mechanical properties of structural steels used in reactor construction.

SUMMARY

To study the mechanisms of deformation hardening and flow localization of radioactive materials, a non-contact "digital marker extensometry" technique has been employed. It allows researchers to easily define plasticity parameters and true stresses in experiments where highly radioactive miniature specimens are used.

The engineering and "true stress – true local strain" relationships of irradiated metal polycrystals during plastic flow and hardening have been investigated experimentally after irradiation in two reactors in Kazakhstan. The true curves were obtained for copper, nickel, iron, molybdenum, as well as for the Russian stainless steels 08Cr16Ni11Mo3 and 12Cr18Ni10Ti. Describing these curves using the equation $\sigma_i = \sigma_0 + k\sqrt{\varepsilon_i}$ demonstrates that the concept of ultimate stress in highly irradiated materials is an artifact arising from flow localization and is not fully informative of the operating hardening mechanisms.

PROGRESS AND STATUS

Introduction

To describe the plastic deformation behavior of polycrystalline metals, it is necessary to utilize dislocation theory [1, 2] combined with elements of thermodynamics [3] and mesomechanics [4]. In some cases, material-specific physical processes involved in plastic flow also need to be taken into account. Examples of such processes are interrupted deformation (dynamic strain aging) [5], microscopic or macroscopic flow localization [1, 2], arising from defect-dislocation interactions, particularly from defects induced by displacive radiation [6].

In such cases the "true" curves of deformation hardening expressed in true stress-true local strain coordinates are used to build a physical picture of the processes operating to produce the deformation. These curves are usually obtained by conducting experiments involving various extensometry techniques [7], but in most cases researchers derive the true curves from the measurement of load vs. elongation, often referred to as an "engineering" curve.

In the case of highly irradiated metals, however, the experimentally recorded "engineering" curves can not always be converted into true curves. This problem arises from the fact that the local flow stress in irradiated metals often develops very specific peculiarities. As a result of irradiation, the metal loses its ability to deform uniformly under tension. A large portion of the highly irradiated specimen does not develop any significant deformation, while the local deformation in the neck area can be very high. In such cases, the engineering curve is inapplicable for studying the kinetics of the deformation processes and, in particular, for defining the character of the relationship between the true stress and strain values.

To obtain an understanding of the events happening in a deforming specimen and, in particular, to study the relationship between the true stresses and strains, one can use special extensometer

^{*} Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO-1830.

techniques during mechanical testing, such as: optical and electron extensometry [8, 9], coordinate network techniques [10], and speckle-interferometry techniques [11].

When radioactive materials are being tested, the use of these extensometry techniques become much more difficult, often limiting their applicability. For very small or "miniature" specimens used to reduce the level of radioactivity, any technique involving physical or close contact of either measurement probes or persons to the specimens often becomes rather impractical. To overcome such problems we have applied a "marker-extensometry" technique that is uniquely suited to examining very small, highly radioactive specimens that are prone to flow localization on a rather small scale.

Materials Under Study

The study was performed on four pure metals – copper, nickel, molybdenum and Armco-iron. Also were examined Russian industrial alloys 12Cr18Ni10Ti and 08Cr16Ni11Mo3, which are widely used in nuclear reactors in the countries of the former Soviet Union. The compositions of these Fe-base alloys are Cr:18%, Ni:10.6%, Mn:1.7%, C:0.1% and Cr:16%, Ni:11.4%, Mn:1.6%, Mo:1.8% C<0.021%, respectively.

Two types of specimens were used in this study. Flat specimens (See Fig.1a) with gauge section dimensions of $10 \times 3.5 \times 0.3$ mm were punched from strips of pure nickel, iron or molybdenum. The specimens were annealed and then irradiated over a range of doses in the core of the WWR-K reactor (located in Almaty, Kazakhstan Republic) to a maximum fluence of 6×10^{20} n/cm² (E > 0.1 MeV). Round tensile specimens (See Fig.1b) of pure copper and 12Cr18Ni10Ti with gauge section 10 mm long and 1.7 mm diameter were also irradiated in WWR-K. All irradiations proceeded over a rather narrow range of temperature but never exceeded 353K.

Additionally, flat specimens of 08Cr16Ni11Mo3 steel with gauge section dimensions of 10×2×0.3 mm were sliced from various axial positions of the faces of the spent fuel assembly wrapper designated H-214(II) that was irradiated in the BN-350 fast reactor in Aktau, Kazakhstan Republic. The damage dose rate and the accumulated dose in this assembly varied along its height. At its centerline a maximum of 15.6 dpa was reached. Unlike the WWR-K data the irradiation temperature of various specimens varied somewhat, ranging from 553 to 600K.

The thermal treatment of the materials and their irradiation conditions are given in Table 1.

Material	Thermal treatment	Irradiation temperature (K), reactor.	Fluence (n/cm ² , E>0.1 MeV) or dose (dpa)
Nickel	Annealing 1223 K, 30 min.	<353, WWR-K	1.4×10 ¹⁹ - 1.3×10 ²⁰
Armco-iron	Annealing 1223 K, 30min.	<353, WWR-K	5×10 ¹⁸ - 1.4×10 ¹⁹
Molybdenum	Annealing 1473 K, 2 hours	<353, WWR-K	1.1×10 ¹⁹ - 6×10 ²⁰
Copper	Annealing 1023 K, 1 hour	<353, WWR-K	2×10 ²⁰
Steel 12Cr18Ni10Ti	Annealing 1323 K, 30 min.	<353, WWR-K	1.4×10 ¹⁹ - 1.3×10 ²⁰
Steel 08Cr16Ni11Mo3	Cold-work 15-20 % + annealing 1073 K, 1 hour.	553-600, BN-350	1.27 - 15.6 dpa

Table 1. Thermal treatment and irradiation parameters of the materials under study

Uniaxial tensile tests of both non-irradiated and irradiated specimens were performed using the "Instron-1195" facility at 293K with a deformation rate of $8.4 \cdot 10^{-4} s^{-1}$. Pneumatic grippers were used for gripping of the specimens.

Details of the "marker-extensometry" technique

To study the kinetics of non-homogeneous deformation of highly irradiated miniature specimens, a "digital marker extensometry" technique was developed. Small drops (0.3-0.5 mm) of dye material from a marking pen were manually applied to the polished specimen surface. The dye was chosen because it demonstrated good adhesive properties and because it deformed easily without debonding. Note, however, that the use of this dye limits the temperature of the experiment to <373K. Because of the small specimen size, the marker dots and their spacing represent our current limit and thereby the spatial resolution of localized deformation areas.

The shape changes of the specimen, as well as the shape change and shift in position of the markers were recorded by digital camera with high resolution (2048×1536 pixels with a resolution of 10 micron/pixels), as shown in Figure 1.



Figure 1. Shape and dimensions in mm of flat (a) and round (b) samples, gauge area of flat specimen before deformation (c) and change of the shape of a single marker as a result of deformation (d).

The easily reproducible and relatively large size markers used in the first cycle of our experiments were chosen as the first stage of development. Later, when more specific algorithms to process the digital images have been established and a stronger optics system has been developed, it will be possible for other, smaller image elements (smaller dots, small scratches, etc) to serve as markers.

In the current marker extensionetry technique, which is similar to the "network technique" [10], the specimen is covered with a spot network with steps of 1-1.5 mm. This allows us to calculate the values of local strain and stress with an error not higher than 5 and 10 %, respectively, for any section of the specimen based on a sequence of pictures, using specially developed computer codes that calculate the distance *L* between the centers of the markers (see Figure 2). The value of the local strain of some chosen local section of the specimen for the *i*-th picture may be defined as $\varepsilon_i = (L_0 - L_i)/L_i$, where L_0 is the initial distance between the markers (defined from the first picture taken before the deformation started), and L_i is the current distance calculated based upon the *i*-th picture.

It is a well known fact that the material density ρ does not change much in the process of deformation ($\Delta \rho < 1$ %). This fact allows us to say that the volume of the specimen V can be considered as constant during the course of a tensile experiment.



Figure 2. The parameters that are being measured using the marker extensionetry technique. The specimen is loaded by the force F. The highlighted section, which has two markers (M); D is the marker's dimension towards the tensile axis; L is the distance between the centers of the markers; d is the width of the specimen; h is the thickness of the specimen (d and h values are defined before the deformation).

Thus, the operating stress σ_i may be obtained based on the constant volume criterion *V* where $(V=S_0 \cdot L_0 = S_i \cdot L_i = \text{const}$, where $S=h \cdot d$) as follows:

$$\sigma_i = \frac{F_i}{S_0 \cdot \left(\frac{L_0}{L_i}\right)} \tag{1}$$

 F_i is the force acting at *i-th* moment of time and is defined from the engineering diagram, S_0 is initial cross section. The marker dimension along the *D* axis might be used instead of the *L* value in the calculations.

This approach allows us to define the stress value acting along the deformation axis but it does not provide an opportunity to define tangential stresses. This paper does not address the analysis of the complex stress state that takes place in the neck region as it develops.

As discussed earlier [7, 8], it is important to note that the method proposed here cannot be used when strain is concentrated in areas smaller than the size of a marker. In addition, at very levels of local strain the "constant volume criterion" will cease to be valid.

Using the experimental values of the true stresses σ_i and the local strain ε_i , one can construct the distribution curve along the operating length of the specimen for various increments of the deformation until failure or to observe the " $\sigma_i - \varepsilon_i$ " relationship for some section of the specimen (see Figure 3).

It is worth noticing that the experimental " $\sigma_i - \varepsilon_i$ " relationships for the irradiated materials [12] are rarely mentioned in the literature. In particular this is true for specimens with high levels of radiation embrittlement. However, the " $\sigma_i - \varepsilon_i$ " curves have great practical value, especially when used in simulation of plastic deformation in calculations using the ANSYS, ABAQUS or LS-DYNA finite element codes.

Experimental Results

08Cr16Ni11Mo3 Steel irradiated in BN-350

Figure 3 shows typical engineering curves obtained through deformation of neutron irradiated 08Cr16Ni11Mo3 steel. The general features of the curves are similar to that of an earlier study [13]. The yield and ultimate stress values and the plasticity obtained from these diagrams, agree well with the results of others [13, 14, and 15]. As seen in Figure 3, the uniform deformation value is very small (2-4%), and immediately after the yield strength one can observe the development of a neck and the engineering curve becomes non-informative concerning the work hardening processes within the neck area. From the scientific point of view it is informative to study the " $\sigma_i - \varepsilon_i$ " relationship in the developing neck (see Figure 3, curves 3 and 3'). The true curve (3') was calculated for the developing neck based on experimental results using the optical extensometer method.

Figure 4 shows the deformation hardening curves for the 08Cr16Ni11Mo3 steel in the "true stresses σ_i – local strain (ε_i)^{0.5}" coordinates, which were calculated based on the digital marker extensometry data. The square root of strain is used, which according to the suggestion of reference [16] results in linearization of the curves.



Figure 3. Engineering curves for 08Cr16Ni11Mo3 steel presented in conventional coordinates: 1 – irradiated to 1.27 dpa at 280 C°; 2 –10.8 dpa at 300 °C; 3 –11.9 dpa at 354 °C; 3' – the true curve of the plastic flow for curve 3; 4 – non-irradiated steel. The various curves are shifted arbitrarily along the strain axis to provide a better view.

As one can see from comparing Figures 3 and 4, the transition from conventional to real deformation and stress values qualitatively changes the view of the flow curves. Thus, the development of the local strain in the neck is accompanied by continual deformation hardening of the material. The operating stresses increase up to the moment of failure, despite the seeming loss of hardening which is registered by the engineering curve immediately after the yield point. According to [17], here we see the "quasi-embrittlement" case, i.e. the suppression of the uniform deformation, and, this case should be differentiated from that of real embrittlement [18], i.e. the complete suppression of the material's capability for plastic deformation.



Figure 4. The "true stress σ_i – local strain (ϵ_i)^{0.5}" relationship for 08Cr16Ni11Mo3 steel. Curves 1-4 correspond to the specimen numbers shown in Figure 3. The experimental data points are not shown for curves 1 and 2.

Analysis of the experimentally obtained $\sigma_i(\epsilon_i)$ relationships showed that they may be described by the following equation:

$$\sigma_i = k \cdot \mathcal{E}_i^{0.5} + \sigma_0, \tag{2}$$

where *k* is the coefficient of the strain hardening and σ_0 is a value close to the yield strength. In " $\sigma - \varepsilon^{0.5}$ " coordinates these curves appear to be linear.



Figure 5. Changes in yield strength (a) and plasticity (b) versus fluence (for Fe, Ni, Mo) or damage dose (for steel 08Cr16Ni11Mo3): $1 - \alpha$ -Fe, 2 - Mo, 3 - Ni, 4 - 08Cr16Ni11Mo3 steel. 1 - 4 -total and 1' - 4' - uniform deformation for the indicated materials.

In this steel we observe monotonic growth of the σ_0 value with increasing dose, while the *k* value in general decreases but not monotonically. To explain this non-monotonic behavior we speculate that in addition to the dose level, factors such as differences in irradiation temperature and dose rate in this data set affect the material's structure and its deformation behavior [19].

Pure metals (Cu, Fe, Ni, Mo) and 12Cr18Ni10Ti stainless steel irradiated in WWR-K

Figure 5 shows strength and plastic engineering properties of the pure metals versus neutron fluence. In this figure one can see that the yield strength of these metals is steadily increasing, while the plasticity is decreasing. The data agree well with data from other studies [20].



Figure 6. Localized deformation and neck formation in molybdenum irradiated by neutrons to 3×10^{20} n/cm².

The decrease in plasticity demonstrates itself most vividly in the bcc metals, for which the uniform deformation values plunges toward zero when the fluence reaches 1.2×10^{20} n/cm² for molybdenum and 1.4×10^{19} n/cm² for iron. Similar to the case of the steel irradiated to > 10 dpa, the uniform deformation value defined from the engineering diagrams does not exceed 4-6%, in agreement with data in [20, 21, 22]. These specimens lose their ability to deform uniformly and plastic flow becomes concentrated in a very narrow area (see Figure 6) which is usually located in the vicinity of one of the grippers. There are only a few cases when two areas of localized deformation develop. It is quite clear that in this situation the engineering diagrams are of little value to study the plastic flow of the irradiated material.

Figures 7-9 show the engineering and true tensile curves obtained for the various metals. Following suggestions in [16] and also for convenience, we continue to use the square root of the local strain value of the " $\sigma_i - \varepsilon_i$ " curves. Once again linearization of the " $\sigma_i - \varepsilon_i$ " curves occur and can be described by the equation $\sigma_i = \sigma_0 + k\sqrt{\varepsilon_i}$.

Comparing the two types of pictures, one can see that the transition from the engineering to the true curve highlights a qualitative change in the nature of the curve. The concept of ultimate strength does not appear to be applicable since hardening continues in the deforming area up to the failure of the specimen. The local strain may reach values that exceed values obtained from the engineering diagrams by at least 1.5 to 2 times.

Analyzing these experimental data one may assume that the " $\sigma_i - \varepsilon_i$ " curves allow us to obtain more reliable information on the kinetics of the deformation processes and on some peculiarities of interactions of dislocations and radiation defects compared to that obtained from the engineering curves. Table 2 presents the values of K and σ_0 obtained from these studies. In particular, from the true curves it is seen that the σ_0 value continually increases with increasing fluence while the hardening coefficient does not change significantly.


Figure 7. Engineering "stress – strain" curves and " $\sigma_i - \varepsilon_i$ " relationships for non-irradiated and neutron irradiated bcc materials. On the top: Armco-iron, 1 – non-irradiated specimen, 2 – 5x10¹⁸ n/cm², 3 – 1.4x10¹⁹ n/cm². On the bottom: molybdenum, 1 – non-irradiated; 2 – 1.1x10¹⁹ n/cm²; 3 – 1.2x10²⁰ n/cm²; 4 – 3x10² n/cm²; 5 – 6.2x10²⁰ n/cm².

Table 2.	Values k and σ_0	obtained for	unirradiated	and	irradiated	materials.
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Material	Fluence (n/cm ²) or damage dose (dpa)	Yield stress σ ₀₂ , MPa	σ_0 , MPa	k, MPa
Steel Cr18Ni10Ti	0	200	180	830
Steel Cr18Ni10Ti	1.4x10 ¹⁹	510	480	790
Steel Cr16Ni11Mo3	15.6 dpa	920	1100	690
Ni	_	59	85	587
Ni	1.4x10 ¹⁹	236	205	470
Ni	1.4x10 ¹⁹	316	265	448
Fe	-	202	215	369
Fe	5x10 ¹⁸	311	250	369
Fe	1.4x10 ¹⁹	399	405	192
Cu	-	50	13	438
Cu	5x10 ²⁰	350	259	110

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Figure 8. " $\sigma_i - \epsilon_i$ " relationships for non-irradiated and neutron irradiated copper (at the left, 1 –non-irradiated specimen, 2 – 2x10²⁰ n/cm²) and nickel (at the right, 1 –non-irradiated specimen, 2 – 1.4x10¹⁹ n/cm²; 3 – 1.3x10²⁰ n/cm²).

As one can see, the *k* value for irradiated nickel is smaller than for non-irradiated nickel and at the same time *k* does not change when the fluence increases from 1.4×10^{19} to 1.3×10^{20} n/cm².



Figure 9. Engineering curves (thick solid lines) and " $\sigma_i - \epsilon_i$ " relationships (with circles) for the nonirradiated (1) and irradiated neutron stainless steels. 2 – 12Cr18Ni10Ti (WWR-K, 1.4x10¹⁹ n/cm²⁾, 3 – 08Cr16Ni11Mo3 (BN-350, 15.6 dpa).

Another aspect of the marker extensionetry method is that it allows visualization of the distribution of strain along the specimen axis. This is particularly useful when the material is just beginning to harden but appears still to be in the uniform elongation regime. Note in Figure 10 that the strain is not uniform along the length of the specimen but appears to indicate some periodicity. This specimen was 12Cr18Ni10Ti irradiated in WWR-K to 1.4×10^{19} n/cm² or ~0.01 dpa. This indicates that some areas initiate plastic deformation before others although subsequent strain rates appear to keep pace at all positions. So the term "uniform" elongation is not a completely correct description of the deformation process. Stress concentrations near the two grips might account for two of the initiation sites but not for the other three sites.



Figure 10. Distribution of strains along the length of 12Cr18Ni10Ti specimen irradiated in WWR-K to 1.4x10¹⁹ n/cm², taken at equal time intervals during the tensile test. The percentages shown are the elongation observed in the engineering curve.

Figure 11 demonstrates that until necking begins to occur the various regions exhibit identical local strain behavior, following the same true "stress-strain" curve. When the ultimate stress is reached, however, necking occurs and the non-necking areas drop out of the deformation process. The true stress decreases and plastic flow stops in these bypassed areas.



Figure 11. Comparison of engineering (black) and true strain curves (designated by colors) for three areas, showing that all three follow the same true curve initially, but as necking develops the other areas drop out of the deformation process.

Conclusions

To study the peculiarities of the deformation hardening and flow localization of radioactive materials, a non-contact "digital marker extensometry" technique has been developed. It allows the researcher to easily define plasticity parameters and true stresses in experiments where highly radioactive miniature specimens are used.

The " $\sigma_i - \epsilon_i$ " relationship during plastic flow and hardening of irradiated metal polycrystals has been investigated experimentally. True curves have been obtained for nickel, iron, molybdenum, as well as for the 08Cr16Ni11Mo3 and 12Cr18Ni10Ti steels. Describing these curves using the

 $\sigma_i = \sigma_0 + k \sqrt{\varepsilon_i}$ equation demonstrates that the concept of ultimate stress is an artifact arising from flow localization and is not fully informative of the hardening mechanisms operating in highly irradiated materials.

Acknowledgements

This work was conducted in Kazakhstan under ISTC K-437 Research Contract and "Government Fund of Fundamental Research of Kazakhstan Republic". The participation of F. A. Garner was sponsored by the US department of Energy, Office of Fusion Energy under Contract DE-AC06-76RLO 1830 at Pacific Northwest National Laboratory.

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10.0 DOSIMETRY, DAMAGE PARAMETERS, AND ACTIVATION CALCULATIONS

No contributions.

11.0 MATERIALS ENGINEERING AND DESIGN REQUIREMENTS

No contributions.

12.0 IRRADIATION FACILITIES AND TEST MATRICES

No contributions.