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FUSION MATERIALS SEMIANNUAL PROGRESS REPORT FOR THE PERIOD ENDING

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FOREWORD

This is the fifty-ninth in a series of semiannual technical progress reports on fusion materials science activity supported by the Fusion Energy Sciences Program of the U.S. Department of Energy. It covers the period ending December 31, 2015. This report focuses on research addressing the effects on materials properties and performance of 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 for an economically and environmentally attractive fusion energy source. Research activities on issues related to the interaction of materials with plasmas are reported separately.

The results reported are the products 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 under the guidance of F. W. (Bill) Wiffen and Stephanie Melton, Oak Ridge National Laboratory. Their efforts, and the efforts of the many persons who made technical contributions, are gratefully acknowledged.

Daniel Clark Research Division Office of Fusion Energy Sciences

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1 FERRITIC/MARTENSITIC STEEL DEVELOPMENT

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Summary of the content of two presentations at ICFRM 17 now in preparation for submission in two open literature publications.

1.2 FABRICATION OF LOW ACTIVATION FERRITIC-MARTENSITIC STEELS CONTAINING ⁵⁴FE ISOTOPE — Y. Yamamoto (Oak Ridge National Laboratory)

Reduction of the mixed oxide steel powder consisting primarily of 54 Fe was successfully conducted via a combination of a hydrogen reduction process, vacuum-melting, and arc-melting with reactive elements. The arc-melted ingot of 54 Fe to date contains 78 wppm oxygen and 70 wppm nitrogen, together with ~1 wt.% of Cr and W, with the total weight of ~200 g. The detailed procedure of each reduction process is summarized in this report. The results were presented in a poster at ICFRM-17.

1.3 ADVANCED BAINITIC STEEL DEVELOPMENT FOR FUSION STRUCTURAL APPLICATIONS — Y. Yamamoto (Oak Ridge National Laboratory)

Four heats of 3Cr-3WV base bainitic steels with or without minor alloying additions of Mn, Si, and N were prepared. Continuous cooling transformation (CCT) diagrams of the bainitic steels were produced by using a Quenching Dilatometer (Material Measuring Corp.). The results indicated successful control of the bainitic transformation kinetics with lower bainitic transformation temperatures in a wide range of continuous cooling rates, compared to those of the base steels. It promoted the formation of "carbide-free acicular bainite ferrite" which improved relatively short-term creep-rupture properties tested at 600°C. Improved oxidation resistance during creep testing was also observed in the modified steels with the Si addition. Weldability screening of the steels has been initiated by using beadon-plate weld together with cross-sectional hardness measurements.

1.4 MICROSTRUCTURE EVOLUTION IN TEMPERED MARTENSITIC STEELS UNDER IN-SITU HE INJECTION EXPERIMENT IN HFIR JP28/29 — Takuya Yamamoto, Yuan Wu, G. Robert Odette (University of California Santa Barbara), Dan Edwards, Rick Kurtz (Pacific Northwest National Laboratory)

TEM studies have been carried out to observe the microstructure evolution in normalized and tempered 8-9Cr martensitic steels (TMS) Eurofer 97 and F82H under in situ helium injection (ISHI) fission reactor irradiation at nominally 500°C to \approx 39 dpa and \approx 2100 appm helium at 500°C. The irradiations were carried out as part of the JP-28&29 US DOE – JAEA collaboration. The cavity microstructure analyses showed cavities with an average size of \approx 2.5 nm and number density of \approx 2.4 x 10²⁴/m³, resulting in a total cavity volume fraction of \approx 0.35%. The corresponding void volume fraction is \approx 0.18%. The magnitude of void swelling is significantly smaller than what was previously observed at 21 dpa and 1230 appm He in JP-27 specimens. The reason for less swelling at higher dpa and He is that the intended 500°C irradiation temperature fell significantly below 500°C during the irradiation.

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1.5 TENSILE FRACTURE MECHANISM OF HFIR-HEAVILY-IRRADIATED F82Hs — H. Sakasegawa, H. Tanigawa, T. Hirose, M. Ando (Japan Atomic Energy Agency), Y. Katoh, C. O. Stevens, and M. R. McAlister (Oak Ridge National Laboratory)

Irradiation embrittlement and hardening of tensile properties were observed in the heavily irradiated F82Hs at high temperatures, though it is still necessary to confirm the result of diametric analysis of silicon carbide passive temperature monitors. For F82Hs irradiated at 573 K, the three dimensional fractography revealed that the fracture mechanism was affected by irradiation. Dimples became smaller and shallower after irradiation, and grain boundary sliding was observed. These results contribute to development of a tensile fracture mechanism model explaining how the fracture is affected by irradiation.

2 ODS AND NANOCOMPOSITED ALLOY DEVELOPMENT

2.1 CHARACTERIZATION OF PROCESSING INDUCED IMPURITY PHASE PRECIPITATES IN THE AS-PROCESSED FCRD-NFA-1 — S. Pal, M. E. Alam and G. R. Odette (UCSB), S. Maloy (LANL), D. Hoelzer (ORNL)

> The NFA-1 contains detrimental impurity phases along with the desirable nanooxides (NOs). The impurity phase precipitate particles appear as black, nearly round features in SEM micrographs, with a size distribution between 10 and 260 nm. The impurity particles are arranged as stringers in the direction of primary deformations during hot extrusion, and cross-rolling. Chemical analysis using electron probe micro-analyzer demonstrates that these particles are either rich in Ti or Y. TEM shows these features are primarily formed on grain boundaries and triple junction. The EDS shows that the particles are primarily Ti-O and fewer Y-O phases. Heat treatment at 1300°C/5 hr shows the complete dissolution of these particles, suggesting they are a metastable phase. The precipitates act as nucleation sites for ductile fracture at high temperature, reducing tensile ductility and fracture toughness.

2.2 MICROSTRUCTURAL AND MECHANICAL BEHAVIOR OF AS-FABRICATED AND ANNEALED 14YWT NFA-1 ALLOY — M.E. Alam, S. Pal, D. Gragg, G. R. Odette (UCSB), D. T. Hoelzer (ORNL) and S. A. Maloy (LANL)

FCRD NFA-1 is a new 14YWT nanostructured ferritic alloy (NFA) processed to form a 12.5 mm thick plate. Ultrafine, nearly equiaxed grains dominate the plate's face (LT), while the front (LS) and side (TS) views contain pancake-shaped, trimodal grains with very large aspect ratios, along with a population of embedded microcracks that are readily visible in profile. Low temperatures tensile tests on the longitudinal (L) direction show a delamination driven ductile fracture, even at liquid nitrogen temperature, with strengths up to 1563 MPa. In contrast, the room temperature tensile specimen loaded in the short thickness (S) direction fails prematurely in its elastic regime, with a flat, faceted fracture surface. Annealing at 1300°C for 1 and 5 hrs helps to alter the grains towards equiaxed in all plane views and heals the microcracks, which results in much improved room temperature tensile ductility. However, microhardness, tensile strength and fracture toughness have been compromised, and the fracture mechanism has also been changed from delamination driven to microvoid coalescence dimple fracture.

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2.3 THE CRYSTAL STRUCTURE, ORIENTATION RELATIONSHIPS AND INTERFACES OF THE NANOSCALE OXIDES IN NANOSTRUCTURED FERRITIC ALLOYS — Y. Wu, S. Kraemer, G. R. Odette (University of California Santa Barbara), J. Ciston (Lawrence Bekeley National Laboratory), N. Bailey, P. Hosemann (University of California Berkeley)

Fast Fourier Transform analysis of focal series images revealed the nano-oxide (NO) crystal structure, including the smallest at < 2 nm in diameter, to be $Y_2 Ti_2 O_7$ pyrochlore in all cases, consistent with both exit wave analysis and scanning transmission Z-contrast imaging of the atomic columns in larger features. The faceted NOs exhibit a quasi-epitaxial orientation relationship to the ferrite matrix: $[110]_{\rm YTO}||[100]_{\rm Fe}$ and $[001]_{\rm YTO}||[010]_{\rm Fe}$, forming a 5x7 near coincidence site interface, and exhibit size-dependent strains in both the oxide and matrix ferrite phases.

2.4 NANOSCALE 3D CORRELATIVE ATOM PROBE-ELECTRON TOMOGRAPHY: CHARACTERIZATION OF MICROSTRUCTURES IN DUAL ION IRRADIATED NFA MA957 — P. B. Wells, S. Krämer, Y. Wu, S. Pal, G. R. Odette and T. Yamamoto (University of California, Santa Barbara)

Transmission Electron Microscopy (TEM) can resolve very small helium bubbles (HB), down to approximately 1 nm, but is not optimal for observing populations of very small nano-oxides (NO) in nanostructured ferritic alloys (NFA). In contrast, atom probe tomography (APT) excels in measuring the location, size and composition of NO, but cannot resolve small bubbles. Because a typical APT tip has dimensions similar to those needed for TEM (on the order of 50-100 nm thickness), it is possible to characterize HB by 3D TEM tomography, hereafter called ET, prior to destructive 3D characterization of the NO by APT. Here, for the first time, APT and ET are used to assess the association between HB and NO in full 3D reconstructions, which also reveal strong NO-HB associations with a grain boundary.

2.5 He IMPLANTATION OF Fe-{110}YTO BILAYERS — T. Stan, Y. Wu, T. Brown, C. Palmstrom, and G.R. Odette (University of California Santa Barbara), and F. Allen, P. Hosemann (University of California Berkeley)

The Fe-Cr matrix nanostructured ferritic alloys (NFAs) are dispersion strengthened by < 5 nm Y-Ti-O nano-oxide (NO) phases. The characteristics of the interfaces between the NOs, such as $Y_2Ti_2O_7$ (YTO), and the surrounding ferrite matrix are critical to trapping He in fine scale bubbles. As a compliment to current characterization efforts of the NOs themselves, a surrogate bulk Fe-YTO interface was fabricated by molecular beam epitaxy (MBE) and electron beam Fe deposition on {110}YTO. Areas of the sample were then implanted with 25 keV He. The He bubble sizes, number densities, and volume fractions are reported. Bubbles at the Fe-YTO interface were on average larger than in the matrix. No bubbles were seen in, but this does not indicate that He is not present in the YTO.

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2.6 SEQUESTRATION OF CAVITIES AT NANOPARTICLE-MATRIX INTERFACES IN HELIUM PLUS HEAVY ION IRRADIATED NANOSTRUCTURED FERRITIC ALLOYS — C. M. Parish^{1*}, K. A. Unocic¹, L. Tan¹, S. J. Zinkle^{1,2}, S. Kondo³, L. L. Snead⁴, D. T. Hoelzer¹, and Y. Katoh¹ - ¹ Oak Ridge National Laboratory, ² University of Tennessee, Knoxville, ³Institute of Advanced Energy, Kyoto University, ⁴Massachusetts Institute of Technology

Abstract of a manuscript being submitted to Journal of Nuclear Materials.

3 CERAMIC COMPOSITE STRUCTURAL MATERIAL DEVELOPMENT

3.1 LOW ACTIVATION JOINING OF SiC/SiC COMPOSITES FOR FUSION APPLICATIONS: MODELING DUAL-PHASE MICROSTRUCTURES AND DISSIMILAR MATERIAL JOINTS — C. H. Henager, Jr., B. N. Nguyen, and R. J. Kurtz; (Pacific Northwest National Laboratory, Richland, WA, USA); M. Ferraris, (Politecnico di Torino, Torino, Italy); Y. Katoh, (Oak Ridge National Laboratory, Oak Ridge, TN, USA)

The international fusion materials community designed miniature torsion specimens for joint testing and irradiation in test reactors with limited irradiation volumes since SiC and SiC-composites used in fission or fusion environments require joining methods for assembling systems. HFIR irradiation results indicated two broad types of joint damage due to irradiation at either 500°C or 800°C to 3 dpa or 5 dpa. One type of damage can be categorized as microcracking within multi-phase joints at the micron length scale. The other type of damage can be categorized as cracking within the miniature torsion sample and within the joint where the cracks are now on the scale of the joint thickness and are not considered to be microcracks. This report discusses methods to model both types of cracking due to differential properties within the joint due to multiple phases or due to the fact that the joint itself is dissimilar from the joined CVD-SiC material. This analysis requires two different models to account for these effects.

3.2 APT AND TEM CHARACTERIZATION OF PRECIPITATES IN Mg⁺ ION IMPLANTED CUBIC SILICON CARBIDE — W. Jiang, J. Liu, D. K. Schreiber, D. J. Edwards, C. H. Henager, Jr., R. J. Kurtz (Pacific Northwest National Laboratory), and Y. Wang (Los Alamos National Laboratory)

This research update reports on the results from our preliminary atom probe tomography (APT) data reconstruction and analysis as well as from our recent transmission electron microscopy (TEM) examinations on Mg⁺ ion implanted cubic silicon carbide (3C-SiC). APT studies have been performed for 3C-SiC implanted with 25 Mg⁺ ions to 9.6×10¹⁶ ions/cm² at 673 K and subsequently annealed at 1073 and 1573 K for 2, 6, and 12 h. TEM examinations have been focused on a lower-dose (5.0×10¹⁵ ions/cm²) 3C-SiC implanted with 24 Mg⁺ ions, followed by annealing at 1573 K for 12 h. The TEM study suggests that some of the nanometer-scale Mg precipitates are associated with Frank loops in the implanted and annealed 3C-SiC, while the APT results show that most of Mg-bearing particles contain both Si and C. Further efforts on APT reconstruction and TEM examination are still in progress.

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3.3 ADVANCED CHARACTERIZATION OF IRRADIATION DEFECTS IN SILICON CARBIDE: POSITRON ANNIHILATION SPECTROSCOPY — X. Hu, T. Koyanagi, Y. Katoh (Oak Ridge National Laboratory)

Positron annihilation spectroscopy (PAS), i.e., positron annihilation lifetime spectroscopy and coincidence Doppler broadening, was used to characterize the small vacancy clusters in 3C-SiC subject to various neutron irradiation conditions by capturing the dependence of irradiation temperature (380~800°C) and dose (0.01~30dpa). The vacancy cluster distribution obtained from PAS investigation is critically important to complement the current understanding of the microstructural evolution in SiC under the abovementioned neutron irradiation conditions, due to the cluster invisibility in TEM characterization. Subsequently, the vacancy clusters are then linked to the measured swelling behavior to provide insight into the correlation between microstructure and physical properties of SiC.

4 HIGH HEAT FLUX MATERIALS AND COMPONENT TESTING

4.1 PRELIMINARY PROGRESS IN THE DEVELOPMENT OF DUCTILE-PHASE TOUGHENED TUNGSTEN FOR PLASMA-FACING MATERIALS: DUAL-PHASE FINITE ELEMENT DAMAGE MODELS — C. H. Henager, Jr., B. N Nguyen, R. J. Kurtz (Pacific Northwest National Laboratory)

A promising approach to increasing fracture toughness and decreasing the DBTT of a W-alloy is by ductile-phase toughening (DPT) [1-3]. In this method, a ductile phase is included in a brittle matrix to prevent fracture propagation by crack bridging or crack deflection. Liquid-phase sintered W-Ni-Fe alloys and hot-pressed and sintered W-Cu composites are two examples of such materials that PNNL and UCSB are investigating. However, there is a need for improved mechanical property models of such composite systems in order to begin to optimize these structural materials with regard to strength and fracture toughness. This report describes such a model that is currently under development at PNNL.

4.2 FABRICATION OF FUNCTIONALLY GRADED TUNGSTEN STEEL LAMINATES 97

- L. M. Garrison (Oak Ridge National Laboratory)

Analysis is underway of the tungsten-steel laminate composites. The composite was fabricated from tungsten foils in thicknesses 250, 100, and 25 μ m and grade 92 steel foils in nominal thicknesses 250, 100, and 76 μ m. The fabrication was by forging and hot rolling at 1000°C. Shear punch tests were completed on the tungsten foils. Tensile and shear punch samples are being machined from the composite.

4.3 NEUTRON ENERGY SPECTRUM INFLUENCE ON IRRADIATION HARDENING 100 AND MICROSTRUCTURAL DEVELOPMENT OF TUNGSTEN — Makoto Fukuda¹, N.A.P. Kiran Kumar², Takaaki Koyanagi², Lauren M. Garrison², Lance L. Snead³, Yutai Katoh², Akira Hasegawa¹, 1- Tohoku University, 2- Oak Ridge

This is the abstract of a paper submitted to The Journal of Nuclear Materials.

National Laboratory, 3- Massachusetts Institute of Technology

4.4 ANALYSIS OF NEUTRON IRRADIATED TUNGSTEN MICROSTRUCTURES — **101** N.A.P. Kiran Kumar, L. M. Garrison, Y. Katoh (Oak Ridge National Laboratory)

There are two components to neutron irradiation response that change the structure of tungsten: neutron created lattice displacement defects such as interstitials and vacancies, and transmutation products, especially rhenium and osmium. This study is examining the effects of both of these on the tungsten microstructure. Tungsten irradiated to four different doses from 0.7 to 4.5 dpa was examined by transmission electron microscopy, scanning transmission electron microscope, and electron dispersive spectrometry. The tungsten types included single crystal tungsten and as-rolled tungsten foils. The Re and Os transmutation products form needle-shaped precipitates preferentially along the <110> direction. The average precipitate and void sizes increased with increasing dose.

4.5 IRRADIATION EFFECTS IN TUNGSTEN-COPPER LAMINATE COMPOSITES 106 L.M. Garrison^{a*}, Y. Katoh^a, L.L. Snead^{a, b}, T.S. Byun^{a, c}, J. Reiser^d, M. Rieth^d, ^aOak Ridge National Laboratory, ^bPresent affiliation-Massachusetts Institute of Technology, ^cPresent affiliation-Pacific Northwest National Laboratory, ^dKarlsruhe Institute of Technology

Extended abstract of a paper ready for journal submission

- 5 **MAGNETIC AND DIAGNOSTIC SYSTEM MATERIALS** No contributions this reporting period.
- 6 FUSION CORROSION AND COMPATIBILITY SCIENCE
- 6.1 COMPATIBILITY OF AN FeCrAI ALLOY WITH FLOWING Pb-Li IN A THERMAL 108 CONVECTION LOOP — S. J. Pawel and K. A. Unocic (Oak Ridge National Laboratory)

This is the abstract of a manuscript that has been submitted to the Journal of Nuclear Materials.

7 MECHANISMS AND ANALYSIS

 7.1 EFFECT OF STRAIN FIELD ON THRESHOLD DISPLACEMENT ENERGY OF TUNGSTEN STUDIED BY MOLECULAR DYNAMICS SIMULATION — D. Wang, N. Gao, (Institute of Modern Physics, Chinese Academy of Sciences) W. Setyawan, R. J. Kurtz (Pacific Northwest National Laboratory), X. Gao, W. H. He (Institute of Modern Physics, Chinese Academy of Sciences)

The influence of hydrostatic strain on point defect formation energy and threshold displacement energy (E_d) in body-centered cubic (BCC) tungsten was studied with molecular dynamics simulations. Two different tungsten potentials (Fikar and Juslin) were used. The minimum E_d direction calculated with the Fikar-potential was <100>, but with the Juslin-potential it was <111>. The most stable self-interstitial (SIA) configuration was a <111>-crowdion for both potentials. The stable SIA configuration did not change with applied strain. Varying the strain from compression to tension increased the vacancy formation energy but decreased the SIA formation energy. The SIA formation energy changed more significantly than for a vacancy such that E_d decreased with applied strain from compression to tension.

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7.2 DAMAGE MECHANISM INTERACTIONS AT THE PLASMA-MATERIALS 114 INTERFACE (*An Early Career Award Project*) — C. M. Parish (Oak Ridge National Laboratory)

This first reporting period of the five-year project has emphasized experimental technique developments as the necessary foundation for all later work, and has begun several valuable collaborations with other institutions. Specifically, tungsten high-purity sheet stock has been obtained and characterized to act as a constant and known baseline for further experiments. Focused ion beam (FIB) methods to prepare samples for transmission electron microscopy (TEM) of plasma-exposed tungsten have been refined. This includes tall (>1000 nm) "nanofuzz" tendrils, which is a significant experimental challenge. A non-FIB technique for nanotendrils has also been developed. Collaborations thus far include UCSD PISCES laboratory, and Dr. D. Donovan, UT-Knoxville.

7.3 A CODE FOR AUTOMATED DERIVATION OF POST NECKING TRUE STRESS-TRUE STRAIN CONSTITUTIVE LAWS FROM STANDARD TENSILE TEST ENGINEERING STRESS STRAIN CURVES — Shuangyu Li, Takuya Yamamoto, G. Robert Odette (UCSB)

We previously developed a self-consistent approach to derive true stress-stain constitutive [$\sigma(\epsilon)$] laws from measured tensile test engineering stress-strain $s(e)_m$ data based on finite element method (FEM) simulations. The simulated $s(e)_s$ were based on trial input $\sigma(\epsilon)_n$ that were adjusted in an iterative fashion until convergence at $s(e)_s \approx s(e)_m$. The adjustments between $\sigma(\epsilon)_n$ and $\sigma(\epsilon)_{n+1}$ were based on experience and judgment but in some cases convergence required many time consuming iterations. Here we report an automated iterative process that is much more efficient and less time consuming for the researcher.

8 MODELING PROCESSES IN FUSION SYSTEM MATERIALS

8.1 OBJECT KINETIC MONTE CARLO SIMULATIONS OF RADIATION DAMAGE 126 IN TUNGSTEN SUBJECTED TO NEUTRON FLUX WITH PKA SPECTRUM CORRESPONDING TO HFIR — G. Nandipati, W. Setyawan, H. L. Heinisch, K. J. Roche, R. J. Kurtz (Pacific Northwest National Laboratory) and B. D. Wirth (University of Tennessee)

We used our recently developed lattice based object kinetic Monte Carlo (OKMC) code, *KSOME* [1], to carry out simulations of radiation damage in bulk W. In this report, we present preliminary results of our study of, the effect of the maximum size of self-interstitial atom (SIA) clusters allowed to rotate on the defect accumulation in bulk tungsten with 1µm grain size when subjected to neutron flux having PKA spectrum corresponding to HFIR at 1025 K for the dose rates in the range 0.17 x 10^{-4} to 0.17 x 10^{-8} dpa/s.

8.2 STABILITY OF SMALL SELF-INTERSTITIAL CLUSTERS IN TUNGSTEN — W. 130 Setyawan, G. Nandipati, and R. J. Kurtz (Pacific Northwest National Laboratory)

Density functional theory was employed to explore the stability of interstitial clusters in W up to size seven. For each cluster size, the most stable configuration consists of parallel dumbbells. For clusters larger than size three, parallel dumbbells prefer to form in a multilayer fashion, instead of a planar structure. For size-7 clusters, the most stable configuration is a complete octahedron. The binding energy of a [111] dumbbell to the most stable cluster increases with cluster size, namely 2.49, 3.68, 4.76, 4.82, 5.47, and 6.85 eV for clusters of size 1, 2, 3, 4, 5, and 6, respectively. For a size-2 cluster, collinear dumbbells are still repulsive at the maximum allowable distance of 13.8 Å (the fifth neighbor along [111]). On the other hand, parallel dumbbells are strongly bound together. Two parallel dumbbells in which the axis-to-axis distance is within a cylindrical radius of 5.2 Å still exhibit a considerable binding of 0.28 eV. The most stable cluster in each size will be used to explore interactions with transmutation products.

8.3 A GENERALIZED ISING MODEL FOR STUDYING ALLOY EVOLUTION UNDER IRRADIATION AND ITS USE IN KINETIC MONTE CARLO SIMULATIONS — Chen-Hsi Huang and Jaime Marian (University of California Los Angeles)

We provide an Ising Hamiltonian for kinetic simulations involving interstitial and vacancy defects in binary alloys. Our model, which we term `ABVI', integrates solute transport by both interstitial defects and vacancies, and thus represents a generalization to the widely- used ABV model for alloy evolution simulations. The Hamiltonian captures the three possible interstitial configurations in a binary alloy: A-A, A-B, and B-B, which makes it useful for irradiation damage simulations. We implement the ABVI Hamiltonian in kinetic Monte Carlo simulations and perform a verification exercise by comparing our results to published irradiation damage simulations in simple binary systems with Frenkel pair defect production and several microstructural scenarios, with matching agreement found.

9 FUSION SYSTEM DESIGN

No contributions this reporting period.

10 IRRADIATION METHODS, EXPERIMENTS AND SCHEDULES

10.1 FUSION MATERIALS IRRADIATION TEST STATION (FMITS) AT SNS — Mark Wendel, Phil Ferguson (Oak Ridge National Laboratory)

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The FMITS is a design concept for installation at the SNS Facility. The project received funding from OFES during FY15 for (1) performing a mockup test on an FMITS-type target seal, (2) augmenting the safety assessment based on the 2014 technical review, (3) analyzing thermal-hydraulic off-normal transients with a full 3D model to assess the performance of the FMITS sensor array, and (4) remote-handling electrical connector operational mock-up, which was successfully completed in FY15. The work was continued in FY16 using residual funding. The main goals of the effort are to remove the project technical risks and prepare for a potential future project.

10.2 A HIGH ENERGY SELF-ION IRRADIATION STUDY OF METALLIC REACTOR MATERIALS AT THE LLNL CENTER FOR ACCELERATOR MASS SPECTROMETRY (CAMS) — N. Almirall, T. Yamamoto, D. Gragg, K. Fields, N. Cunningham, P. Wells, G. R. Odette (University of California, Santa Barbara), S. Tumey, T. Brown (Lawrence Livermore National Laboratory)

The LLNL CAMS accelerator experiment was designed to irradiate a range of reactor materials (~80 samples per condition) with 70 MeV Fe⁺⁹ ions to a dose of 3 dpa at two dpa rates that differ by a factor of 10. The experiment also explores ion versus neutron irradiation effects by cross-comparing the CAMS results with previous neutron and charged particle irradiation (CPI) data for the same alloy. Following a prototype test on 10/8/15, the actual CAMS irradiation was successfully conducted beginning on 12/3/2015. Extensive PIE is planned for the FeCr alloys, NFA, TMS and other fusion reactor relevant alloys, including W. One objective is to explore the concept of using precipitation as a damage meter to evaluate the relative effects of neutron irradiating particle. Here some preliminary ion versus neutron results are reported.

 10.3
 METHOD FOR ANALYZING PASSIVE SILICON CARBIDE THERMOMETRY WITH A CONTINUOUS DILATOMETER TO DETERMINE IRRADIATION TEMPERATURE — Anne A. Campbell (ORNL), Wallace D. Porter (ORNL), Yutai Katoh (ORNL), Lance L. Snead (MIT)
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This is the abstract of a paper published in Nuclear Instruments and Methods in Physics Research B, 370, (2016) 49-58.

10.4 IRRADIATION STUDY OF ADVANCED CERAMICS: STATUS OF IRRADIATION EXPERIMENTS — T. Koyanagi, C.M. Petrie, N.O. Cetiner, Y. Katoh (Oak Ridge National Laboratory)

HFIR Rabbit capsules were designed for irradiation of various advanced ceramics. The materials include isotopically-controlled ultra-high temperature ceramics such as TiB_2 and ZrB_2 , MAX phases such as Ti_2AIC , Ti_3AIC_2 , and Ti_3SiC_2 , SiC with various qualities, AIN, TiC, YAG, glassy carbon, and Si. The first phase of the irradiation has been completed.

10.5 HFIR IRRADIATION EXPERIMENTS – J.P. Robertson, Y. Katoh and J. McDuffee **173** (Oak Ridge National Laboratory)

HFIR completed 3.2 cycles during the second half of 2015. Cycle 460C (July 6 – July 11, 2015) added 406 MWdays to complete this cycle. Cycle 460 started on June 9, 2015, but there was a manual shutdown on June 13, 2015, in response to a reactor setback. The cycle was restarted on June 15, but the reactor was again forced to shut down due to abnormal fluctuations in the primary temperature. Cycles 461 (July 21 – August 15), 462 (October 6 – October 31), and 463 (November 17 – December 11) were completed without incident.

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1. FERRITIC/MARTENSITIC STEEL DEVELOPMENT

1.1 STATUS AND IMPROVEMENT OF REDUCED ACTIVATION FERRITIC-MARTENSITIC STEELS FOR HIGH TEMPERATURE SERVICE — L. Tan and Y. Katoh (Oak Ridge National Laboratory), A.-A.F. Tavassoli and J. Henry (CEA), M. Rieth (KIT), H. Sakasegawa and H. Tanigawa (JAEA), Q. Huang (INEST)

Summary of the content of two presentations at ICFRM 17 now in preparation for submission in two open literature publications.

Reduced activation ferritic-martensitic (RAFM) steels are candidate structural materials for fusion reactors. After about three decades of research and development, RAFM steels have achieved technological maturity with representative RAFM steels including 9Cr-2WVTa (United States), F82H (Japan), Eurofer97 (European Union), and CLAM (China), as well as similar steels being developed in South Korea and India, which evolved from small lab heats to large industrial scale heats of steel larger than 20 tons. A comprehensive set of properties of the RAFM steels have been investigated, including the recent stringent code qualification activity of Eurofer97 to the RCC-MRx edition 2015, and the ongoing materials qualification of F82H and CLAM. Long-term thermal aging resulted in reductions in strength and ductility and degradation of Charpy impact toughness for aging temperatures above about 500°C for F82H and CLAM. An increase of plate thickness from ~10 to 110 mm resulted in some reductions in Charpy impact energy but little influence on tensile properties of F82H and CLAM. Recent addition of fracture toughness data of Eurofer97-1 in the transition regime increased the scatter in the database, which vielded modification of Master curve but retained the same T₀ of -90°C. Comparable fatigue resistance was observed for F82H, Eurofer97, and CLAM at room temperature. However, CLAM with ~9Cr seems to possess somewhat superior fatigue resistance in air at 550°C compared to F82H with ~8Cr.

The current RAFM steels primarily contain $M_{23}C_6$ (M=Cr-rich) and small amounts of MX (M=Ta/V, X=C/N) precipitates, which are not adequate to maintain strength and creep resistance above 500°C. Thermomechanical treatments, including non-standard heat treatments, and alloy chemistry refinement or modification have been employed to development next generation RAFM steels for superior performance. Non-standard heat treatments using lower temperatures of normalization and tempering (e.g., 980 and 700°C) were found to produce similar balanced strength and Charpy impact toughness compared to Eurofer97 normalized and tempered at higher temperatures (e.g., 1150 and 760°C).

Cast nanostructured alloys (CNAs) were recently developed at ORNL with the aid of computational alloy thermodynamics coupled with strength modeling. The new alloys are designed to significantly increase the amount of MX nanoprecipitates, which are manufacturable through standard and scalable industrial steelmaking methods. Either MN or MC nanoprecipitates are favored in the CNAs with designed amounts in the range of ~0.4–0.6 vol%, which is lower than the oxide nanocluster content (>~0.7 vol%) in 9–20Cr oxide dispersion-strengthened (ODS) alloys, but significantly higher than the MX (<0.2 vol%) in the current RAFM steels. The experimental heats of CNAs demonstrated significantly refined MX nanoprecipitates (<~7 nm) with a high density (on the order of 10^{22} m^{-3}), as well as a refined sub grain structures and a high density of free dislocations (~3×10¹⁴ m⁻²), leading to improvements in strength, creep resistance, and Charpy impact toughness.

The CNAs exhibited ~100–300 MPa higher yield strength than the RAFM/FM steels at test temperatures up to 800°C, and comparable or slightly superior strength to PM2000 at temperatures above ~500°C. The enhanced strength was achieved at the cost of a modest reduction in ductility. Preliminary creep tests indicated superior creep resistance compared to RAFM steels, which approached the lower bound of the scatter data of ODS-Eurofer. The CNAs showed Charpy impact toughness comparable to or significantly greater than Grade 91, in terms of higher USE and lower DBTT. The improvement levels were even greater when compared to 9–20Cr ODS alloys.

The CNAs with noticeably increased amount of MX nanoprecipitates are expected to have radiation resistance and helium management performance superior to the current RAFM steels because of the

increased defect sinks at the nanoparticle-matrix interface. Preliminary neutron irradiation results on one of the CNAs showed radiation hardening comparable to the large database for Eurofer97 and F82H irradiated in a variety of fission reactors to ~70 displacements per atom at ~300–325°C. Small radiation hardening (<80 MPa) did not impair the ductility of the CNA at low radiation damage. More post irradiation examination and HFIR neutron irradiation experiments on CNAs are in progress or are planned, to provide a more complete picture of radiation resistance. Ongoing research and development activities on RAFM steels and CNAs will provide a solid foundation for their deployment in DEMO and later fusion reactors.

The content of this topic was presented in two presentations at 17th International Conference on Fusion Reactor Materials (ICFRM-17), October 11-16, 2015. Detailed information is reported in Refs. [1,2].

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- [1] L. Tan, Y. Katoh, A.-A.F. Tavassoli, J. Henry, M.Rieth, H. Sakasegawa, H. Tanigawa, Q. Huang, Status and improvement of reduced activation ferritic-martensitic steels for high temperature service, Journal of Nuclear Materials (2016), to be submitted.
- [2] L. Tan, L.L. Snead, Y. Katoh, Development of new generation reduced activation ferritic-martensitic steels for advanced fusion reactors, Journal of Nuclear Materials (2016), submitted.

1.2 FABRICATION OF LOW ACTIVATION FERRITIC-MARTENSITIC STEELS CONTAINING ⁵⁴**FE ISOTOPE** — Y. Yamamoto (Oak Ridge National Laboratory)

OBJECTIVE

This primary goal is to evaluate the effect on the irradiation microstructure and mechanical properties of the 9Cr base reduced activation ferritic-martensitic (RAFM) steels, such as EUROFER 97 and cast nanostructured alloys (CNA), prepared by using ⁵⁴Fe isotope reduced from the oxide powder that KIH provided. The ⁵⁴Fe isotope should accelerate the helium bubble formation during fast neutron exposure at HFIR which allow simulating the high dose conditions within relatively short period of exposure time.

SUMMARY

Reduction of the mixed oxide steel powder consisting primarily of ⁵⁴Fe was successfully conducted via a combination of a hydrogen reduction process, vacuum-melting, and arc-melting with reactive elements. The arc-melted ingot of ⁵⁴Fe to date contains 78 wppm oxygen and 70 wppm nitrogen, together with ~1 wt.% of Cr and W, with the total weight of ~200 g. The detailed procedure of each reduction process is summarized in this report. The results were presented in a poster at ICFRM-17.

PROGRESS AND STATUS

Introduction

There are no test facilities available with a neutron spectrum that matches D-T fusion. Various methods are used to simulate fusion reactor conditions and evaluate irradiation effects in structural materials for fusion reactors. For reduced-activation ferritic-martensitic (RAFM) steels doped with B or Ni have been used in fission test reactors to produce helium through (n, α) reactions while the fast neutrons produce displacement damage. However, both B and Ni tend to segregate at grain boundaries, compromising the simulation of uniform irradiation damage. It has been proposed to replace all natural Fe with the isotope ⁵⁴Fe in selected RAFM steels to expect acceleration of the He bubble formation dispersed uniformly within relatively short period of irradiation time, as previously attempted at High Flux Isotope Reactor (HFIR) with ⁵⁵Fe by Liu et al. [1]. HFIR neutron irradiation will achieve simultaneous He and dpa production throughout the bulk of specimens in a damage evaluation study.

About 400 g of mixed oxide steel powder was delivered from Karlsruhe Institute of Technology (KIT) which consisted primarily of ⁵⁴Fe together with small amounts of Cr, W, and other alloying elements. The origin of the powder material was a trial heat of EUROFER 97 with ⁵⁴Fe made at KIT. However, the heat was accidentally contaminated with high amount of B and C so that the material was fully dissolved into an acid and turned into oxide powders during the recovery process [2]. Reduction process of the oxide powders was applied at ORNL, in order to extract the ⁵⁴Fe with reasonably low oxygen content. In this report, the efforts on reducing the oxide powders were summarized.

Experimental Procedure

Four bottles containing ⁵⁴Fe oxide powders (~100 g for each) were delivered from KIT. The oxide powders were reduced by using multiple steps as follows; (1) hydrogen annealing (at 1100°C in a flowing H₂ gas for 24h), (2) cold compaction (to make a pellet, x4), (3) hydrogen sintering (to sinter the pellet, x4), (4) arc-melting (to make a button ingot, x4), (5) vacuum melting (to merge four button ingots into one piece), and (6) arc-melting with reactive elements (to reduce oxygen level by melting with Al). Oxygen content of the ingot at each step was determined by using inert gas fusion analysis (conducted by DIRATS), after the step #6. The step #6 repeated 5 times until the oxygen level became sufficiently low (less than 80 wppm.).

Results

All steps in the reduction process are summarized in Table 1. There were total 10 different steps, and the measured oxygen levels at each step after #6 were also listed. The last arc-melt (the step 6-5) resulted in obtaining the button ingot with 79 wppm oxygen and 70 wppm nitrogen, together with ~1 wt.% of Cr and W, with the total weight of ~200g. The ingot will be sectioned into two pieces, and then mixed with the required elements to fabricate EUROFER97 and CNA steels by arc-melting.

Step	Procedure	O, wppm.	Remarks
1	Hydrogen reduction	-	Fluffy powder
2	Cold-press	-	Pressed at 12 ksi to make pellets (x4)
3	Hydrogen sintering	-	Sintered pellets (x4)
4	Arc melting	-	Button ingots with Cr-rich oxides (x4)
5	Melting in a vacuum furnace	-	One large ingot with lots of Cr-rich oxides
6-1	Arc melting	2180	A button ingot with lots of Cr-rich oxides
6-2	Arc melting with reactive elements (I)	1700	A button ingot with scales
6-3	Arc melting with reactive element (II)	741	A button ingot with a few scales
6-4	Arc melting with reactive element (III)	413	A button ingot with a few scales
6-5	Arc melting with reactive element (IV)	79	A button ingot with a few scales
Next	Mix with required element by arc melting	-	Planned

Table 1 . List of the reduction process and analyzed oxygen con
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The reduction process was initiated from the hydrogen annealing. The powders were spread on an alumina boat as shown in Figure 1, and kept them in a tube furnace with a flowing hydrogen gas at 1100C for 24h. The powders in four different bottles were reduced separately, and the contents before and after annealing were analyzed by using the powder X-ray diffraction. The obtained spectra are shown in Figure 2. The as-received powder mostly consisted of Fe_2O_3 type oxides with no metal Fe, whereas the hydrogen annealing resulted in reducing the oxides significantly. However, the powders still contained 7~16% of mixed oxides (Fe_2O_3 , Fe_3O_4 , Cr_2O_3 , etc.). Since the majority of the powders were metal Fe, a melt process was proposed in order to separate these mixed oxides from metal Fe.



Figure 1. The powders after hydrogen annealing.



Figure 2. The powder XRD results before and after hydrogen annealing.

The powders were cold-pressed at 12 ksi to make pellets with ~29mm diameter and ~25mm height, and then sintered in a flowing hydrogen gas at 1100C, as shown in Figure 3. This process was applied to prepare the following arc-melting process since the powders would be difficult to arc-melt (e.g. potential explosion during evacuation or melting).

Each pellet was arc-melted several times to make sure to eliminate any residual powders and to form one piece of the ingot. The metal Fe typically showed a spherical shape during arc-melting process, as shown in Figure 4a, together with the agglomerate of the mixed oxides fringed the metal Fe. The resultant button ingots were covered by the mixed oxides, so that they were mechanically separated by using a hammer, as shown in Figure 4b. Some of the oxide pieces could not be removed from the ingots since they were "bitten" inside of the metal ingots. This could potentially be due to lower melting point of Fe-rich oxides compared to that of metal Fe, which resulted in solidifying the metal and oxides almost the same time and difficult to make a clear separation.



Figure 3. (a) The pellet made from the cold-press powders, and (b) the pellet after sintering.



Figure 4. (a) The pellet during arc-melting, and (b) the button ingot and separated oxide scales.

A melting in a vacuum was also attempted. After several trial melt with a dummy (natural) Fe, an MgO crucible was selected for the melting process. Four ingots were melted at once this time in order to make a large ingot. The crucible with the ingots were kept in a vacuum chamber, slowly heated up to 1600C and held for 30min, and then furnace cooled to room temperature. The ingots were fully melted to form one large ingot, although the surface was not smooth and lots of mixed oxides were bitten at the top of the ingot, as shown in Figure 5. After removing the mixed oxides as possible, the ingot was arc-melted again to make a large button ingot. A part of the ingot was accidentally separated from the main body during arc-melting, so that there were two ingots after this process step, as shown in Figure 6. A lot of mixed oxide agglomerates were removed from the arc-melted ingot, and a small piece (~5g) was sectioned from the large ingot for the chemical analysis. The analyzed result indicated that the metal contained not only oxygen with 0.218 wt.% but also 0.93 wt.% of Cr and 0.80 wt.% of W in it.



Figure 5. The ingots melted in an MgO crucible in a vacuum; (a) before and (b) after melting



Figure 6. Arc-melted ingots and removed oxide agglomerates

From the chemical analysis result, it was hypothesized that most of oxygen was combined with Cr to form chromium oxide. It would be difficult to separate the chromium oxide from molten Fe, so that another reduction method was proposed; melting the ingot with reactive elements such as Al and/or Si which would form more stable oxides compared to chromia as well as easier to separate from molten Fe because of their higher melting points. Based on this idea, the required amounts of Al and Si (to form Mullite, $Al_6Si_2O_{13}$) or Al (to form Al_2O_3) to compensate the oxygen in the ingot were calculated, and then arc-melted with the ingot.

It was found that the Si addition was not effective to form Mullite but the AI addition was beneficial to separate the oxides from molten Fe, as shown in Figure 7a (after the first mixing, or step 6-2). The Cr content increased after the first mixing, suggesting that the AI successfully captured the oxygen from chromium oxide and increased free Cr in the metal Fe ingot. Since excess AI could be poisons for the fabrication of RAFM steels later (e.g. interfering with the nitrogen addition), relatively small amount of the AI addition was made in the following steps. Total four times mixing of the ingot with AI resulted in reducing the oxygen content up to 78 wppm. together with 1.34 wt.% of Cr. Note that the AI content was below the detection limit (<0.01 wt.%) after the step 6-5.



Figure 7. The ingot after mixing with reactive elements; (a) after the step 6-2, (b) 6-3, (c) 6-4, and (d) 6-5.

The ingot after the step 6-5 will be sectioned into two pieces, and then melted with the required elements to fabricate two different RAFM steels. The progress will be summarized in the next semi-annual report.

These contents were presented at the 17th International Conference on Fusion Reactor Materials held at Aachen, Germany on October 12th to 16th, 2015, as a poster presentation entitled "FABRICATION OF LOW ACTIVATION FERRITIC-MARTENSITIC STEELS CONTAINING ⁵⁴Fe ISOTOPE".

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1.3 ADVANCED BAINITIC STEEL DEVELOPMENT FOR FUSION STRUCTURAL APPLICATIONS — Y. Yamamoto (Oak Ridge National Laboratory)

OBJECTIVE

This work aims to develop new bainitic steel, based on 3Cr-3WV(Ta) steels originally developed at ORNL, with mechanical properties of both base metal and weldments superior to those of existing commercial bainitic steels or ferritic-martensitic (F-M) steels. The target applications are high temperature structural components in fusion reactors such as the vacuum vessel, the structural ring which supports the blanket modules, and magnet shields, to be used at or above the 400-500°C range. Improvement of long-term creep properties by introducing additional fine, stable second-phase dispersions, as well as maintaining good weldability, is targeted via optimization of alloy composition and thermo-mechanical heat treatment.

SUMMARY

Four heats of 3Cr-3WV base bainitic steels with or without minor alloying additions of Mn, Si, and N were prepared. Continuous cooling transformation (CCT) diagrams of the bainitic steels were produced by using a Quenching Dilatometer (Material Measuring Corp.). The results indicated successful control of the bainitic transformation kinetics with lower bainitic transformation temperatures in a wide range of continuous cooling rates, compared to those of the base steels. It promoted the formation of "carbide-free acicular bainite ferrite" which improved relatively short-term creep-rupture properties tested at 600°C. Improved oxidation resistance during creep testing was also observed in the modified steels with the Si addition. Weldability screening of the steels has been initiated by using bead-on-plate weld together with cross-sectional hardness measurements.

PROGRESS AND STATUS

Introduction

With the alloy design strategy of improving creep performance, two new bainitic steels based on 3Cr-3WV and 3Cr-3WVTa [1,2] with minor alloying additions of Mn, Si, and N were proposed with guidance from computational thermodynamics. The calculation predicted that the minor alloying additions result in formation of stable MN (M: mainly V) in a wide temperature range below ~1100°C and increase the stability of $M_{23}C_6$ (M: mainly Cr) relative to M_7C_3 (M: mainly Cr). Since both MN and $M_{23}C_6$ are the key strengthening phases of the bainitic steels at elevated temperatures, the proposed steels would have a potential of improved creep properties compared to the base steels. An improved oxidation resistance would also be expected due to the Si addition [3]. In addition, the calculated continuous-cooling-transformation (CCT) diagram predicted wider austenite stable regions (retarding the transformation to ferrite or pearlite) with lower bainitic transformation start temperature compared to the base steels, indicating that the transformation would occur at relatively lower temperature range even with air cooling which is equivalent to the lower bainite formation during isothermal annealing in TTT diagram (Figure 1).



Figure 1. Schematic illustration of TTT and CCT curves for a bainitic steel

This new design of bainite transformation kinetics through alloying additions would result in enhancing the formation of "carbide-free acicular bainite ferrite formation" which also plays an important role of improving the creep properties as well as toughness of the bainitic steels [2]. In this report, the experimental efforts to verify the predicted transformation kinetics, microstructure, and the creep-rupture performance have been summarized by comparing the base and the modified steels. The first trial of weldment by using bead-on-plate gas tungsten arc weld is also discussed.

Experimental Procedure

The 55 kg forged plates of two base bainitic steels and two modified steels have been prepared using a vacuum induction melting by Carpenter Technology Corporation. The heat identifications and the base compositions are listed in Table 1. The ingots were homogenized and forged at 1100° C to make plates with a size of 25 mm thickness x 15 cm width x ~40 cm length. The forged plates were austenitized at 1100° C, followed by air cooling (normalization). A part of each plate was sectioned, and applied annealing at 700°C for 1h, followed by air cooling (tempering).

Iup		
Heat	Base composition, wt.%	Remarks
2750	Fe-3Cr-3W-0.2V	Base 3WV
2751	Fe-3Cr-3W-0.2V-0.1Ta	Base 3WVTa
2752	Fe-3Cr-3W-0.2V + Mn, Si, and N	Modified 3WV
2753	Fe-3Cr-3W-0.2V-0.1Ta + Mn, Si, and N	Modified 3WVTa

 Table 1. Heat identifications and base alloy compositions of the steels

Continuous cooling transformation diagrams were produced by using Quenching Dilatometer (Material Measuring Corp., MMC) refurbished at ORNL. Columnar specimens with a size of 3 mm diameter x 10 mm length were machined from the steels for the dilatometry analysis. The specimens were kept at 1100°C for 30 s in a vacuum chamber, and then cooled down to room temperature by using a controlled He gas blow in order to achieve various cooling rates in a range of from 1°C/s to 180°C/s. The bainitic transformation start and finish temperatures were determined from the obtained dilatometry curves. Microstructure of the specimens cooled at a cooling rate of 1°C/s were characterized by using light optical microscope (OM), and the same metallographic specimens were used for micro-Vickers hardness analysis with 1kg load. A series of creep-rupture tests of the base and the modified steels after tempering was conducted at 600°C and various constant loads in a range of 170 to 250MPa in a laboratory air. The test was conducted with sub-sized sheet dog-bone shape specimens with the gage dimension of 0.7 mm thickness x 3.2 mm width x 13 mm length. The extensometer was not attached to the specimens but the pull-rod to measure the creep-deformation, so that the creep-test was semi-quantitative. Bead-on-plate welding (gas tungsten arc weld, GTAW) was performed on the selected steel plates with the conditions of both as-normalized and tempered. Cross-sectional microstructure characterization was conducted by

using OM, and the Vickers hardness of the as-welded materials was measured with 300g load across the base metal – heat affected zone – weld metal, in order to produce a hardness distribution map.

Results

Continuous cooling transformation (CCT) diagrams of the base and the modified bainitic steels are shown in Figure 2. The bainitic transformation start (B_s) and finish (B_t) temperatures before and after alloy modification were compared in Ta-free (Figure 2a) and Ta-containing (Figure 2b) steels. Alloy modification resulted in lowering both B_s and B_t with ~20-100°C in the cooling rates studied, as expected from the alloy design strategy described above. There was no significant difference in the transformation temperatures between Ta-free and Ta-containing steels, indicating that the addition of Ta would have little effect on controlling bainitic microstructure (i.e. formation of carbide-free acicular bainite ferrite) but be more effective on the second-phase precipitation (MX/MC) which would contribute to improving creep properties significantly [2]. Optical micrographs of the steels cooled at 1°C/s (shown in Figure 3) indicates that there was no ferrite or pearlite formation at the cooling rate which was quite slower than a typical cooling rate of air-cooling (~10°C/s). This result suggests that the formation of locally weakened microstructure (= ferrite or pearlite) would not be expected during cooling after a typical welding, either at the heat affected zone or in the weld metal. The Vickers hardness increased with the alloy modification in both Ta-free and Ta-containing steels, which supported that the hardenability was successfully improved by controlling the microstructure with the stable carbide-free acicular bainite ferrite as expected.



Figure 2. Continuous cooling transformation diagrams of (a) Ta-free, and (b) Ta-containing steels.



Figure 3. Optical micrographs of the bainitic steels after cooling at 1°C/s; (a) #2750, (b) #2752, (c) #2751, and (d) #2753.

Comparison of creep-rupture properties of the base and the modified bainitic steels were summarized in Figure 4. The creep-rupture life of the 3Cr bainitic steels at 600°C/200MPa were quite longer than that of P92 (9Cr-2W-0.5Mo base) ferritic-martensitic steel (Figure 4a), and the Ta-containing steels showed almost doubled creep-life compared to the Ta-free steels. However, no apparent or consistent effect of alloying additions on the creep-rupture properties was observed at the test condition. At 600°C/170MPa (Figure 4b), on the other hand, only the Ta-containing steels exhibited longer creep-life compared to that of P92, although the alloy modification resulted in ~10-20% improvement of creep-rupture life in the bainitic steels. These results suggested that the effect of alloy modification on creep-properties would be more apparent in the milder creep test conditions. Since 600°C test temperature is quite aggressive and the creep-rupture life is in a range of "short-term" compared to the target applications of the developing steels, further evaluation of creep properties in a range of more than "mid-term (= several thousand hours)" would be required. The creep tests of the steels at slightly lower temperature (550°C) have been initiated and are currently in progress.



Figure 4. Creep-rupture test results of the 3Cr bainitic steels compared with the result of P92; tested at (a) 600°C/200MPa (creep-life), and (b) 600°C/170MPa (creep-rupture curves)

The Si addition improved the surface protection during creep-rupture testing, as shown in Figure 5. The base 3Cr-3WV with 0.16 wt.% Si showed rusty specimen surface, especially at the gage portion, and the cross-sectional near the surface exhibited the formation of thick oxide layers. The oxidation resulted in not only consuming the material volume but also a formation of a wedge-shape oxide penetration along the grain boundary which would also affect to the mechanical properties such as crack initiation site. On the other hand, the modified steel with 0.5 wt.% Si addition do not show such thick oxide layers after the same creep-rupture test condition as the base metal. This Si effect was reported by Ishitsuka et al. [3] in case of Grade 92 steel in a steam exposure. However, as far as the PI is aware of, no such effect of Si addition was reported in the heat-resistant bainitic steels. Further systematic study would be required to understand the oxidation characteristics after long-time exposure at elevated temperatures as well as the potential benefits or limitations in the new bainitic steels, and the test planning is currently in progress.



Figure 5. Creep-ruptured specimens of the steels #2750 and #2752 tested at 600°C and 200MPa, together with cross-sectional microstructure near the specimen surface showing the surface oxide layers.

Trial GTAW was conducted by using bead-on-plate weld on the 3Cr-3WVTa steels after tempering. Cross-sectional microstructures of the welded samples are shown in Figure 6. There are two weld beads on the samples, and the weld metals locate inside the yellow lines in the pictures. The boundary between the heat affected zone and the base material can easily be identified because of abrupt change in the contrast. There was no delta-ferrite or martensitic microstructure was observed in the weld metal or the

heat affected zone. The hardness distributions across the weld metal are also shown by using contour color maps which were obtained from the area with the white rectangle in the picture. The tempered base metals exhibited ~320-350Hv, and the hardness of the modified 3Cr-3WVTa showed slightly higher hardness compared the base steels. The weld metal and the heat affected zone, on the other hand, showed the hardness of ~370-400 Hv and ~390-440Hv for the base and the modified steels, respectively, which were much higher than the base materials. Such high hardness could possibly be beneficial for the high temperature creep properties similar to as-normalized materials [2], but may have a significant impact on the ductility, toughness, or potential residual stresses. Further characterization efforts is planned.



Figure 6. Cross-sectional microstructure of the 3Cr-3WVTa base bainitic steels with bead-on-plate weld (GTAW), together with the contour color map of the hardness distribution across the weld metal; (a) #2751, tempered, and (b) #2753, tempered.

This material was presented at ICFRM 17 with the title "Development of Advanced 3Cr-3WV(Ta) Bainitic Steels for Fusion Structural Applications".

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1.4 MICROSTRUCTURE EVOLUTION IN TEMPERED MARTENSITIC STEELS UNDER IN-SITU He INJECTION EXPERIMENT IN HFIR JP28/29 — Takuya Yamamoto, Yuan Wu, G. Robert Odette (University of California Santa Barbara), Dan Edwards, Rick Kurtz (Pacific Northwest National Laboratory)

OBJECTIVE

The objective of this research is to characterize cavities and other microstructural evolutions in candidate 9Cr tempered martensitic steels under in situ He injection and displacement damage in HFIR.

SUMMARY

TEM studies have been carried out to observe the microstructure evolution in normalized and tempered 8-9Cr martensitic steels (TMS) Eurofer 97 and F82H under in situ helium injection (ISHI) fission reactor irradiation at nominally 500°C to \approx 39 dpa and \approx 2100 appm helium at 500°C. The irradiations were carried out as part of the JP-28&29 US DOE – JAEA collaboration. The cavity microstructure analyses showed cavities with an average size of \approx 2.5 nm and number density of \approx 2.4 x 10²⁴/m³, resulting in a total cavity volume fraction of \approx 0.35%. The corresponding void volume fraction is \approx 0.18%. The magnitude of void swelling is significantly smaller than what was previously observed at 21 dpa and 1230 appm He in JP-27 specimens. The reason for less swelling at higher dpa and He is that the intended 500°C irradiation temperature fell significantly below 500°C during the irradiation.

PROGRESS AND STATUS

Introduction

Predicting and mitigating the effects of a combination of large levels of transmutant He and displacement damage (dpa), produced by high energy neutrons on the dimensional stability and mechanical properties of structural materials is one of the key challenges in the development of fusion energy [1]. The fundamental overriding questions about He-dpa synergisms include: a) What are the basic interacting mechanisms controlling He and defect transport, fate and consequences, and how are they influenced by the starting microstructure and irradiation variables (dpa rate, He/dpa ratio, temperature and applied stress); and, b) how can the detrimental effects of He-dpa synergisms be mitigated and managed by proper microstructural design?

We have previously demonstrated that in situ He implantation (ISHI) in mixed spectrum fission reactor irradiations provides a very attractive approach to assessing the effects of He-dpa synergisms, while avoiding most of the confounding effects associated with Ni- or B-doping type experiments [1-8]. Another approach to study He-dpa synergism is to use dual ion (DI) beams to simultaneously implant He and create displacement damage with heavy ions [1,9-12]. In spite of an apparent similarity, the two techniques have many differences that include the dpa rate, the spatial distribution of damage and He and the proximity of a free surface. Nevertheless, our earlier study [10,11] indicated

- Swelling incubation dose ≈ linearly decreases with He/dpa in DI
- Larger swelling with He/dpa is consistent with limited observations in ISHI
- Swelling incubation dose in ISHI is significantly lower than in DI presumably due mainly to dpa and He implantation rates
- Post-incubation trend of swelling is nearly common when the above data are plotted on a incubation normalized dose scale

Development of a microstructure database from ISHI and DI irradiation experiments over wide range of irradiation variable conditions is an important objective of this research, and provides a basis to inform, calibrate and validate predictive models. Here we report the most recent results from the ISHI experiment carried out in the HFIR JP-28 and 29 irradiations.

Experimental Procedure

Irradiation conditions

ISHI experiments have been included in US-JAEA collaboration JP-26, 27, 28/29 and 30 target capsules and DOE-Japan MEXT collaboration TITAN program rabbit capsules both in HFIR, as well as the UCSB ATR-1 experiment. The details of ISHI method is described elsewhere, but in summary the experiment is carried out using TEM discs with a thin NiAl intermetallic coating that was electron beam deposited at UCSB. The coated discs were paired with adjacent uncoated discs as illustrated in Figure 1, so that He atoms generated in the NiAl via two-step Ni thermal neutron reactions are injected up to \approx 9 µm deep from the surface regions of both coated and uncoated discs. Target coating thicknesses of 0.8, 1.6 and 4 µm produced nominal He/dpa ratios of 11, 22, and 55 at 39 dpa in the case of JP-28/29 capsules. Some results from the JP-26 and JP-27 capsules have been reported previously, while new JP-28/29 capsules provided specimens at higher dose and He conditions, nominally 39 dpa and 2430 appm, respectively. Table 1 summarizes those materials and irradiation conditions.

$ \begin{array}{c} 58\text{Ni} + n_{th} \rightarrow 59\text{Ni} + \gamma \\ 59\text{Ni} + n_{th} \rightarrow 56\text{Fe} + 4\text{He} (4.76\text{MeV}) \end{array} $	Table 1. Irradiation conditions for ISHI experiments in HFIR						
	Irr. ID	T(°C)	dpa	He(appm)	He/dpa(appm)	Spec ID	Material
n _{th}	JP26	500	9	169	18.8	R25	Eurofer 97
n _{th}	JP26	500	9	190	21.1	H24	F82H mod.3 (AT)
$\alpha \longrightarrow \alpha$	JP26	500	9	372	41.3	R26	Eurofer 97
	JP26	500	9	372	41.3	R27	Eurofer 97
	JP26	500	9	380	42.2	H27	F82H mod.3 (AT)
	JP26	500	9	380	42.2	UN27	F82H mod.3 (CW20)
specimen 1 substrate	JP27	500	21	510	24.3	H57b	Eurofer 97
	JP27	500	21	510	24.3	UN56	F82H mod.3 (CW20)
Ni (B, Li.) layer	JP27	500	21	1230	58.6	R56	Eurofer 97
	JP27	500	21	1250	59.5	UN57	F82H mod.3 (CW20)
Figure 1. Schematic of in	JP28/29	500	39	858	22.0	O84	F82H_IEA
situ He injection technique	JP28/29	500	39	2145	55.0	R86	Eurofer 97

Materials

We included various materials in the experiment with emphasis on two major material groups, tempered martensitic steels (TMS) and nano-structured ferritic alloys (NFA). This report focuses on some TMS alloys with emphasis on high dose swelling trends and effects.

The TMS material group includes two heats (IEA and Mod.3) of F82H and Eurofer97 [12,13]. F82H mod.3 is one of the F82H steel variants. The base chemical composition of F82H-IEA (nominally, 7.5%Cr 2%W 0.2%V 0.1%C 0.1%Si 0.02%Ta 60ppmN), Mod. 3 is a high purity (14 ppm N and 0.001% Ti) variant of F82H with high 0.1% Ta [13]. Both heats were austenitized at 1040°C for 30 min, normalized (air-cooled), and tempered at 740°C for 1.5 h. The F82H mod.3 was also included in the 20% cold worked (CW20) condition in addition to the as tempered (AT) condition. The composition of the 6.25 mm Eurofer97 plate used in this study is: 8.93Cr, 1.08W, 0.49Mn, 0.20V, 0.12C, 0.04Si, 0.021N, < 0.01(P, Cu, Co, Ti, Nb, B), bal. Fe (wt%) [14,15]. The plate was austenitized at 980°C for 27 minutes and air-cooled prior to tempering at 760°C for 90 minutes.

PIE methods

TEM specimens were prepared by focused ion beam micromachining (FIBing) at a low final current of 5.5 pA and voltage of 2 keV. The cavities were characterized using through-focus sequence imaging. They appear as white regions surrounded by a dark ring in the under-focused condition (typically -500 to -1000

nm) and as dark regions surrounded by white rings in the over-focused condition. Cavities were identified by careful comparative image analysis of the under and over-focused micrographs. Cavities were not observed in un-implanted regions, consistent with the well-known high swelling resistance of Eurofer97 and F82H in the absence of sufficient helium. The absolute diameters of the bubbles cannot be determined precisely, especially at small sizes, without detailed corrections. The cavity diameters reported here are the nominal values for the white spot diameter in the under-focused condition. Foil thicknesses were determined by convergent beam electron diffraction.

Results

Cavity Microstructure

Figure 2a and Figure 2b show representative TEM cavity microstructure images in Eurofer 97 at (a) 21 dpa and 1230 appm He in JP-27 and (b) 39 dpa and 2145 appm He in JP28/29, both at a nominal temperature of 500°C. Fig. 3a and 3b show the corresponding size distributions of the cavities in the Eurofer 97 samples. Surprisingly, the lower dose and He condition showed more numerous large faceted cavities, which are growing voids. At higher dose, smaller \approx 2 nm, more numerous (~3x) cavities are observed

Figure 4a and Figure 4b show TEM cavity microstructures in TMS alloys at lower He/dpa ratio \approx 22 to 25. Figure 4a is taken from previous JP27 results on Eurofer 97 at 21 dpa and 510 appm He while Figure 4b shows the cavity microstructures in F82H IEA in JP28/29 irradiated to 39 dpa and \approx 860 appm He, at He/dpa \approx 22. The corresponding cavity size distributions are shown in Fig. 5a and 5b, respectively. While we do not have exactly matching specimen pairs for the He/dpa ratios, these irradiated alloys basically show similar cavity evolution behavior (shown later in Figs. 6 and 7 as general trends). We observe fewer large cavities, especially those > 10 nm, while the small cavity population seems to have grown in size and in number density at the higher dose.







Figure 4. TEM cavity microstructure images in (a) Eurofer 97 at 21 dpa and 510 appm He in JP-27 and (b) F82H IEA at 39 dpa and 860 appm He in JP28/29, both at a nominal temperature of 500°C.



Figure 6 shows overall trends of average diameter, <d>, number density, N, and volume fraction, f, of two groups of cavities, bubbles and voids, in Eurofer 97. Here we defined voids as cavities larger than 2.25 nm, based on our earlier bi-modal distributions analyses [11]. The figures show stop of growth or even shrinkage of voids from 21 dpa to 39 dpa as well as an accelerated increase in the bubble number density.

Figure 7 shows the void evolution trends in the TMS materials. General trends are gradual (N and <d>) or rapid (f) increase from 9 to 21 dpa, while it stops or reverses from 21 to 39 dpa.



Figure 6. Dpa trends of average diameter, <d>, number density, N, and volume fraction, f, of two groups of cavities, bubbles and voids, in Eurofer 97. Voids are defined as cavities larger than 2.25 nm.



These observations are inconsistent with the observed trend of cavity evolution between 9 and 21 dpa. Preliminary analysis of the SiC temperature monitor in another 500°C sub-capsule in the JP-28/29 capsules suggests that the irradiation temperature may have fallen off significantly, presumably due to swelling of internal parts, which reduced or closed heat transfer gaps. These observations are consistent with lower irradiation temperature conditions.

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1.5 TENSILE FRACTURE MECHANISM OF HFIR-HEAVILY-IRRADIATED F82Hs — H. Sakasegawa, H. Tanigawa, T. Hirose, M. Ando (Japan Atomic Energy Agency), Y. Katoh, C. O. Stevens, and M. R. McAlister (Oak Ridge National Laboratory)

OJECTIVE

The objective of this work is to study the tensile fracture mechanism of F82Hs heavily irradiated up to about 87 dpa at high temperatures in HFIR (JP 28&29) using three dimensional fractography [1]. This work is part of the U.S. Department of Energy – Japan Atomic Energy Agency fusion materials collaboration.

SUMMARY

Irradiation embrittlement and hardening of tensile properties were observed in the heavily irradiated F82Hs at high temperatures, though it is still necessary to confirm the result of diametric analysis of silicon carbide passive temperature monitors. For F82Hs irradiated at 573 K, the three dimensional fractography revealed that the fracture mechanism was affected by irradiation. Dimples became smaller and shallower after irradiation, and grain boundary sliding was observed. These results contribute to development of a tensile fracture mechanism model explaining how the fracture is affected by irradiation.

PROGRESS AND STATUS

Introduction

The current design technology is based on the guarantee that it is safe to ignore effects of defects which cannot be detected through normal non-destructive inspecting techniques, and to assume the fracture mode is plastic collapse. Namely, it presupposes that the structural material has adequate ductility [2]. However, it is well known that the ductility of reduced activation ferritic/martensitic steels drastically degrades and uniform elongation becomes near zero accompanying significant irradiation hardening after irradiation around 573 K to less than a few dpa. Therefore, it is important to study the tensile fracture mechanism after irradiation. The result should be considered in the design technology of test blanket modules for the actual usage of F82H as a blanket material with appropriate structural soundness.

Experimental Procedure

The materials evaluated are F82H-IEA (Fe-8Cr-2W-0.2V-0.04Ta-0.1C), F82H-MOD3 (Fe-8Cr-2W-0.2V-0.09Ta-0.1C), and F82H-1.4 % Ni (Fe-8Cr-2W-0.3V-0.02Ta-0.07C-1.4Ni⁵⁸ or Ni⁶⁰). These were irradiated up to around 87 dpa at 573, 673, and 773 K (JP 28&29). After disassembling the capsules, high temperature tensile tests were performed in the cell 2 in the Building 3025E of Oak Ridge National Laboratory using the SS-J3 type tensile specimen (thickness: 0.75 mm, width: 1.25 mm, and gage length: 5 mm) at their irradiated temperatures in vacuum under a cross head control of 0.002 s⁻¹. After tensile test, three dimensional fractography was performed using the JEOL JSM-6010LA in the cell 4, and the software Alicona imaging Mex5.1 [1].

Results

Figure 1 shows the result of high temperature tensile tests at irradiated temperatures of 573, 673, and 773 K [3]. In all the results, irradiation hardening and embrittlement were observed. F82H-MOD3 showed tensile properties comparable to that of F82H-IEA, though it had higher tantalum content. F82H-1.4%Ni⁵⁸ which produced 900 appm of helium demonstrated the minimum ductility, but F82H-1.4%Ni⁶⁰ still showed ductility larger than 10 %.



Figure 1. High temperature tensile test results of irradiated F82H alloys. [3]

Table 1 shows the result of diametric analysis of silicon carbide passive temperature monitors. For the irradiation at 573 K, no significant differences were observed between planned and analyzed temperatures. However, for the other irradiation temperatures, significant differences were observed. In future work, it is necessary to confirm this result performing hardness test and room temperature tensile test. In the present work, we focused on the specimens irradiated at 573 K only.

Figure 2 shows the result of three dimensional fractography of F82H-IEA and F82H-MOD3 before and after irradiation [2]. For the unirradiated F82H-IEA, a few large and deep equiaxed dimples were observed. On shear fracture surfaces, small elongated dimples were mainly observed. For the irradiated F82H-IEA, a few small and shallow equiaxed dimples were observed, and for the unirradiated F82H-MOD3, large and deep equiaxed dimples with inclusions were observed. Small elongated dimples were observed in F82H-IEA. For the irradiated F82H-MOD3, small and shallow equiaxed dimples were observed in F82H-IEA. For the irradiated F82H-MOD3, small and shallow equiaxed dimples were observed. In both F82H-IEA and F82H-MOD3, smaller and shallow equiaxed dimples were observed. In both F82H-IEA and F82H-MOD3, smaller and shallower dimples were observed after irradiation. These obtained results conform to the observed irradiation hardening and embrittlement, as shown in Figure 1.

Planned temperature	Specimen ID	Analyzed median
(K)		temperature
		(K)
573	JP29TM0704	591.6
	JP29TM0708	557.3
673	JP28TM0702	593.5
	JP28TM0704	587.7
773	JP28TM0902	620.2
	JP28TM0904	612.3

 Table 1. Diametric analysis result of passive temperature monitors.



(b)F82H-MOD3

Figure 2. Fracture surface of F82H specimens tested at 573 K. [2]

Figure 3a shows the side of specimen of F82H-IEA after irradiation. Grain boundary sliding was observed. In Figure 3b, grain boundary sliding was more clearly observed in F82H-1.4 % 58Ni. These are representative results and grain boundary sliding was also observed in other irradiated F82Hs irradiated in JP 28&29. The irradiation hardening within the grain possibly caused relative strength degradation on grain boundaries. Grain boundary sliding can give a crack initiation site and enhance the degradation in ductility after irradiation. Though further observations are still necessary, grain boundary sliding possibly has an important role in tensile fracture mechanism.



(a) F82H-IEA



(b) F82H-1.4 % 58Ni

Figure 3. Grain boundary sliding in F82H samples tested at 573 K.

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2. ODS AND NANOCOMPOSITED ALLOY DEVELOPMENT

2.1 CHARACTERIZATION OF PROCESSING INDUCED IMPURITY PHASE PRECIPITATES IN THE AS-PROCESSED FCRD-NFA-1 — S. Pal, M. E. Alam and G. R. Odette (UCSB), S. Maloy (LANL), D. Hoelzer (ORNL)

OBJECTIVE

This study is aimed at characterizing the microstructure and chemistry of the impurity phase precipitates produced in the as-processed NFA-1 alloy and determining their corresponding effect on mechanical properties.

SUMMARY

The NFA-1 contains detrimental impurity phases along with the desirable nano-oxides (NOs). The impurity phase precipitate particles appear as black, nearly round features in SEM micrographs, with a size distribution between 10 and 260 nm. The impurity particles are arranged as stringers in the direction of primary deformations during hot extrusion, and cross-rolling. Chemical analysis using electron probe micro-analyzer demonstrates that these particles are either rich in Ti or Y. TEM shows these features are primarily formed on grain boundaries and triple junction. The EDS shows that the particles are primarily Ti-O and fewer Y-O phases. Heat treatment at 1300°C/5 hr shows the complete dissolution of these particles, suggesting they are a metastable phase. The precipitates act as nucleation sites for ductile fracture at high temperature, reducing tensile ductility and fracture toughness.

PROGRESS AND STATUS

Introduction

Nanostructured ferritic alloys (NFAs) are designed in such a manner to contain 1-3 nm fine dispersions of Y-Ti–O nano-oxides to achieve both a high radiation tolerance by managing helium, and exceptionally high thermal stability up to ~1000°C [1-3]. The alloy also possesses a very high tensile strength and high temperature creep strength [1, 3]. It has been postulated that the excellent creep and radiation tolerance of this alloy is due to the presence of these fine scale nano oxides, which impede dislocation and boundary movements during high-temperature deformation. On the other hand, they can effectively trap helium in nanometer scale bubbles and prevents the formation of large voids [1, 2]. An enormous effort has been put forward to characterize the structure and chemistry of these nano-oxides using different characterization also reveals that the alloy consists of some larger sized precipitates 10-150 nm, rich in either Ti or Y [6, 7]. Chemical analysis of these precipitates using EDS and EELS suggest that they are composed of Ti-C-O-N or sometimes pure Y_2O_3 , originating as a processing-induced inhomogeneity [1, 6, 7]. A little effort has been given to characterize the exact structure and chemistry of these precipitates, as well as its role on determining the mechanical properties of this alloy. The present investigation is a prelude towards that path.

Materials

The present investigation was carried out on a newly develop NFA alloy, FCRD-NFA-1, a variant of ODS class of steel. This alloy has been developed with a close collaboration between UCSB, LANL, and ORNL. The nominal composition of the alloy is 14Cr-3W-0.4Ti-0.3Y and balance Fe. The alloy powder is first ball milled, then canned and degassed at 400°C, and hot extruded (HE) at 850°C, which is further annealed for 1 hr and cross-rolled perpendicular to the HE direction, both at 1000°C. Microstructural characterizations were carried out using SEM and TEM. The elemental chemical analysis was performed using an electron probe micro-analyzer (EPMA) and an energy dispersive spectroscopy attachment on a TEM. Thin TEM lamellas are prepared using FIB lift-out methods. In order to characterize the thermal stability of the impurity phase precipitates, as-processed alloy sample were annealed at 1300°C for 5 hr inside a vacuum furnace.

Results

Figure 1b shows a representative SEM micrograph of the side surface (LS) of NFA-1 plate, where the grains are elongated in the extrusion direction. The impurity phase precipitates appear as black particle-like features, and collectively those are arranged as strings along the extrusion direction. The particles appear as near circular shaped. Size distribution and the average spacing between two particles, measured from the SEM micrographs of the top, side and front surfaces, are listed in Table 1.



Figure 1. (a) A schematic of the NFA-1 plate showing longitudinal (L), transverse (T) and short thickness (S) directions. Planes parallel to the side surface is defined as LS, parallel to the top LT and parallel to the front face as TS. Extrusion and cross-rolling of the plate was carried out along the L and T direction as marked accordingly. (b) SEM micrographs of the LS view or plane parallel to the top surface of NFA-1 as processed plate shows impurity phase precipitates as a black particle like feature. Extrusion direction is marked with a white arrow.

Table 1. Statistics of particles size and interparticle spacing for planes parallel to the top (LT), side (LS) and front (TS) of as-processed NFA-1 plate.

Sample Orientation	Ti/Y rich particle size (nm)	Interparticle spacing along x (nm)
LT/ Top surface	57 ± 33 Range: 10-262	228 ± 106
LS/Side surface	62 ± 32 Range: 11-188	303 ± 210
TS/ Front surface	68 ± 33 Range: 22-180	279 ± 160

Figure 2a-f and Figure 3a-f display the compositional maps of the plane parallel to the side (LS) and top (LT) surfaces of the NFA-1 plate, measured using an electron probe micro analyzer. The Fe, Cr, and W are homogeneously distributed throughout the map; whereas, Ti and Y form clusters. The SEM micrographs together with EPMA maps confirm that those precipitates are rich in Ti and Y. The numbers of Ti-rich features far exceed Y rich particles.



Figure 2. a-e) Elemental compositional maps for the LS view, and f) the cracked region of interest.



Figure 3. a-e) Elemental compositional maps for the LT view, and f) the region of interest.

An in-depth microstructural characterization and chemical analysis of these impurity phase precipitates were performed using TEM. Similar to SEM micrographs, these precipitates are also appeared as dark particle-like features in an STEM-HAADF image (Figure 4). The BF-TEM images of two of these precipitates are shown in Figure 5a and Figure 5b. From the micrographs, it is clearly evident that those precipitates are nucleated at either grain boundary or grain boundary triple junction. Both the precipitates have a size of ~ 50 nm.



Figure 4. STEM–HAADF image of the NFA-1 alloy shows impurity phase precipitates as black particles.



Figure 5. a), and b) BF-TEM image of an impurity phase precipitate nucleated at a grain boundary and triple junction, respectively.

Lattice fringe image of the precipitate, shown in Figure 6a, clearly displays that the interface between the matrix and precipitate is completely incoherent. The shape of the precipitate is not spherical; rather it takes a faceted polyhedral shape. The Fast Fourier Transform (FFT) pattern of the precipitate captured from the region, marked as 2, displays that the precipitate has a different structure than NOs of $Y_2Ti_2O_7$ or $Y_2Ti_2O_5$, seen in Figure 6b [5]. The amorphous-like appearance of the region, marked as 1, implies that this portion of the precipitate does not satisfy a zone axis condition, whereas region 2 does satisfy a near zone axis condition. This gives an indication of strongly faceted nature of the precipitate. A higher magnification view of the lattice fringe, shown in Figure 7, does not exhibit continuous lattice fringes. Even within the precipitate, regions of discontinuous lattice fringes with a dark contrast are clearly visible. A STEM-HAADF image of the same particle also shows some white features inside the precipitates (Figure 8a). The EDS spectrum collected from the whole particle, shown in Figure 8b, indicates that this particle is enriched with Y and O.



Figure 6. a) HR-TEM image of the precipitates shown in Figure 5a). b) FFT pattern of the PPT captured from the location, marked as 2 in Figure a).



Figure 7. Higher magnification view of the lattice fringe image of the precipitates shown in Figure 5a.



Figure 8. a) STEM-HAADF image of a Y-rich precipitates b) corresponding EDS spectrum of the whole particle.

The STEM-HAADF imaging coupled with an EDS line profile also shows that there are precipitates, which are rich in Ti (Figure 9). A dark contrast inside these precipitates has been observed, which shows higher oxygen concentration compared to the brighter portion of the precipitates. The Ti signal has an opposite trend compared to oxygen. Fe and Cr signal have not been detected.



Figure 9. a) STEM-HAADF image of an impurity phase precipitates, b) corresponding EDS composition profiles of different elements present in the alloy, captured along the marked line in Figure 9a).

The effect of high-temperature heat treatment on the impurity phase precipitates:

Effect of high-temperature heat treatments on these precipitates is quite profound, and, it has been observed that these precipitates are not thermally stable. Figure 10a shows that the large precipitates do not even exist after a heat treatment of 1300°C for 5 hr.



Figure 10. a) STEM-HAADF image of 1300°C/5 hr. heat treated sample. b) Magnified view of the precipitate marked in Figure 10a using a black circle.



Figure 11. Composition profile of the different elements presents in the NFA alloy measured along the marked line in Figure 10b).

The EDS line profile analysis, shown in Figure 11, depicts that after heat treatments of 1300° C/5 hr, Ti and Y content of the precipitates are significantly reduced; whereas, in the as-processed condition precipitates are enriched with either Ti or Y, seen in Figure 7 and Figure 8b. The measured average ratio of Y, Ti and O is ~ 1/1/3.5. This suggests that the imaged precipitate is not the same impurity phase precipitate; rather, it is a nano-oxide of $Y_2Ti_2O_7$ which coarsens during the heat treatment. On one hand it is well known that growth kinetics of NOs are extremely sluggish, therefore coarsening of a NOs up to a size of ~ 60 nm (ure 11b), is extremely difficult for the present heat treatment conditions [1]; rather, it is more probable for the precipitates to transform into NOs. Figure 11b also shows that inside NOs significant amounts of Fe and Cr coexist, suggesting a core-shell kind of structure. This kind of core-shell kind of structure of NOs is also reported by other researchers [6, 7]. Though the kinetics of dissolution and thermal stability of the impurity phase precipitates are metastable. Surprisingly for the present instance, we have not found any of the impurity phase precipitates in 1300°C/5 hr annealed sample.

Effect of impurity precipitates on high-temperature tensile behavior:

Figure 12 shows the variation of yield strength with temperature for the FCRD-NFA-1 alloy, where test specimens were made from three different orientations of the plate top, side and front surfaces. The plots suggest that there might be two different mechanisms operative: one from room temperature to 400°C and another one above 400°C. A similar kind of dependence of fracture toughness of NFA alloys on temperature is also reported by Byun et.al [8]. At room temperature fracture of the alloy is controlled by mesoscopic features; whereas, above 200°C continuous reduction in the toughness is caused by the shallow plastic zone formation due to the nanostructure of the alloy itself. It was also observed that at 700°C fracture occurs through de-bonding of low toughness grain boundaries [8].



Figure 12. Yield strength of NFA-1 alloy tested at different temperatures.

Fractography of the 600°C tensile tested specimen clearly demonstrates that the failure of the alloy at elevated temperature occurs by ductile failure mode with dimple formation. A closer observation of the fracture surface (Figure 13a and Figure 13b) reveals that fracture processes at high temperature occur through de-bonding of the grain boundary, which initiates from those impurity phase precipitates. Notably, all these impurity phase precipitates are only observed at the grain boundaries and are incoherent in nature. This altogether suggests that this impurity phase precipitates have an important role on determining the high-temperature behavior of this alloy.



Figure 13. a), and b) show the both low and high mag image of the fracture surface of a tensile sample tested at 600°C. Particles are marked using a white circle in Figure 13b).

SUMMARY

Experimental evidence clearly demonstrates that the large size precipitates are not same as the NOs, usually found in the NFA alloys. These precipitates are neither oxynitride nor oxycarbaide particles as previously reported [6, 7]. They are usually bigger in size and lesser in number compared to the NOs and they form only at the grain boundary. These precipitates are incoherent in nature and do not have any significant effect on the room temperature mechanical properties of these alloys; but decohesion of these precipitates during high-temperature deformation may degrade the high-temperature mechanical properties of the alloy.

Future Work

- Accurate determination of the chemistry and crystal structure of these precipitates will be performed using electron energy loss spectroscopy and convergent beam diffraction techniques.
- High-temperature mechanical properties of this alloy degrade through decohesion of these precipitates from grain boundary during deformation. Post-deformation TEM characterization of the grain boundary will also be performed on the high temperature tensile tested sample.

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2.2 MICROSTRUCTURAL AND MECHANICAL BEHAVIOR OF AS-FABRICATED AND ANNEALED 14YWT NFA-1 ALLOY — M.E. Alam, S. Pal, D. Gragg, G. R. Odette (UCSB), D. T. Hoelzer (ORNL) and S. A. Maloy (LANL)

OBJECTIVE

The objective of this study is to perform statistical analysis of grains, precipitates and microcracks of asfabricated 14YWT FCRD NFA-1 material, and to explore the effects of annealing on the microstructural and mechanical properties.

SUMMARY

FCRD NFA-1 is a new 14YWT nanostructured ferritic alloy (NFA) processed to form a 12.5 mm thick plate. Ultrafine, nearly equiaxed grains dominate the plate's face (LT), while the front (LS) and side (TS) views contain pancake-shaped, trimodal grains with very large aspect ratios, along with a population of embedded microcracks that are readily visible in profile. Low temperatures tensile tests on the longitudinal (L) direction show a delamination driven ductile fracture, even at liquid nitrogen temperature, with strengths up to 1563 MPa. In contrast, the room temperature tensile specimen loaded in the short thickness (S) direction fails prematurely in its elastic regime, with a flat, faceted fracture surface. Annealing at 1300°C for 1 and 5 hrs helps to alter the grains towards equiaxed in all plane views and heals the microcracks, which results in much improved room temperature tensile ductility. However, microhardness, tensile strength and fracture toughness have been compromised, and the fracture mechanism has also been changed from delamination driven to microvoid coalescence dimple fracture.

PROGRESS AND STATUS

Materials and Methods

The nanostructured ferritic alloys (NFAs) are a promising candidate alloy class for the advanced nuclear fission and future fusion reactor applications, since they have high tensile, fatigue and creep strengths over a wide range of temperature, as well as unique irradiation tolerance and outstanding thermal stability up to 1000°C. These attributes derive from the presence of submicron size grains, high dislocation densities and especially an ultrahigh population of nanometer size Y-Ti-O rich multifunctional nano-oxides (NOs) [1]. NFA-1 was developed in collaboration between UCSB, ORNL and LANL to explore including Y in the Fe-14Cr-3W-0.4Ti-0.2Y melt prior to gas atomization by ATI Powder Metals (Pittsburgh, PA). However, the Y was phase separated after atomization. Thus, a low interstitial alloy powder (15 kg) variant was ball milled for 40 hours with FeO (52.5 g) to increase the O content and to mechanically alloy the Y into solution. The milling was carried out by Zoz GmbH (Wenden, Germany) using a CM100b attritor mill with a ball to-powder mass ratio of 10:1 and ball size of 5 mm. The milled powders were then consolidated at ORNL by hot extrusion at 850°C. The extruded bar was annealed for 1 hour and then hot cross-rolled to a $\approx 50\%$ thickness reduction, both at 1000°C, to produce a ≈ 12.5 mm thick plate [2]. The basic microstructural and mechanical properties of the as-fabricated plate have been reported elsewhere [3-4]. However, due to the anisotropic nature of the plate along with through-thickness grain variation, the measured grain size of three different planes (face: LT, front: LS and side: TS, see Figure 1) were found inconsistent since the specimens were selected randomly. Therefore, in this present study, a 5mm 5mmx5mm cube has been EDM cut from the middle of the plate thickness and grain size of all three plane views was characterized. In detail crack statistics as well as processed induced impurities were also analyzed. Low temperature tensile tests were performed. Later, as-fabricated specimens from the plate were wrapped in a molybdenum getter foil and annealed in vacuum at 1300°C for 1 and 5 hrs. Microstructural and mechanical characterizations were also performed on the annealed specimens.

Metallurgically ground (up to 1500 grit sand paper) and polished (up to 20 nm colloidal silica) asfabricated and annealed specimens were observed in scanning electron microscope (SEM, FEI x30) equipped with energy dispersive spectroscopy (EDS) to characterize the pre-test surface morphology. Polished samples were then etched with Kroll's reagent (92% distilled water, 6% nitric acid and 2% hydrofluoric acid) prior to imaging of grains using SEM and dual beam Scanning Electron Microscope/Focused Ion Beam (SEM/FIB, FEI Helios 600). Longest (I) and shortest (s) dimensions of ~ 500 individual grains from each planes were tabulated from the micrographs using 'ImageJ64' software. The effective grain diameter was taken as d = (1+s)/2 and the aspect ratio as r = 1/s. Coarser precipitates were identified using both the SEM and transmission electron microscopy (TEM), equipped with EDS. SEM images were used to measure the average precipitate size, inter-precipitate spacing and stringer spacing. Precipitates were found to be arranged in stringers, rather than random. Therefore, the interprecipitate spacing along the stringer and stringer spacing along the thickness was considered. Microcracks were also characterized in terms of crack width, crack separation distance, crack length and number density of crack per unit area. Relatively low magnification (x1000) SEM images were chosen to characterize the crack length and their number. Vickers microhardness measurements were performed on polished coupon surfaces at a 500g load using LECO M-400A semi-automated hardness tester, based on the average of 10 to 15 indents. Tensile tests were performed on flat dog-bone shaped sub-sized specimens with a gage section length, width, and thickness of 5.0x1.2x0.5 mm³. The tensile tests were performed for the as-fabricated longitudinal (L) directions as illustrated in Figure 1, from room temperature down to liquid nitrogen temperature, on an 810 MTS servo-hydraulic universal testing machine equipped with a cooling chamber. Controlled liquid nitrogen-air mixture was injected into the cooling chamber to achieve the targeted cryogenic temperature, and held for 30 to 45 minutes before testing. However, both L and short (S) oriented as-fab and annealed tensile specimens were tested at room temperature. The tensile specimens were sanded with 1500 grit to remove surface contamination, minor defects and local residual stresses due to the EDM used to fabricate them. Loading was carried out at a crosshead speed of 0.30 mm/min, or a strain rate of $\approx 10^{-3}$ /s. Except for the small size of the specimens, the tensile properties were determined in accordance with ASTM Standard E8M-13. Fracture toughness tests of asfabricated and annealed specimens were conducted at room temperature on the L-T oriented fatigue precracked single-edged notch three point bend (3PB) bar specimens with nominal dimensions of 16 mm in length, 3.3 mm in width and 1.65 mm in gross thickness and a/W ≈ 0.5. The same 810 MTS servohydraulic testing machine was used for this purpose. The toughness (K_{Jc}) was calculated at the maximum load. Fracture surfaces of the broken tensile and toughness specimens were extensively characterized by SEM.



Figure 1. NFA-1 specimen orientations labeled with respect to the extrusion, cross-rolling and plate thickness directions.

Results

Microstructure

The microstructure of the as-fabricated FCRD NFA-1 material has been characterized in terms of: (a) grain morphology, (b) presence and distribution of coarser precipitates, and (c) crack statistics at all three different planes (see Tables 1 to 3 and Figures 1 to 3). Figure 2a and Figure 2b show the low magnification SEM, and high magnification SEM/FIB images of the as-fabricated and pre-test NFA-1 at different planes, respectively. Plate's face (LT) reveals crack or pore free surface. High magnification SEM/FIB images also characterize nearly uniform, equiaxed and ultrafine grain morphology of the corresponding plane (see Table 1). In contrast, the front (LS), and side (TS) views reveal a number of microcracks embedded on planes normal to the plate thickness direction. The corresponding plane's grains are elongated and pancake-shaped that oriented parallel to the extrusion (LS) or cross-rolling (TS) direction with a tri-modal grain size distribution (many are <1 μ m, some are 1-10 μ m and few are >10 μ m, see Figure 3a). Through thickness grain size variation has also been observed. Relatively smaller grains are found near the top and bottom of the plate's thickness while the larger grains at the middle.



Figure 2. Different plane views of the as-fabricated NFA-1 plate captured by: (a) SEM at low magnification, and (b) SEM/FIB at high magnification.

Planes	Long, l (µm)	Short, s (µm)	Avg, d= l+s)/2 (μm)	Aspect ratio, r = I/s	Microhardness, HV, (Kg/mm²)
LT (Face)	0.767 ± 0.566	0.517 ± 0.355	0.642 ± 0.450	1.5 ± 0.4	376 ± 18
LS (Front)	0.792 ± 0.638	0.301 ± 0.108	0.546 ± 0.343	2.7 ± 1.6	368 ± 25
TS (Side)	0.799 ± 0.833	0.296 ± 0.180	0.548 ± 0.482	2.7 ± 1.3	352 ± 39

Table 1. Grain morphology and hardness of as-fabricated NFA-1 specimens

Despite having uniformly distributed Y-Ti-O rich nano-oxides (NOs) (size: 2.1 nm, number density: 1.6 x 10²³ m⁻³ and volume fraction: 0.25%) all over the NFA-1 matrix, reported elsewhere [2], the material also reveals the presence of relatively coarser precipitates (Figures 2b and 3b) in the matrix, summarized in Table 2. These precipitates are predominantly located at or near the grain boundaries in the form of stringers (Figure 3b). EDS equipped with SEM and TEM, identify them mostly as Ti-rich (darker) with some as Y-rich (relatively gray) oxides [5]. These stringers are oriented randomly at the plates' face but parallel to the extrusion or cross-rolling direction at the front and side views, respectively, with an average

stringer separation distance 2.6 to 2.8 μ m (Table 2 and point 1 of Figure 3b). Average precipitate size is \approx 60 nm, ranging from 10 to 262 nm. Figure 3c shows the distribution of coarser precipitate size. Table 2 also summarizes the spacing among the precipitates that averaged ~ 200 to 300 nm.







Figure 3. (a) Distribution of grain's length, I, (b) point 1, 2 and 3 showing the inter-stringer spacing, crack width and crack separation distance, respectively, (c) coarser particle size distribution, and (d) crack length distribution of as-fabricated NFA-1 plate at different plane views.

Planes	Ti/Y rich particle size (nm)	Interparticle spacing along x (nm)	String spacing along thickness (µm)
LT (Face)	57 ± 33	228 ± 106	Random
LS (Front)	62 ± 32	303 ± 210	2.6 ± 1.0
TS (Side)	68 ± 33	279 ± 160	2.8 ± 1.0

Table 2. Ti/Y rich precipitates of as-fabricated NFA-1

Figure 2 also shows the presence of microcracks running normal to the plate thickness direction both for the front (LS) and side (TS) plate views and their statistics are summarized in Table 3. The micromechanism of these crack formation has been reported elsewhere [5]. The average crack width (point 2 in Figure 3b), which is believed to be the initiation of crack front, is ~250 nm. The crack separation distance is measured between the layers of crack in the short thickness direction (point 3 in Figure 3b) and found almost same (~16 μ m) for both the front and side views. Length of the cracks is also recorded and averaged ~10 μ m (front) to 15 μ m (side) with a span ranges from 2 μ m to 105 μ m. Smaller cracks might join together to form the larger cracks. In some cases, cracks are separated by a very small ligament (<1 μ m) and might have minimal resistance during loading, and thus considered as a single large crack. Figure 3d shows almost similar crack size distribution for both front and side planes and

found ~75% cracks are below 15 μ m with very few over 50 μ m. Nevertheless, these larger cracks are supposed to serve as weaker links during fracture. The number density of cracks is also measured and found to be 2.5 times higher at the front than the side plane.

Planes	Crack opening width (nm)	Crack separation distance (µm)	Crack length (μm)	Crack density (m ⁻²)
LS (Front)	252 ± 142	16.3 ± 4.7	10.2 ± 8.9	3.45 x 10 ⁹
TS (Side)	205 ± 130	15.2 ± 4.8	14.9 ± 12.6	1.34 x 10 ⁹

Table 3. Side surface crack statistics of as-fabricated NFA-1

Since the front and side plate view shows almost similar microstructural features for as-fabricated conditions, only the plates' side view (TS) has been considered for annealing along with its face (LT) view. Figure 4 and Tables 4 and 5 show the grain morphology and statistics of the face and side planes after annealing at 1300°C for 1 and 5 hrs. Results show that the introduction of annealing (1300 °C/1hr) increases the grain size up to 10%, which further increases with time (5hrs) \approx 25% when compared with the as-fabricated condition. Aspect ratio of the side plane reduces from 2.7 for the as-fabricated condition to 1.8 for annealed at 1300°C/5h condition (Table 5). Grains larger than 10 µm were also not observed for any annealed specimen. Higher annealing temperature might recrystallize the larger grains. High temperature annealing also appears to heal the cracks, presumably by surface diffusion, perhaps assisted by recrystallization and grain boundary migration [6]. However, crater-like pores were observed in all the annealed specimens, and the size of these pores increases while their number decreases with annealing time.

Table 4. Grain morphology and hardness of NFA	1 as a function of annealing cor	ndition and plate views
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Planes [*]	Long, I	Short, s	Avg, d= l+s)/2	Aspect	Microhardness,
	(µm)	(µm)	(µm)	ratio	HV, (Kg/mm²)
LTa131	0.842 ± 0.493	0.547 ± 0.285	0.695 ± 0.367	1.6 ± 0.4	294 ± 13
TSa131	0.849 ± 0.544	0.354 ± 0.144	0.602 ± 0.320	2.4 ± 1.3	304 ± 17
LTa135	0.979 ± 0.481	0.694 ± 0.325	0.837 ± 0.390	1.4 ± 0.4	252 ± 7
TSa135	0.963 ± 0.371	0.537 ± 0.197	0.750 ± 0.266	1.8 ± 0.5	247 ± 13

LT: As-fabricated, LTa131: Annealed at 1300°C for 1 hr, LTa135: Annealed at 1300°C for 5 hrs

Microhardness

Vicker's microhardness (H_v) data for the as-fabricated and annealed NFA-1 are summarized in Tables 1 and 4, respectively. H_v averages 376 ± 18 (kg/mm²) and 352 ± 39 (kg/mm²) when indented at face and side plane, respectively. Hardness reduces \approx 30% with the annealing for 1300°C/5hr. These differences can probably be attributed to the presence of pores and grain coarsening. However, unlike as-fabricated condition, hardness variation among different planes is negligible for annealed specimen.



Figure 4. SEM/FIB images of the as-fabricated (a,b) and annealed (c-f) NFA-1 specimens for face (left column), and side (right column) planes, respectively.

Planes	Range (µm)	Length, I (µm)	Aspect ratio, r	No. freq. of grains, (%)	Area fraction, (%)
	0-1	0.57 ± 0.20	1.5 ± 0.4	80	60
LT (Face)	1-10	1.57 ± 0.80	1.6 ± 0.4	20	40
	10+	-	-	-	-
	0-1	0.60 ± 0.19	2.2 ± 0.7	79.3	64.6
LS (Front)	1-10	1.42 ± 0.50	4.5 ± 2.0	20.5	33.2
	10+	11.3	15.8	0.2	2.2
	0-1	0.56 ± 0.22	2.2 ± 0.9	79.3	59.5
TS (Side)	1-10	1.59 ± 0.94	4.1 ± 1.5	20.5	37.9
	10+	12.94	10.0	0.2	2.6
	0-1	0.63 ± 0.19	1.5 ± 0.4	72.6	56
LT131 (face)	1-10	1.40 ± 0.60	1.8 ± 0.6	27.4	44
LT131 (face)	10+	-	-	-	-
	0-1	0.60 ± 0.20	2.0 ± 0.7	72.8	55.2
TS131 (side)	1-10	1.51 ± 0.61	3.5 ± 1.7	27.2	44.8
	10+	-	-	-	-
	0-1	0.71 ± 0.19	1.4 ± 0.4	61.1	45.2
LT135 (Face)	1-10	1.39 ± 0.50	1.5 ± 0.3	38.9	54.8
	10+	-	-	-	-
	0-1	0.72 ± 0.16	1.7 ± 0.4	59	45.6
TS135 (Side)	1-10	1.31 ± 0.29	2.0 ± 0.5	41	54.4
	10+	-	-	-	-

Table 5. Grain aspect ratio, number and area fraction as a function of plates view, for as-fabricated and annealed conditions

Tensile Properties

Results of low temperature uniaxial tensile test on L oriented specimens are shown in Table 6 and their engineering stress-strain s(e) curves at Figure 5. Unlike most of the metallic materials, the NFA-1 material shows a concurrent increase in strengths and ductility (except at -196°C) at sub-zero temperatures. For example, ~32% higher yield strength (YS) and ~65% higher uniform elongation (UE) has been observed for -150°C when compared to room temperature test. This exceptional phenomenon can be attributed to the presence of microcracks that creates delamination during the test (see Figure 6a). These delaminations split the thickness of the tensile specimen and drive them towards plane stress conditions, and thus, suppress the effect of friction stress or Peierls force. Strengths continue to increase (1469 MPa YS and 1563 MPa UTS) at liquid nitrogen temperature, while both the uniform and total elongation decreases to 1.0% and 8.4%, respectively. Relatively lower ductility at -196 °C might be due to the activation of Peierls stress, which might take control over delamination, or it might only happen to this particular specimen. Low magnification fracture image for -196°C, shown in Figure 6a, shows a relatively shiny fracture surface. Nevertheless, higher magnification images of the fractured specimens tested at all

different temperatures reveals almost identical flake-like shallow dimples, attributed to ductile tearing (Figure 6b). It is worth noting that the NFA-1 material showed remarkably low ductile brittle transition temperature (\approx -185 °C), reported previously [3], which makes the NFA-1 material to achieve near record strength-toughness combination. In contrast, The S tensile specimen tested at room temperature fails in a complete brittle manner, mostly in its elastic zone, with almost 0% ductility. The fractured surface shows a very flat, shiny face with cleavage like brittle features (see Figures 6 and 7). Upon loading, the pre-existing micro cracks that run perpendicular to the loading direction propagate by brittle cleavage.

Temperature (°C)	0.2%YS (MPa)	UTS (MPa)	UE (%)	TE (%)
20	970	1062	6.4	13.9
-50	1046 ± 64	1143 ± 37	9.2 ± 0.3	16.1 ± 0.4
-100	1123	1249	9.9	16.0
-150	1283	1380	10.6	16.6
-196	1469	1563	1.0	8.4

Table 6. Low temperature tensile test results of L oriented NFA-1 specimens

YS= Yield strength, UTS= ultimate tensile strength, UE = uniform elongation, TE= total elongation.



Figure 5. Engineering stress-strain curves of L-oriented NFA-1 specimens tested at lower temperatures.



Figure 6. Low (a), and high (b) magnified SEM images of the L and S-oriented tensile fracture surfaces.

The room temperature tensile s(e) curves and their respective SEM fractographs of as-fabricated and annealed (with varying times) conditions for L and S oriented NFA-1 specimens are shown in Figure 7. Figure 8 also plots the summary of their properties. Annealing at 1300°C for 1 and 5 hrs lower the tensile strength for L by ~14% and ~24%, respectively, than their as-fabricated condition. Uniform and total elongation remain almost similar at all conditions though the fracture mechanism changes from delamination driven for as-fabricated specimens to microvoid coalescence dimple fracture with some presence of crater-like features for annealed specimens. These craters might be partly responsible for lower strength along with higher grain size compared to the as-fabricated specimens. While the asfabricated S oriented tensile specimen failed in the elastic region at room temperature, the corresponding 1h annealed specimen has a large total elongation of \approx 18% with a significantly higher UTS of \approx 874 MPa compared to the as-fabricated condition (≈ 652 MPa). Annealing at 1300°C for 5h further improves the total ductility to 23%, while tensile strength drops slightly (≈ 802 MPa), but still high enough when compared with the as-fabricated condition. Fracture surface has also been changed from flat, shiny brittle fracture for as-fabricated specimens to dimple dominated ductile fracture with some craters for annealed specimens. The crater-like features may partially heal microcracks and help to increase the ductility. The room temperature strength and ductility of the L and S oriented annealed specimens are comparable to each other. These improvements in strength and ductility are associated with the absence of microcracks and grains larger than 10 µm (see Table 5 and Figure 4).



Figure 7. Room temperature engineering stress-strain curves for the as-fabricated and annealed L (red) and S (blue) oriented tensile specimens and their respective SEM fractographs. Codes 101, 131 and 135 mean as-fab, annealed at 1300°C/1hr and annealed at 1300°C/5hr conditions, respectively.

Fracture toughness

Room temperature fracture toughness test were conducted on L-T oriented as-fabricated and annealed $(1300^{\circ}C/1hr)$ specimens and their load-displacement curves along with fracture surfaces are shown in Figure 9. The results show that the toughness reduces $\approx 22\%$ for the annealed specimen when compared with the as-fabricated specimen. This lower toughness for annealed specimen might be associated with the relatively higher grain size, lower strength, and formation of crater-like pores and absence of microcracks in favourable orientations. Fracture mode has also been changed from delamination driven for the as-fabricated specimens to the classical dimple fracture by micro void coalescence for annealed specimen.

SUMMARY

The statistical analysis of microstructural features of as-fabricated and annealed NFA-1 material has been studied. High temperature annealing at 1300°C for 1 and 5 hrs appears to heal the microcracks and alters the pancake-shaped grains towards more equiaxed than exist in the as-fabricated plate. Annealing for 1 and 5 hrs also increases the average grain size by $\approx 10\%$ and $\approx 24\%$, reducing the microhardness by $\approx 18\%$ and $\approx 30\%$, respectively. The room temperature L loaded tensile strengths also lower by up to 24%. Interestingly, the strength increases up to $\approx 34\%$ for the S loaded annealed tensile specimens. Total ductility was also observed $\approx 23\%$ for the annealed condition, when compared to the as-fabricated condition that showed $\approx 0\%$ ductility. The room temperature tensile properties are more isotropic after annealing.



Figure 8. Room temperature ultimate tensile strength (UTS) and total elongation (TE) of L (red) and S (blue) oriented tensile specimens as a function of annealing conditions.



Figure 9. Room temperature fracture toughness test for L-T oriented specimens: (a) load-displacement curves, (b) delamination driven fracture for the as-fabricated specimen, and (c) dimple fracture surface for annealed at1300°C/1hr specimens.

The effect of different annealing temperatures (1100 and 1200 °C) and times (1 and 5 hrs) will be explored and more detailed observations on microcrack healing will be obtained along with the corresponding effects on the grains, dislocations and NO nanostructures.

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2.3 THE CRYSTAL STRUCTURE, ORIENTATION RELATIONSHIPS AND INTERFACES OF THE NANOSCALE OXIDES IN NANOSTRUCTURED FERRITIC ALLOYS — Y. Wu, S. Kraemer, G. R. Odette (University of California Santa Barbara), J. Ciston (Lawrence Bekeley National Laboratory), N. Bailey, P. Hosemann (University of California Berkeley)

OBJECTIVES

The objective of this study is to use aberration-corrected high-resolution transmission electron microscopy to characterize the nanoscale oxides in four NFA conditions, including severe deformation and extreme neutron radiation exposure.

SUMMARY

Fast Fourier Transform analysis of focal series images revealed the nano-oxide (NO) crystal structure, including the smallest at < 2 nm in diameter, to be $Y_2Ti_2O_7$ pyrochlore in all cases, consistent with both exit wave analysis and scanning transmission Z-contrast imaging of the atomic columns in larger features. The faceted NOs exhibit a quasi-epitaxial orientation relationship to the ferrite matrix: $[110]_{YTO}||[100]_{Fe}$ and $[001]_{YTO}||[010]_{Fe}$, forming a 5x7 near coincidence site interface, and exhibit size-dependent strains in both the oxide and matrix ferrite phases.

BACKGROUND

Fusion reactors will require advanced materials with tolerance to intense high-energy neutron fluxes that generate helium concentrations reaching thousands of atomic parts per million and hundreds of atomic displacements per atom over the operating lifetime. Neutron damage leads to void swelling, embrittlement and irradiation creep [1-3]. Managing helium is a grand challenge for turning the promise of C-free fusion power into a reality. Nanostructured ferritic alloys (NFAs) are promising candidate materials, which are dispersion strengthened by an ultrahigh density ($\approx 5 \times 10^{23}/m^3$) of Y-Ti-O nano-oxides (NOs) averaging \approx 2.5 nm in diameter, with volume fractions of $\approx 0.75\%$ [1-3]. NOs result in unique irradiation tolerance because they pin dislocations, help to self-heal vacancy and self-interstitial damage; and, most significantly, trap otherwise highly damaging helium in harmless nm-scale interface bubbles [1-3]. Notably, NFAs can manage very high concentrations of transmutation product helium produced in fusion reactors. Thus understanding of NOs is essential to developing, qualifying and optimizing NFAs.

PROGRESS AND STATUS

Experimental Procedure

Alloy information

The TEM studies were carried out on three conditions of NFA MA957 and a 14YWT heat recently developed in the DOE Fuel Cycle Research and Development Program called FCRD NFA-1. The variants of MA957 included as-extruded (AE), friction stirred weld and annealed (FSWA), and irradiated (IR) conditions. The AE MA957 was obtained from Pacific Northwest National Laboratory in the form of extruded 25-mm-diameter rods [4]. The FSW was prepared by Edison Welding Institute in collaboration with UCSB, by joining two MA957 AE coupons, followed by post-weld annealing at 1150°C for 1h [5,6]; annealing was intended to relax residual stresses and to recover any potential damage to the NOs that might be caused by severe plastic deformation. The IR condition is another MA957 heat irradiated to 109 dpa at 412°C in the Fast Flux Test Reactor [7]. FCRD NFA-1 is a best practice heat of 14YWT in the form of an extruded and cross-rolled plate [8]. Various combinations of APT, SANS, TEM and mechanical property measurements have been used to extensively characterize these four NFA conditions; further details can be found in [5-8, 9-11].

TEM characterization

Electron transparent TEM specimens were prepared by either the focused ion beam (FIB) lift-out technique, using FEI Helios and Quanta microscopes, or by wedge polishing, followed by ion-milling, both at successively lower energies down to 2kV to minimize the gallium and argon ion damage. Most of the HRTEM images were recorded using the TEAM 0.5 FEI-Titan-class microscope with aberration correction to third order in both TEM and STEM modes [12]. HRTEM data was collected at 300 kV using monochromation to 0.1 eV with the corrector tuned to optimize bright atom contrast (C3 = -6 um, C5 =2.5mm) and recorded on a 2048x2048 pixel CCD camera. Focal series were recorded with a defocus step of -1.72 nm ranging from -34.4 nm under focus to 34.4 nm over focus. Exit wave reconstruction was performed using the Gershberg-Saxton algorithm [13] as implemented in the MacTempasX software [14]. Exit wave reconstruction is a holographic technique that can provide both the amplitude and phase of the electron wave after passing through the sample. Once the complex wave is known, all residual aberrations of the microscope can be corrected in software [15], improving the interpretability of the HRTEM data. Furthermore, at the limit of the weak phase object approximation, the exit wave phase is directly related to the projected potential of the object. MacTempasX was also used to perform multi-slice HRTEM simulations using the experimental parameters and a cutoff frequency of 10/nm. Atomic coordinates of the Fe- Y2Ti2O7-Fe slab are provided in Supplemental Materials. TEAM 0.5 was also used in STEM mode to record high angle annular dark field (HAADF) images with a 17.1 mrad convergence semi-angle and a collection semi-angle ranging from 75-150 mrad. Finally, electron energy loss spectroscopy (EELS) was used to characterize Ti-profiles for a limited number of NOs. The HRTEM images and exit waves were analyzed by FFT power spectrum lattice indexing. Individual FFT were first calculated and then collectively averaged using MATLAB. The lattice spacing's and inter-planar angles were measured using Image J.

Results

The microstructures of the 4 NFA conditions were characterized by aberration corrected TEM: MA957 in as-extruded (AE), friction stir welded and annealed (FSWA) and irradiated (IR) conditions; and a new developmental heat of 14YWT (NFA-1). Note that the FSWA and IR conditions represent extreme conditions of deformation and neutron irradiation exposure, respectively. Figure 1a is a bright field TEM image of the MA957 FSWA condition, showing the NO features. The NOs have elongated cuboidal shapes with sizes widely ranging from \approx 1 to 12 nm.



Figure 1. a) A bright field TEM image at low magnification of FSWA MA957 showing faceted, cuboidal oxide particles with a wide size distribution; b), representative HRTEM images from the focal series for a large NO and the corresponding power spectra for: i) under-; ii) near; and, iii) over-focus; and, c), the averaged FFT from all HRTEM images of the NO shown in Figure 1b, where the larger high-intensity reflections and their multiples are from the Fe-Cr ferrite matrix (Fe) while the white circles mark the major reflections of $Y_2Ti_2O_7$ pyrochlore (YTO) with corresponding zone axes of [100]_{Fe} and [110]_{YTO}.

The left side of Figure 1b shows three HRTEM images of the same NO, as examples of a larger series representing (i) under-; (ii) close-to-; and, (iii) over-focused conditions. The NO is sharply faceted and the Moiré patterns indicate that it is crystalline. The right side of the Figure 1b shows the associated FFT for each of these focal condition examples. The overlay of stronger and weaker lattice spots represent reflections of the ferrite matrix and the NO, respectively. The weak NO reflections vary in amplitude with the focal condition and, in some cases, even disappear. This is a result of the strong image modulations introduced by the contrast transfer function of the TEM objective lens.

Taking the average over all fast Fourier transforms (FFTs) in a focal series minimizes contrast transfer function effects and provides a higher signal-to-noise ratio. The corresponding averaged FFT is shown in Figure 1c. The strong reflections (with a red spot in the middle) are the <100> zone-axis pattern of the bcc ferrite matrix. The primary reflections from the NOs, marked by white circles, are consistent with $Y_2Ti_2O_7$ pyrochlore with a <110>-zone axis. Detailed analysis shows that all other spots arise from multiple scattering.

The in-focus electron wave phase obtained from exit-wave reconstruction (EWR) in Figure 2 takes into account the transfer function modulations, and provides a more interpretable representation of the projected crystal structure.



Figure 2. a). The phase of the reconstructed exit wave from of the focal series in Figure 1b. b) the corresponding HAADF STEM image where the dashed lines highlight the periodicity of the Moiré pattern in the overlap region. c) magnified views of the periodic structure in the exit-wave reconstruction image, and d), in the corresponding HAADF STEM image. The dashed lines show the periodic repeated pattern of 5x7 Fe unit cells, while the colored balls represent lateral positions of Y (green) and Ti (blue) columns relative to Fe (yellow) matrix.

Figure 2a displays the phase of the reconstructed HRTEM exit wave, with white atom contrast, while Figure 2b shows the corresponding HAADF STEM image. In both cases a periodic image pattern is observed in the central region of the large NO, reflecting the overlap of the ferrite matrix and the $Y_2Ti_2O_7$ pyrochlore crystal structures. The in-focus phase of the exit wave and HAADF STEM images are both interpreted as projected atomic columns, as supported by corresponding HRTEM simulations (not shown here). Corresponding overlays of an ideal $Y_2Ti_2O_7$ pyrochlore atomic model with the observed OR are shown in Figures 2c and 2d. The dashed lines correspond to a periodic array of 5x7 Fe periodic cells, while the colored balls represent lateral positions of Y (green) and Ti (blue) atoms relative to the Fe matrix (yellow), based on a visual best fit position adjustment of the image intensities. Note the visible atoms represent columns of pure Y, pure Ti and mixed Y and Ti. The bulk $Y_2Ti_2O_7$ model is very well matched to the EWR and STEM column patterns, when displaced relative to the ferrite matrix, based on simple visual pattern matching. The periodic pattern corresponds to a 5x7 Fe periodic cell near coincident site lattice.

A HAADF STEM image of AE MA957 is shown Figure 3a. The faceted oxides are significantly smaller in this case, many less than 2 nm. Clearly imaging the smallest NOs in HRTEM is very difficult due to reduced atomic mass contrast, the dominance of interfaces, as well as the possibilities of complex chemical oxide terminations, mismatch strains, solute segregation and the presence of both ferrite matrix lattice and oxide defects. The averaged FFT of one somewhat larger NO in the AE condition, shown in Figure 3b, deviates from those in for the FSWA MA957 in Figure 1c, since there are {100} indexed spots lying on a line between the major {110} type Fe reflections, which would be forbidden in an ideal bulk crystal. These extra spots may occur due to a symmetry-breaking sharp truncation of the bcc Fe crystal at the small NOs interface and possible lattice defects. The other reflection spots visible on the line between the Fe reflections are consistent with a $Y_2Ti_2O_7$ pyrochlore crystal orientated along [100] with a [100]_{YTO} || [010]_{Fe} and [011]_{YTO} || [100]_{Fe} OR, which is also found by both Dawson et al.[16] and Ribis et al. [17].



Figure 3. TEM images for AE MA957: a) a HAADF STEM overview image with arrows marking some oxide particles; b) a HRTEM image of a larger particle; and, c) an averaged FFT of all the images in the corresponding focal series. White circles mark the major reflections of $Y_2Ti_2O_7$ pyrochlore (YTO). The corresponding zone axes are [100]_{Fe} and [001]_{YTO}.

Structural information was also obtained from the extra spots in the FFT for a larger image area containing a sufficient volume fraction of NOs, even if they could not be individually indexed due to signal to noise limitations for individual embedded NOs. Note that in the MA957 IR condition, the individual NOs were not indexed, but this will be part of future research. The collage in Figure 4 is a summary of corresponding power spectra for all the NFA conditions in this study. Each spectrum is based on the average of all the individual images in the focal series. For comparison purposes, Figure 1c is repeated in 4a. Figures 4b and 4c are power spectra from two other regions in FSWA MA957. Figure 4b is for a NO that is 1.8 nm high and 3.2 nm wide. The large aspect ratio can be seen as an elongation of the corresponding reflections along the vertical axis. Due to the smaller size of these NOs, multiple scattering

is reduced compared to the larger crystal shown in Figure 1a. The Fe region next to the particle contains no discernible features. The corresponding FFT in Figure 4c mainly contains ferrite matrix spots, with only very minimal indications of any other structures in the background.



Figure 4. A summary of the averaged FFTs for all the NFA conditions studied. The top row is the FSWA MA957 for: a) the large NO shown in Figure 1c; b) a smaller 3.2x1.8 nm² NO; and c) the area next to the small NO in b. The bottom row is for MA957 in the: d) AE MA957; e) IR MA957 conditions; and f) NFA-1.

Figures 4d and 4e are FFT for the AE and IR MA957 conditions, respectively, and Figure 4f is for NFA-1. All the FFT for a larger area of the foil show the same characteristic extra spot features, i.e. weak peaks in between and close to the $\{200\}$ -type Fe reflections. The spots near the Fe peaks are at the same locations that were previously assigned to $Y_2Ti_2O_7$ pyrochlore in Figure 1. The detailed analysis results of Figure 3 and Figure 4 are summarized in Table 1. Note Ribis et al. also reported pyrochlore structure is stable after irradiation [17]. However, in contrast to the other images, these spots are streak-like broadened, as discussed in the next section.

A careful analysis of NOs in MA957 and 14YWT NFA-1 heat reveals strongly facetted shapes and a welldefined OR to the ferrite matrix. All of the recorded and indexed power spectra are consistent with a *cube-on-edge* OR as illustrated in Figure 5a with $[110]_{YTO} \parallel [100]_{Fe}$ and $[001]_{YTO} \parallel [010]_{Fe}$ for all of the alloy conditions.

		$Y_2Ti_2O_7$		
Figure	d (Å)	d ₁ (2-22)	d ₂ (22-2)	α ₁₂ (°)
Fig. 4d	Measured	2.83±0.09	2.83±0.09	68.7±0.9
Fig. 4e	Measured	2.85±0.07	2.85±0.07	71.9±1.3
Fig. 4f	Measured	2.81±0.07	2.80±0.07	69.4±1.8
	$Y_2Ti_2O_7$	2.90	2.90	70.5
Fig. 3c	d (Å)	d ₁ (400)	d ₂ (040)	α ₁₂ (°)
	Measured	2.60±0.08	2.60±0.08	90.6±1.8
	$Y_2Ti_2O_7$	2.52	2.52	90

 Table 1. Summary of d-spacing's and plane angles measured in the indicated figures compared to bulk

Due to the two-fold symmetry of the <110>-zone axis there are three possible variants of overlapping ferrite and $Y_2Ti_2O_7$ pyrochlore diffraction patterns. Figure 5b i) shows possible peak locations in the power spectrum assuming an equal mix of three cube-on-edge rotations. Figures 5b ii) and iii) correspond to <110>-type $Y_2Ti_2O_7$ pyrochlore patterns rotated 90°, while iv) shows a <100>-type pattern that is 45° rotated relative to $[100]_{Fe}$. Notably, Figures 4d, 4e and 4f show streaking of the corresponding $Y_2Ti_2O_7$ reflections that are consistent with a combination of these three rotation variants.



Figure 5. a) A schematic illustration of the cube on edge OR of $Y_2Ti_2O_7$ pyrochlore (small cube) relative to the Fe matrix (large cube); b) i) all possible peak locations in the FFT assuming a cube-on-edge OR where ii) and iii) represent $<110_{YTO}$ orientations rotated with respect to each other by 90° and, iv) is $<100_{YTO}$ rotated 45° around the zone axis. c) The 5 x 7 array of Fe matrix unit cells in near-coincidence periodicity with the $Y_2Ti_2O_7$ pyrochlore (cation) lattice.

The strong OR between ferrite matrix and $Y_2Ti_2O_7$ pyrochlore is intriguing given the incommensurate bulk unit cells of the two crystals. Nevertheless, it is noted that the overlapped crystal structures with the specified OR show a near CSL between Fe atoms and Y and Ti cations that spans 5x7 ferrite periodic cells, as illustrated in Figure 5c. Note, Figure 5c represents an yet to be published first principles calculation of an embedded NO, provided by Y. Jiang at the South Central University In China, which was inspired by the TEM results reported here. The atomic positions, including O, in a 525 atom supercell are fully relaxed from a bulk pyrochlore structure with the 5x7 CSL interface with the ferrite matrix. The first principles minimization resulted in only small movements of the atoms, suggesting that this interface represents a highly stable structure. Details of this very recent modeling research will be the subject of a future publication, including corresponding interface energies, as well as a full oxygen potential and temperature dependent interface phase diagram. These repeat units in Figure 5c correspond exactly to the observed periodicity seen in Figure 2b and the coherent structures are consistent with the EWA. The lattice mismatch is remarkably low across these periodic distances, at only +0.45% along the horizontal and -0.57% along the vertical directions. The corresponding strains in the fully relaxed DFT model are horizontal/vertical: 1/1.05% in Fe and -1.77/-0.7% in Y₂Ti₂O₇. Due to the symmetry of the OR, the lattice strains along horizontal and the third, out of plane, direction are equivalent.

The interfaces between the NO and ferrite matrix are also remarkably flat, as is especially seen in the FSWA condition shown in Figure 1; note the other alloy conditions also show faceted NOs. The example of the larger particle in the MA957 AE condition in Figure 3c is most striking. Nevertheless, upon close inspection one can also recognize similar faceting for the smaller particles. Note that the direction of the arrows in Figure 3a correspond to <100> directions of the ferrite lattice. Presumably optimally matched interfaces between low-energy planes on both the oxide and iron matrix sides are self-selected. However, the exact shape of the particles cannot be determined from the projection images we have obtained and need to be further characterized by electron tomography, for example.

We conclude that: a) the NO are predominantly $Y_2Ti_2O_7$ pyrochlore that persist to small sizes even in the face of severe deformation and extreme irradiation exposure and in all four alloy conditions; b) the NOs observed here have a predominantly cube on edge $[110]_{YTO} \parallel [100]_{Fe}$ and $[001]_{YTO} \parallel [010]_{Fe}$ OR relationship in all conditions; c) the atomic scale interface in a larger NO can be described as a 5x7 near CSL.

A pertinent question is how general are these results? Even wide area TEM FFT measurements only sample a small volume of material. Unfortunately, classical techniques for crystal structure analysis in larger volumes, like XRD, have serious limitations when dealing with low volume fractions of nano-scale crystals, with sizes of order of one to several nm. However, new synchrotron based techniques like the partially or not known structures (PONKS) Rietveld Refinement approach to fit the peak broadened background of the XRD spectra [18] has been recently demonstrated for Ni- Mn-Si nano precipitates in reactor pressure vessel steels at the new NSLS II synchrotron light source at Brookhaven National Laboratory [19]. Application of XRD PONKS to NFAs and NOs will lead to further understanding. Indeed, it is notable that the our preliminary XRD results on AE MA957 show weak peaks and enhanced background that are consistent with the presence of $Y_2Ti_2O_7$ and Y_2TiO_5 NOs, along with much larger TiO features. These results are also consistent with several previous XRD studies that characterized greater volume fractions of larger or extracted NOs [20-22]. Furthermore, a very recent glancing angle XRD study found only $Y_2Ti_2O_7$ peaks in a MA957-like 14YWT NFA [23]. Finally, a combination of SAXS and SANS was used to identify the NOs in another 14YWT alloy, showing that they are consistent with $Y_2Ti_2O_7$ or Y_2TiO_5 [24].

We have focused on the $Y_2Ti_2O_7$ and, in the case of the larger pyrochlore oxide, the detailed atomic structure of its ferrite matrix interface. However, we should emphasize that, as noted above, other oxides are often present in NFAs, and different cube-on-cube ORs have also been reported [25]. Further, while we believe that the HRTEM images suggest that they are similar, we have not resolved the detailed interface structures in the smallest NOs. We also note that in the other limit of µm-scale bilayers of Fe grown on (100) $Y_2Ti_2O_7$ pyrochlore, the edge-on-cube OR is accompanied by interface dislocations with a spacing of 1.4 nm, which are not observed in small embedded NOs that do not experience a semi-infinite in-plane strain condition.

It is useful to emphasize the critical importance of the detailed observations reported here. For example, the presence of interface strains has important implications to the NO interactions with helium. This is especially the case to support modeling efforts to better understand the nature of NOs, their functionality and the corresponding overall performance of NFAs. The first principles result in Figure 5c is an example of the opportunity for close coupling of modeling and experiment. This work also provides "ground truth" to a series of first principles and atomistic studies that have explored: a) initial clustering energetics of Y-Ti-O solutes [26-28]; b) the structure and physical properties of $Y_2Ti_2O_7$ and Y_2TiO_5 [29]; c) the corresponding remarkable ability of NO to sequester helium, in internal interstitial sites and subsequently in associated interface bubbles [30,31]; d) the free surface and embedded interface energies of $Y_2Ti_2O_7$ [32]; and, e) the solubility of Y both in the matrix and at dislocations [33], that mediates the truly

remarkable long-term, high-temperature thermal stability of NOs, as modeled by cluster dynamics methods [4].

A detailed high resolution TEM study was conducted to answer unresolved questions about the nature of the NOs present in NFAs. The results suggest that even the smallest cubic and cuboidal NOs are predominately $Y_2Ti_2O_7$ pyrochlore in all the 14YWT alloy conditions we studied. The NOs have a cube on edge, apparently coherent, interface that manifests a well-ordered 5x7 near CSL oxide-bcc ferrite-matrix boundary structure in a larger oxide. The NOs are under compressive stress while the Fe-matrix is under tension. With the exception of APT measurements, the more detailed results reported here are generally in good agreement with the preponderance of corresponding evidence in the literature although other phases and ORs also occur. The results of this study represent an important step in supporting detailed modeling efforts, such as the first principles simulation of the 5x7 near CSL example in Figure 5c, that will help to develop, optimize and qualify NFA for fusion and advanced fission energy service.

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2.4 NANOSCALE 3D CORRELATIVE ATOM PROBE-ELECTRON TOMOGRAPHY: CHARACTERIZATION OF MICROSTRUCTURES IN DUAL ION IRRADIATED NFA MA957 — P. B. Wells, S. Krämer, Y. Wu, S. Pal, G. R. Odette and T. Yamamoto (University of California, Santa Barbara)

OBJECTIVE

The objective of this study is to use a combination of atom probe (APT) and 3D electron tomography (ET) to characterize nm-scale helium bubbles (HB) and nano-oxides (NO) in dual ion irradiated MA957 to characterize their mutual associations, as well as their associations with other microstructural features, such as grain boundaries.

SUMMARY

Transmission Electron Microscopy (TEM) can resolve very small helium bubbles (HB), down to approximately 1 nm, but is not optimal for observing populations of very small nano-oxides (NO) in nanostructured ferritic alloys (NFA). In contrast, atom probe tomography (APT) excels in measuring the location, size and composition of NO, but cannot resolve small bubbles. Because a typical APT tip has dimensions similar to those needed for TEM (on the order of 50-100 nm thickness), it is possible to characterize HB by 3D TEM tomography, hereafter called ET, prior to destructive 3D characterization of the NO by APT. Here, for the first time, APT and ET are used to assess the association between HB and NO in full 3D reconstructions, which also reveal strong NO-HB associations with a grain boundary.

BACKGROUND

Structural materials for use in fusion reactors must be able to withstand neutron doses in the hundreds of dpa and manage high concentrations of He generated in neutron-alpha reactions. Insoluble helium atoms cluster in steels to form nm-scale pressurized bubbles [1, 2]. When helium bubbles reach a critical size, they transform and grow unstably as voids, causing swelling. Helium on grain boundaries also promotes intergranular fracture by both fast crack propagation, at low to intermediate temperatures, and creep rupture at high temperatures.

It is well established that helium can be managed in NFAs, which contain a high density of Y-Ti-O NO. The NO trap helium in a high density of harmless nm-scale bubbles at the ferrite matrix interface [2]. Dual ion irradiations (DII) can be used to study helium behavior and related mechanisms in fusion relevant alloys. Heavy ions, such as Fe, are used to create displacement damage, while He ions are simultaneously injected to mimic n,α transmutation reactions [3]. The DII have shown that NFA with NO have a much larger number density of finer bubbles, compared to conventional 9Cr tempered martensitic steels [4–6].

The TEM has previously been used to show the association between NO and HB for a fraction of larger sizes in a population of NO [5, 7, 8], or for a single smaller NO [9]. Characterizing the general association between HB and a population of smaller NO is challenging in that it is generally not practically possible to find an imaging condition that can resolve both features at small sizes, except in special cases. Further, conventional TEM is also limited to imaging 2D projections of features in a 3D foil. Thus, for example, quantifying the relationship of HB and NO with angled grain boundaries is difficult.

New ET techniques seek to eliminate these limitations by taking a series of images over a wide range of tilt angles on a rotated cylindrical specimen. The tilt series can then be used to reconstruct a 3D representation of the microstructure, including HB. APT tips meet the cylindrical geometry requirement for ET, and then can be characterized by APT to observe the NO. Note while there are claims that APT can indirectly observe cavities, like HB, we have not found this to be the possible.

PROGRESS AND STATUS

Experimental Procedure

Materials and Irradiation Conditions

The NFA MA957, that contains a high density of NO, was DII at 500°C with 6.4 MeV Fe³⁺ and 1 MeV He⁺ ions in the DuET facility at the Institute of Advanced Energy of Kyoto University in Japan. MA957, which has been commonly used as a reference NFA, was first produced by INCO in the late 1970s [2]. The composition in wt.% of the heat studied here is; 13.6Cr, 0.30Mo, 0.98Ti, $0.26Y_2O_3$, with trace impurities and the balance of Fe. The character and thermal stability of the NO in MA957, and their ability to refine the He bubble microstructure has been the subject of numerous studies [3–6, 10, 11].

The DII dpa and appm He as a function of depth in MA957, calculated using SRIM 2008, is shown in Figure 1. The APT TIPS were FIBed from liftouts taken from near the peak helium implanted damage region. The liftouts were mounted on a 5-post TEM grid and sharpened into APT tips using a 30 kV ion beam, followed by cleanup steps at 5 kV and 2 kV to minimize Ga contamination and damage. After cleanup, the tip of the APT needle was ~ 1 um from the original irradiated sample surface, nominally corresponding to \approx 80 dpa and \approx 4300 appm He.





Electron Tomography

A series of 140 bright field images were taken in a 200 keV FEI T20 Cryo TEM over a tilt range of -70° to +70° in 1° increments at a magnification of 50kx with an underfocus of 1um. While this defocus reduces the resolution of the images, the Fresnel white-black ring pattern improves the visibility of the bubble significantly. Simulation by Yao et al found that the optimum underfocus for imaging 1-3 nm bubbles is 750 nm, but 1µm is still near optimal [12]. The simulation suggested that the 1 µm underfocus results in a nominal bubble size that is \approx 90% of its actual dimension. The series of images was then imported into a MATLAB code, using a custom weighted back projection algorithm that reconstructs the 140 ET data sets into a single 3D tomogram. Details of the reconstruction algorithm will be reported elsewhere.

Atom Probe Tomography

Following ET, the APT tip was run in a LEAP 3000x HR in voltage mode at 40K with a pulse fraction of 20%. The APT data was reconstructed using the CAMECA Instruments Integrated Visualization and Analysis Software (IVAS) 3.6.2 software. The TEM images of the specimen were used to determine the radius as a function of depth as input to the reconstruction. The [110] pole planes used in the reconstruction, were only visible in one region, because of a grain boundary in the center of the tip.

Correlative Tomography

The electron tomogram was imported into IVAS and the cluster analysis algorithm was used to determine the center of mass and size of both the HB and NO. The two datasets are initially reconstructed in separate arbitrary coordinate systems. The x, y, z coordinate systems were adjusted to align and overlay the HB and NO. An initial eyeball 3D overlay of the population HB and NO showed a 1:1 association. A refined overlay algorithm was then used to minimize the distance between the entire populations of correlated HB-NO pairs. Note because x, y, z adjustments were exactly the same for all off the HB and NO the statistical likelihood of false associations is virtually zero. Finally, the two datasets were imported into MATLAB for visualization.

Results

The 1 µm under focused bright field image of the DII MA957 in Figure 2 shows an extremely high density of 2-3 nm HB. No HB or NO is seen in the unirradiated control MA957 (not shown). The DII needle contained 3 grains, with one boundary roughly parallel and the other boundary roughly perpendicular to the tip axis. Two-dimensional projections of both the ET and APT tomograms are shown in Figure 3, for views parallel and perpendicular to the vertical grain boundary. Note the APT reconstruction volume is smaller than that for the ET. The grain boundaries can clearly be seen in the profile view parallel to the boundary planes. These results demonstrate the capability of ET to image and analyze HB. For example, the density of HB on the grain boundary is much higher than in the matrix and there is a \approx 5 nm wide denuded zone on both sides of the horizontal boundary. Note a standard 2D TEM projection would not image the denuded zones unless the grain boundary was fully normal to the projection plane.

The superimposed ET and APT datasets is shown in Figure 4 where the red and blue isosurfaces represent the NO and HB, respectively. While in almost all cases, the surfaces of the bubbles and NO overlap, or are in close proximity, there are a few cases where there is clear separation between the two features. As seen in Figure 5, the center to center separations of HB and NO are larger at both the top and bottom of the tip. This is thought to be due to a slight miscalibration of either the APT reconstruction or the spatial superposition of the ET and APT, or both.

Future Work

While in a very preliminary stage, this work has shown for the first time on a large population of features, that there is a 1:1 correlation between HB and NO. A number of improvements will be pursued to further improve the quantitative correlation of the two techniques. Notably, improvements in the accuracy of APT reconstructions, both globally and locally, are constantly being made by the community. The combination of ET and APT also offer a way to further improve APT reconstructions. For example, trajectory aberrations associated with the local tip topology at an ET imaged void can be fully quantified in terms of the atom densities or local magnification factor. These experimental observables can be compared to and used to refine APT ion emission simulations. Further, future work will explore using additional information from both techniques to improve the individual correlation accuracy. For example, ET provides grain orientation information by local area diffraction measurements and real space images of other microstructures features, such as the grain boundaries, that can be tied to plane spacing and solute distributions measured in APT.



Figure 2. One of the 140 TEM bright field micrographs from the irradiated MA957 showing the size and Locations of HB. The lower figure is 5x time higher magnification.



Figure 3. Two-dimensional projections of the ET and APT datasets parallel and normal to the grain boundaries. Note the volume of material in the APT reconstruction is smaller than the region imaged by ET.



Figure 4. Projection views of the 3D correlated-superimposed ET and APT reconstructions parallel and normal to the grain boundaries showing the close association between the HB (blue) and NO (red) features.



Figure 5. Center-to-center distances between the pairs of correlated NO and HB as a function of distance along the tip axis.

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2.5 He IMPLANTATION OF Fe-{110}YTO BILAYERS — T. Stan, Y. Wu, T. Brown, C. Palmstrom, and G.R. Odette (University of California Santa Barbara), and F. Allen, P. Hosemann (University of California Berkeley)

OBJECTIVE

The objective of this work is to fabricate mesoscale $Fe-Y_2Ti_2O_7$ interfaces in the form of bilayers that are amenable to detailed characterization techniques and He implantation experiments.

SUMMARY

The Fe-Cr matrix nanostructured ferritic alloys (NFAs) are dispersion strengthened by < 5 nm Y-Ti-O nano-oxide (NO) phases. The characteristics of the interfaces between the NOs, such as $Y_2Ti_2O_7$ (YTO), and the surrounding ferrite matrix are critical to trapping He in fine scale bubbles. As a compliment to current characterization efforts of the NOs themselves, a surrogate bulk Fe-YTO interface was fabricated by molecular beam epitaxy (MBE) and electron beam Fe deposition on {110}YTO. Areas of the sample were then implanted with 25 keV He. The He bubble sizes, number densities, and volume fractions are reported. Bubbles at the Fe-YTO interface were on average larger than in the matrix. No bubbles were seen in, but this does not indicate that He is not present in the YTO.

PROGRESS AND STATUS

Introduction

Materials for nuclear fusion applications must reliably perform at high temperatures and manage high levels of helium (He). Nanostructured Ferritic Alloys (NFAs) are a promising class of Fe-Cr-based stainless steels that have remarkable mechanical properties, are thermally stable up to 1000 °C, and are irradiation tolerant [1-3]. NFAs contain a high density (~10²³/m²) of 2-3 nm Y-Ti-O nano-oxides (NOs) which help impede dislocation climb and glide, stabilize dislocation and grain structures, and trap He in fine-scale bubbles at matrix-NO interfaces, preventing void swelling and He embrittlement. Indeed, NFAs may turn He from a liability to an asset. For example, He bubbles act as recombination sites for vacancies and interstitials, thus promoting self-healing. The high density of matrix-NO interfaces prevents He from collecting at grain boundaries, which would otherwise degrade creep and fracture properties.

There is ongoing research to determine the compositions, structures, and orientation relationships (ORs) for the NOs themselves. A summary of these studies and other NFA properties was recently published by Odette [1]. The most common reported NO is $Y_2Ti_2O_7$ (YTO) fcc pyrochlore. Characterization and analysis of the NO-matrix interfaces is needed to develop first principles and atomic interface models that predict NFA performance in fusion reactor environments. YTO-matrix ORs are of interest because they affect interface defect structures, misfit strains, and energies.

The NO-matrix interfaces are difficult to characterize in NFAs using conventional microscopy techniques due to the nm size scale. The research approach in this study is to deposit Fe on bulk oriented YTO single crystal substrates to create surrogate mesoscopic-scale interfaces. Even if the bilayers do not have same characteristics as the embedded ones, this study will further the general understanding of metal-oxide interfaces. Bilayers are also amenable to irradiation studies such as interactions with point defects and He.

Studies of Fe deposited on {111}YTO were previously published by Stan et al. [7], while Fe on {100}YTO and {110}YTO were reported in other Fusion Semi Annual Reports [8-10]. This study is a continuation of the previous results by characterizing a new Fe deposition on {110}YTO, and the associated He implantation.

Experimental Procedure

The details of sample fabrication and the characterization instruments used are covered in a previous publication [7]. In summary, a YTO single crystal was grown by the Chelkowski method at University of Tennessee. The crystal was then {110} surface oriented and 2 mm thick wafers were cut. An Allied Multiprep instrument was used to polish the wafer using a sequence of diamond lapping films, followed by a final 15 minute polishing step using a 0.02 μ m non-crystallizing colloidal silica suspension. The wafer was placed under running deionized (DI) water, followed by a sequential series of 5 min sonic bath treatments in: 10 vol% Micro-Organic soap and 90 vol% DI water, acetone, isopropanol, and finally DI water.

The Fe film was grown in the UCSB Palmstrom laboratory interconnected molecular beam epitaxy (MBE) system. The wafer was inserted into the system and pumped down to ultra-high vacuum (~10⁻¹¹ Torr). The substrate was then outgassed by annealing at 700 °C for 1 hour. The first 20 nm of Fe were MBE grown at room temperature. The first 5 nm were grown slowly with a deposition rate of 0.5 Å/min, while the remaining 15 nm were grown with a faster rate of 1.35 Å/min. The sample was then annealed at 300 °C for 1 hour to allow the film to equilibrate. An extra 200 nm of Fe was then deposited on top of the MBE-grown layer using an electron beam system with 2 Å/sec at 300 °C. The 220 nm Fe layer was capped with 5 nm of electron beam grown AIO_x to prevent Fe oxidation. The Fe-YTO bilayer was then moved into an Oxford FlexAL assisted layer deposition (ALD) instrument at the UCSB Nanofab facility. 9 nm of Pt was uniformly deposited on the entire sample. In total, the sample is composed of 2 mm thick YTO, 220 nm Fe, 5 nm AIO_x, and 9 nm Pt.

The sample was then He implanted using a 25 keV ion beam using a Zeiss ORION NanoFab microscope at UC Berkeley. A 10 pA beam was rastered over a 10 x 10 μ m area, with the sample tilted at 7° to prevent channeling, for a total dose of 4E15 He/cm². Stopping and Range of Ions in Matter (SRIM) simulations indicate a peak concentration of ~2000 ppm He at a depth of 120 nm into the Fe film, and a total implantation range of ~200 nm, roughly the same as the total Fe film thickness.

The bilayer was characterized using an FEI Quanta 400F field-emission scanning electron microscope (SEM) with an electron backscatter diffraction (EBSD) detector. The sample was placed into an FEI HELIOS Focus Ion Beam (FIB) tool and 5 μ m of protective platinum were deposited over areas of interest. Lift-outs <30 nm thick of the Fe-YTO interface were extracted, and a low energy 2 keV 5.5 pÅ gallium beam was used for the final cleaning. Transmission electron microscopy (TEM) observations were performed on a 300 keV FEI Titan.

Results

SEM and EBSD Characterization

Figure 1 shows EBSD data from the Fe film. Figure 1a is an EBSD band contrast (BC) image showing the Fe grain sizes and shapes. The sub-micron grains range in size from ~20 nm to ~200 nm. Figure 1b shows an EBSD inverse pole figure (IPF) map depicting the out-of-plane crystallographic orientation of the Fe grains. The range of colors indicates no clear preferred texturing normal to the film surface. Figure 1c shows the same data as Figure 1b but represented as Euler maps indicating the full orientation of the Fe grains. The large variation in coloring indicates no preferred in-plane orientation.

Figure 1d shows four pole figures (<100>, <110>, <111> and <112> reflections) of the data from the IPF map in Figure 1b, colored according to the out-of-plane grain orientation (IPFZ). The streaks in the pole figures (PFs) indicate axiotaxial texturing, and are further seen in the contour PFs in Figure 1e. This texturing is characterized by the alignment of planes in the Fe grain and in the YTO substrate that lie off-normal to the sample surface. Axiotaxial texturing results in an interface that is periodic in one dimension. The red spot in the <110>Fe PF in Figure 1e indicates a high concentration of aligned planes. PFs from the {110}YTO substrate are represented in Figure 1f. The off-centered green spot in

the <100>YTO PF overlaps with that seen for <110>Fe, but not at the same distance away from the center. Thus, the axiotaxial matching is close to <110>Fe\\<100>YTO. Last, Figure 1g shows 3D renderings of some selected Fe grains, and the {110}YTO substrate.



Figure 1. a) Band contrast, b) inverse pole figure map and c) Euler map of the Fe film. d) Fe pole figures colored according to the out-of-plane orientation, and e) contour mapping. f) YTO substrate pole figures. g) 3D renderings of some Fe grains (top two) and YTO substrate (bottom).

TEM Characterization

Transmission electron microscopy was used to characterize the He-implanted Fe film. Figure 2a is a schematic showing the Pt + AIO_x coating, four Fe grains, and {110}YTO substrate for the TEM micrographs in over-focus (Figure 2b) and under-focus (Figure 2c) conditions. He bubbles are seen as dark dots in the over-focus condition, and as white dots in the under-focus condition. Bubbles are found within the Fe grains and at all boundaries including AIO_x -Fe, Fe-Fe grain boundaries, and Fe-YTO interface. No bubbles were observed in the YTO substrate, however, this does not mean that He did not reach the YTO substrate (discussed later).



Figure 2. a) Schematic showing the Pt + AIO_x coating, four Fe grains, and YTO substrate for the b) over-focus and c) under-focus TEM images.

Figure 3 is a TEM image taken from the top half of an Fe grain. The red circles indicate the size and location of He bubbles. The bubble number density and volume fraction was calculated as a function of depth by first splitting the image into 10 nm tall and 90 nm wide sections, indicated by the white boxes in Figure 3. The top-most 10 nm box shows the He bubble distribution close to the AIO_x -Fe interface. It has a high number density of small He bubbles. However, not all grains had this bubble-rich area. This effect may be due to the axiotaxy, which causes the crystallographic Fe orientation to vary from grain to grain. The area between 10 nm and 20 nm has fewer but larger bubbles. Below the 20 nm depth, the average bubble size and number density generally increases. This is consistent with SRIM calculations that indicate a peak He concentration at ~120 nm.



Figure 3. TEM image from an Fe grain. Red circles show the sizes and locations of He bubbles. The Fe-YTO interface is not shown in this image.

The under-focus TEM image in Figure 4 shows part of the Fe-YTO interface. A total of 26 bubbles are seen in the ~125 nm wide figure. The bubbles range in size from 1.2 nm to 4 nm, with an average diameter of <d> = 1.8 nm. There does not appear to be a periodic spacing between the bubbles. However, interphase boundaries are difficult to image using conventional TEM due to spherical aberrations and defocus effects. It is possible that under-focusing the beam caused some He bubbles to

appear grouped as one large bubble (such as the horizontally elongated red bubble in the center of Figure 4). Furthermore, no bubbles were observed in the YTO substrate. It is possible that no He entered the YTO through the interface or the He diffused out of the YTO all together. Alternatively, the He in the YTO may be dissolved throughout the structure, or the He bubbles are too small to see in TEM. More quantitative measurements of the He depth profile are required. Secondary ion mass spectroscopy (SIMS) was used to measure the He concentration in the YTO, but the results were inconclusive and thus not reported here.



Figure 4. Under-focus TEM image from the Fe-YTO bilayer. Red circles show the sizes and locations of He bubbles at the Fe-YTO interface. No bubbles were observed in the YTO.

Three random Fe grains were chosen for bubble analysis. They have slightly different ORs. The nine graphs in Figure 5 show the average He bubble size <d>, number density <N>, and volume fraction <f> for three random areas in the Fe film. A depth of 0 nm indicates the top surface of the grain, while 200 nm indicates the bottom near the Fe-YTO interface. The bubble size graphs for the three areas are all plotted on the same scale to allow for direct comparison. The same is true for number density and volume fraction graphs.

Area 1 had the largest bubbles with an average size of $\langle d \rangle = 1.7$ nm, while Area 2 had $\langle d \rangle = 1.4$ nm bubbles, and Area 3 had $\langle d \rangle = 1.5$ nm bubbles. All three areas show a roughly flat bubble size profile, with smaller bubbles at the top of the Fe and at the Fe-YTO interface. The average bubble size in all three Fe areas are smaller than at the interface where $\langle d \rangle = 1.8$ nm.

The number density plots follow a u-shape trend. $\langle N \rangle$ is large at shallow depths into the Fe (except for Area 1), is minimum at ~ 50 nm, and steadily increases towards the Fe-YTO interface. Overall, Area 3 had the largest number density of bubbles compared to Areas 1 and 2. The third column of graphs indicates an increase in bubble volume fraction as a function of depth. For all three graphs, the average volume fraction is ~ 0.2% at the top of the grain, and the value increases with depth. In Area 1, <f> has a maximum value of 0.45% at 150 nm, then drops to 0.2% at 170 nm. Area 2 has a maximum <f> of 0.32% at 175 nm. Area 3 had the largest overall volume fraction of bubbles, with a maximum of 0.48% at 130 nm into the Fe. This depth is consistent with the expected He concentration profile calculated by SRIM. The He profiles are different between the three areas likely due to the Fe grains not having the same orientation with respect to the He implantation beam axis.

Summary and Future Studies

In summary, a YTO single crystal was cut, polished, and cleaned in preparation for deposition. 20 nm of Fe was deposited using MBE, followed by 200 nm of electron beam deposited Fe. The sample was then capped with 5 nm of AlO_x and coated with 9 nm of Pt. EBSD analysis showed sub-micron Fe grains with an axiotaxial orientation relationship with the underlying {110}YTO substrate. The bilayer was then implanted with 25 keV He with a dose of 4E15 He/cm². TEM images show a range of He bubble sizes, number densities, and volume fractions. The bubbles within the Fe grains ranged in size among the three areas studied, but the bubbles at the interface were overall larger with an average size of <d> = 1.8 nm. No bubbles were seen in the YTO substrate, however, this does not indicate that He was not present in the YTO. The bilayers are being prepared for future He implantation studies. The results will help inform first principle models of metallic oxide interfaces, as well as reaction-rate theory models for predicting NFA behavior.



Figure 5. Graphs showing the average He bubble size <d>, number density <N>, and volume fraction <f> for three analyzed areas (Area 1, 2, and 3).

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2.6 SEQUESTRATION OF CAVITIES AT NANOPARTICLE-MATRIX INTERFACES IN HELIUM PLUS HEAVY ION IRRADIATED NANOSTRUCTURED FERRITIC ALLOYS — C. M. Parish^{1*}, K. A. Unocic¹, L. Tan¹, S. J. Zinkle^{1,2}, S. Kondo³, L. L. Snead⁴, D. T. Hoelzer¹, and Y. Katoh¹ - ¹ Oak Ridge National Laboratory, ² University of Tennessee, Knoxville, ³Institute of Advanced Energy, Kyoto University, ⁴ Massachusetts Institute of Technology

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Four ferritic alloys: one cast-nanostructured alloy containing Ti-W-Ta carbides, one 9Cr alloy containing Y-Ti-O nanoclusters, and two Fe-12Cr-5Al alloys containing Y-Zr-O or Y-Hf-O clusters, were subjected to simultaneous dual-beam Fe+He ion implantation at 650°C to ~50 dpa at ~15 appm He/dpa ratio, to simulate fusion-reactor irradiation conditions. Post-irradiation examination using scanning/transmission electron microscopy revealed small, high-number-density helium bubbles of ~8 nm, ~10²¹ m⁻³ in the cast nanostructured alloys (CNA) and ~3 nm, 10^{23} m⁻³ in the three nanocluster-strengthened alloys. Advanced X-ray mapping methods combined with data mining of the X-ray maps using multivariate statistical analysis (MVSA) showed that the precipitates in all alloys serve as effective helium trapping sites while precipitates survived the ~50 dpa irradiation at 650°C. All four alloys appear to be viable candidates for future fusion energy systems, although the nanocluster-strengthened alloys appear to sequester the helium into smaller bubbles and away from the grain boundaries more effectively than the cast nanostructured alloys.

3. CERAMIC COMPOSITE STRUCTURAL MATERIAL DEVELOPMENT

3.1 LOW ACTIVATION JOINING OF SIC/SIC COMPOSITES FOR FUSION APPLICATIONS: MODELING DUAL-PHASE MICROSTRUCTURES AND DISSIMILAR MATERIAL JOINTS — C. H. Henager, Jr., B. N. Nguyen, and R. J. Kurtz; (Pacific Northwest National Laboratory, Richland, WA, USA); M. Ferraris, (Politecnico di Torino, Torino, Italy); Y. Katoh, (Oak Ridge National Laboratory, Oak Ridge, TN, USA)

OBJECTIVE

Finite element continuum damage models (FE-CDM) have been developed to simulate and model dualphase joints and cracked joints for improved analysis of SiC materials in nuclear environments. This report extends the analysis from the last reporting cycle by including results from dual-phase models and from cracked joint models.

SUMMARY

The international fusion materials community designed miniature torsion specimens for joint testing and irradiation in test reactors with limited irradiation volumes since SiC and SiC-composites used in fission or fusion environments require joining methods for assembling systems. HFIR irradiation results indicated two broad types of joint damage due to irradiation at either 500°C or 800°C to 3 dpa or 5 dpa. One type of damage can be categorized as microcracking within multi-phase joints at the micron length scale. The other type of damage can be categorized as cracking within the miniature torsion sample and within the joint where the cracks are now on the scale of the joint thickness and are not considered to be microcracks. This report discusses methods to model both types of cracking due to differential properties within the joint due to multiple phases or due to the fact that the joint itself is dissimilar from the joined CVD-SiC material. This analysis requires two different models to account for these effects.

PROGRESS AND STATUS

Introduction

The international fusion materials community has irradiated and is currently irradiating several SiC joint types and compositions in the HFIR reactor at ORNL [1]. PNNL is working with Politecnico di Torino (POLITO) and ORNL using miniature torsion specimens that have been specifically designed for pre- and post-irradiation joint shear strength testing [2]. To elucidate how cracks initiate and propagate in the torsion joint specimens, finite element analyses of these specimens subjected to torsion were performed using a continuum damage mechanics (CDM) model previously developed at PNNL for elastic materials for which any nonlinearity in stress/strain response is due solely to damage and not to other irreversible processes such as plasticity [3-5]. The CDM model was implemented in the ABAQUS[®] finite element code via user defined subroutines. This CDM model [3] was now applied at the submicron scale by creating a dual-phase FE mesh within the joint region. The constitutive behavior of each phase in the modeling domain was described by the CDM model to explore the effects of differential material responses within the joint to external forces, such as thermal expansion, swelling, and applied loads. In addition, the previous model was also exercised but now including pre-cracked joints to simulate observed HFIR cracking patterns [1]. Although the joints survived the HFIR irradiation with reasonable properties, there was degradation observed in SEM images taken post-irradiation at ORNL. This report discusses methods to understand the sources for the observed cracking and subsequent joint degradation so that improved joints can be fabricated for fusion applications.

Model Formulation

<u>Approach</u>

This section summarizes the damage model and method for modeling the joints [3-7] in the joined CVD-SiC that has been previously reported. Damage in an elastic and damageable material, for which any nonlinearity in stress/strain response is due solely to damage and not to other irreversible processes, can be described by a scalar variable, D, that can be related to the level of damage accumulation in the material [6]. Damage affects the material stiffness according to a stiffness reduction law. Using the concepts of thermodynamics of continuous media [6, 8], a thermodynamic potential is defined to derive the constitutive relations and the thermodynamic force associated with the damage variable. This damage model uses the density of the elastic deformation energy as the thermodynamic potential that provides a coupling between damage and elasticity. A damage criterion dependent on a damage threshold function is defined and the damage evolution law is obtained. Damage evolves with the deformation according to the damage evolution law until a critical (saturation) state at which $D=D_{\rm cr}$ ($0 < D_{\rm cr} < 1$) and failure occurs.

 $D_{\rm cr}$ is small for brittle materials, and this is the case for ceramic materials studied in this work. In this

work, failure at damage saturation $(D=D_{cr})$ leading to crack initiation and propagation is modeled by a

vanishing finite element technique [9] that reduces the stiffness and stresses of the failed element to zero [3, 10]. We choose to implement the damage model for brittle ceramics in shear loading. The thermodynamic and CDM approach adopted is phenomenological and it does not describe the detailed frictional sliding of crack ligaments but the magnitude and effect of shear damage on the material response are *phenomenologically* captured by the damage variable, *D*, driven by the associated thermodynamic force, *F*(*D*), and the damage evolution law.

As discussed in Ref. [1] miniature torsion joints were irradiated in HFIR at ORNL and examined postirradiation using SEM and then tested in torsion. Archival joints were imaged and tested pre-irradiation for comparison. Joint images showed two types of damage that is assumed to have originated from the neutron irradiation in HFIR for several of the joints (but not all). One type of damage can be categorized as microcracking within multi-phase joints at the micron and sub-micron length scale. The other type of damage can be categorized as cracking within the miniature torsion sample and within the joint where the cracks are now on the scale of the joint thickness and are not considered to be microcracks. This FE-CDM requires two different models at two different length scales to account for these observed effects.

First, a pattern of cracks at the joint/specimen scale are created within the joined sample so that the joint region consists of a homogenized layer containing incipient damage in the form of either planar cracks, which are cracks parallel to the joint plane, or transverse cracks perpendicular to the joint plane. These two types of cracks are shown in Figure 1. The homogenization method uses the previously described Eshelby-Mori-Tanaka approach (EMTA) [11] to model cracks as elongated inclusions with zero stiffness and provide a tensor description of defect orientations for the homogenized material. We anticipate that these two types of crack patterns will behave differently due to this directionality with regard to the applied torsion strains. A crack volume fraction of 25% is assumed as an estimate.



Figure 1. SEM images from Ref. [1] showing planar cracking in (a) between the joint and the CVD-SiC and transverse cracking in (b) within the glass-ceramic joint region. Both joints were irradiated at 800°C to 5 dpa in HFIR and examined at ORNL post-irradiation prior to torsion testing.

Second, the origin of the intra-joint microcracking was investigated by creating a finite element mesh of the joint microstructure using the $OOF2^1$ public domain software. A digital image that was 14.1 µm on a side (910 x 910 pixels) was input and OOF2 was used to create a two-phase FE mesh consisting of 230k

¹ Software developed at the National Institute of Standards and Technology

FE nodes, both triangular and quadrilateral elements. This allowed a high resolution meshing of the microstructure at the phase boundaries and provided the ability for ABAQUS to assign individual constitutive laws to each phase. The meshed microstructure and image are shown in Figure 2.



Figure 2. The FE mesh is shown in (a) superimposed on the image of the microstructure. Inset in (a) shows the high-resolution mesh at the interfaces between the SiC (black) and the ternary MAX Ti_3SiC_2 (white) phase. Shown in (b) is the image with the two phases identified within the joint.

Results

Model Results

The damage models are implemented in ABAQUS[®] as a FE analysis of the miniature torsion specimen containing 1) a homogenized layer with incipient cracks in two orientations and 2) a region within the joint containing regions of SiC and regions of Ti_3SiC_2 meshed from a digital image. The assumed mechanical properties of the CVD-SiC for both models are shown in Figure 3.



Figure 3. Assumed constitutive laws for CVD-SiC and Ti_3SiC_2 for this report. Failure occurs for SiC at a strain of 0.001 and 0.002 for Ti_3SiC_2 .

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Material	Elastic Modulus (GPa)	Poisson Ratio	Strength (MPa)	Failure Strain	Damage Variable Critical Value
SiC	460	0.2	368	0.001	0.2
Ti₃SiC₂	300	0.2	480	0.002	0.2

Table 1. Material properties for CVD-SiC and Ti₃SiC₂ phases

The FE-CDM was exercised for both the planar and transverse cracked joint and the damage fracture pattern is shown in Figure 4 for both cases. The CDM model predicts that the planar cracks are more deleterious to the joint degradation compared to the transverse and nearly vertical cracks, which is a consequence of the crack orientation with respect to the applied torque. Also, in comparison to assumed porous joints that were previously modeled the planar cracks are quite efficient in reducing the joint failure strength. Joints that prior to irradiation would be predicted to fail within the CVD-SiC are now predicted to fail in the joint plane [1, 4, 5].



Figure 4. Predicted fracture patterns (red regions) using an elastic damage model for the torsion joint specimens containing 25% volume fraction of planar cracks in (a) and (b) and 25% volume fraction of transverse cracks in (c) and (d). In each case an initial damage and final damage pattern are shown.

Figure 5 shows results from the micromechanical two-phase model under bi-axial loading. For this case, the left/bottom boundaries are fixed and the right/top boundaries are displaced with either $u_x/u_y = 3$ or 1/3 displacement ratio. The displacements u_x and u_y are expressed in the xyz coordinate system shown in Figure 5. Bi-axial tension can be considered as a substitute for volumetric swelling in the absence of a swelling model for Ti₃SiC₂. The hypothesis being explored here is that a dual-phase microstructure has some liabilities when it comes to incompatibility strains within the joint. This behavior can account for the observation of microcracking within the joint after HFIR irradiation exposure [1]. The model clearly shows that differential strain within the joint can account for cracking at the microscale in the joint, which qualitatively agrees with observations for this joint following HFIR irradiation.



Figure 5. Damage accumulation within the joint using the mesh shown in Figure 2 and the constitutive properties in Table 1 and Figure 3. Shown in (a) is the case for $u_x/u_y=3$ and in (b) the ratio is 1/3. The red regions of damage saturation are considered to be crack nuclei or microcracked regions. Note that this cracking occurs adjacent to the SiC phase within the joint and also at the joint interface with the CVD-SiC. This result supports the thesis that a dual-phase joint might develop a system of microcracks due to differential strain response to either thermomechanical loads or volumetric swelling.

Discussion

Model Predictions and Comparisons

The FE-CDM model appears to be able to account for two key observations from the HFIR joint irradiation study reported in Ref. [1]. One observation was the change in torsion sample failure mode from CVD-SiC body failure to in-plane joint failure. As shown in Figure 1, planar cracks were observed in the irradiated joint between the dual-phase joint and the CVD-SiC specimen body. This was thought to be the cause for the observed transition from out-of-plane to in-plane torsion test failure mode. Results from the FE-CDM model including an assumed 25% planar crack distribution in the joint and homogenized using EMTA support this hypothesis. As shown in Figure 4a and Figure 4b, planar cracks act to concentrate crack damage in the plane of the joined specimen, which shifts the failure location from the CVD-SiC base material to within the joint material, or out-of-plane to in-plane fracture². Further, as shown in Ref. [1], the presence of transverse cracks does not quite have the same effect since that joint retained some portion of failure in the CVD-SiC material.

Microcracking within the dual-phase PNNL joint was also observed following HFIR irradiation at 800°C to 5 dpa. Figure 6 shows an image from Ref. 1 that reveals microcracking within the dual-phase joint material and that the cracking appears to coincide with the dark features in the joint, which are the SiC phase regions. The FE-CDM model constructed here, even though it does not contain all the detailed

² In Ref. [1] this is referred to as base material (B) or joint plane (J) fracture.

deformation modes experienced by joints irradiated in HFIR, such as thermomechanical and swelling loads, demonstrates that deformation of the joint regions might cause microcracking in the joint and that the origin of the microcracking is probably associated with the SiC/Ti₃SiC₂ incompatibility strains at the phase interfaces. This is shown clearly in Figure 5 where the damage accumulation in the form of crack nuclei is predicted to occur at the interfaces between the SiC and Ti₃SiC₂ phases within the joint at micron or submicron length scales. This illustrates a potentially key weakness of multi-phase joints where the mechanical properties of constituent phases are significantly different.



Figure 6. SEM images taken from Ref. [1] showing the pre-irradiated and post-irradiated joint microstructures. The larger planar cracks are shown in C and the micron-scale microcracks are shown in D. The model discussed here captures both types of cracking using the FE-CDM approach on a dual-phase FE mesh (See Figure 2 and Figure 5).

Conclusion

A modification of the PNNL FE-CDM model [4, 5, 11] implemented in the ABAQUS FE package has been shown to provide qualitative agreement with experimental observations following SiC joint irradiations in HFIR. Both in-plane and transverse cracks are simulated and the overall response of the torsion sample with this type of incipient damage agrees well with torsion test data obtained at ORNL following HFIR irradiation. In addition, SEM observations of irradiated joints indicated microcracks were nucleating within the dual-phase joint region at SiC/Ti₃SiC₂ interface boundaries and the PNNL FE-CDM model captures this type of damage when a microstructural scale FE-CDM model containing two phases is strained in biaxial loading.

Future Work

The developed FE-CDM model will be modified to account for thermophysical and swelling loads consistent with the HFIR irradiation conditions.

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3.2 APT AND TEM CHARACTERIZATION OF PRECIPITATES IN Mg⁺ ION IMPLANTED CUBIC SILICON CARBIDE — W. Jiang, J. Liu, D. K. Schreiber, D. J. Edwards, C. H. Henager, Jr., R. J. Kurtz (Pacific Northwest National Laboratory), and Y. Wang (Los Alamos National Laboratory)

OBJECTIVE

This study aims to characterize precipitates and defect structures in Mg⁺ ion implanted and high-temperature annealed cubic silicon carbide (3C-SiC).

SUMMARY

This research update reports on the results from our preliminary atom probe tomography (APT) data reconstruction and analysis as well as from our recent transmission electron microscopy (TEM) examinations on Mg⁺ ion implanted cubic silicon carbide (3C-SiC). APT studies have been performed for 3C-SiC implanted with ²⁵Mg⁺ ions to 9.6×10^{16} ions/cm² at 673 K and subsequently annealed at 1073 and 1573 K for 2, 6, and 12 h. TEM examinations have been focused on a lower-dose (5.0×10^{15} ions/cm²) 3C-SiC implanted with ²⁴Mg⁺ ions, followed by annealing at 1573 K for 12 h. The TEM study suggests that some of the nanometer-scale Mg precipitates are associated with Frank loops in the implanted and annealed 3C-SiC, while the APT results show that most of Mg-bearing particles contain both Si and C. Further efforts on APT reconstruction and TEM examination are still in progress.

PROGRESS AND STATUS

Introduction

Elemental transmutation of silicon in silicon carbide due to high-energy neutron irradiation leads to production of magnesium, a major non-gaseous transmutant as predicted by Sawan, *et al.* [1]. The presence of the transmutants and irradiation-induced defects in 3C-SiC are expected to affect its thermomechanical properties, which needs to be investigated prior to application of the material in fusion reactors. As an on-going study, we continue to investigate the formation and behavior of Mg-bearing precipitates in 3C-SiC using ion implantation and thermal annealing methods. Our previous study [2] suggests that precipitates of cubic Mg₂Si and tetragonal MgC₂ are likely formed in 3C-SiC implanted to $9.6 \times 10^{16} \, {}^{25}$ Mg⁺/cm² at 673 K and subsequently annealed at 1573 K for 12 h. These precipitates were not observed directly, but derived from fast Fourier transformation (FFT) of an atomic-level resolution high-angle annular dark field (HAADF) scanning TEM (STEM) micrograph [2]. The APT method is currently being used to examine the possible precipitates. To facilitate APT analysis for differentiating Mg from ${}^{12}C_2$ clusters using time-of-flight mass spectrometry, isotope 25 Mg⁺ ion implantation has been performed. In addition, low ion fluence was also implanted for STEM studies of both initial Mg states in the nucleation process and possible formation of low-concentration voids that could be individually resolved.

Experimental Procedure

3C-SiC samples were implanted 7° off the surface normal with 200 keV 25 Mg⁺ ions at 673 K to a high ion fluence of 9.6×10¹⁶ ions/cm². This fluence corresponds to ~6 at.% 25 Mg and 54 dpa at their respective peak maxima (depths of 280 and 220 nm) based on SRIM simulations [3]. The isotope 25 Mg was obtained from the National Isotope Development Center (NIDC) at Oak Ridge and the implantation was performed at Los Alamos National Laboratory (LANL). An additional 24 Mg⁺ ion implantation was also performed at LANL to a lower fluence of 5×10^{15} ions/cm² at the same ion energy and sample temperature. The implanted samples were cleaved into smaller pieces for thermal annealing under different conditions. Each set of the low and higher dose samples was annealed at 1573 K for 2, 6 and 12 h in flowing Ar gas, respectively. Additional annealing of the 25 Mg⁺ ion implanted samples were placed inside a chimney made of a Ta metallic foil to reduce the oxygen partial pressure.

Both TEM and APT samples were prepared using a focused ion beam (FIB) microscope at the Pacific Northwest National Laboratory. Once finished, the APT samples were quickly put into the ultrahigh vacuum chamber of the APT to avoid contamination. APT examinations were carried out at a sample temperature of 44 K and a bias voltage ranging from 5.5 to 8.5 kV with a laser power of 60 - 80 pJ/pulse at a frequency of 125 kHz. The detection efficiency was 36% with an average detection rate of 0.4%, i.e., 4 detected evaporation events in 1000 pulses. Three to four APT needles were prepared from each of the unimplanted, as-implanted, and implanted and annealed samples. The total ions collected for each needle range from 3 to 5 M ions. Some of the needles fractured during APT measurements. The measured C and Si concentrations are not calibrated. For unimplanted high-purity 3C-SiC single crystals, Si to C ratio is shown as being about 60:40 and this ratio can change slightly for different measurements due to selective loss of C at the detector. TEM was performed using a Cs-corrected JEOL ARM 200 CF TEM/STEM microscope. Equipped with a cold field emitter, the microscope is capable of sub-Å spatial resolution under HAADF STEM imaging. The high-brightness source coupled with a ~0.3 eV energy resolution allows for a fast acquisition of electron energy loss spectroscopy (EELS) and energy dispersive x-ray spectroscopy (EDS) analyses. EELS and EDS utilize the latest Gatan Quantum 965 spectrometer with Dual EELS and a proprietary JEOL Centurio Si-drift EDS detector with 0.98 Sr collection angle from a detection area of 100 mm², respectively. EDS measurements in selected areas and elemental mapping with automatic sample drift corrections were performed at both 200 kV and 80 kV, the latter of which was used to minimize sample damage.

Results

Figure1(a) shows a bright-field TEM image from the peak damage region in 3C-SiC implanted to 5.0×10¹⁵ ²⁴Mg⁺/cm² and subsequently annealed at 1573 K for 12 h. A high-concentration of small Frank loops is



Figure 1. (a) Bright-field TEM image, (b) EDS map for implanted Mg, and (c) and (d) EDS spectra from Mg-deficient and Mg-rich areas, respectively, in the Mg profile peak region of 3C-SiC implanted to 5.0×10^{15} ²⁴Mg⁺/cm² and annealed at 1573 K for 12 h.

observed. Over the same area, EDS mapping for Mg was performed and the result is shown in Figure 1(b). Although the concentration of the implanted Mg at the peak is small (~0.1 at./cm³ Mg), Mg clustering to a size on the order of a few nanometers is evident in the sample. The brighter area represents a higher local Mg concentration. Figures 1(c) and 1(d) show EDS spectra at spots #1 and #2 from Mg-rich and Mg-deficient regions, respectively. A close inspection reveals that some of the Mg clusters exhibit a location correspondence with the Frank loops. An example is shown at spot #2 in Figures 1(a) and 1(b). A more detailed study of the location relationship between Mg clusters and dislocation loops is currently being pursued using the APT method. Further atomic-level resolution TEM examinations are planned to study the initial states of Mg nucleation in 3C-SiC and the possible formation of voids in 1573 K annealed samples.



Figure 2. SEM image of the final APT needle, prepared using FIB from 3C-SiC implanted to 9.6×10^{16} 25 Mg⁺/cm² and annealed at 1573 K for 12 h.

The APT measurements have been performed for various 3C-

SiC samples, including as-received (unimplanted), as-implanted $(9.6 \times 10^{16} {}^{25}Mg^+/cm^2 at 673 K)$, and postimplantation annealed at 1073 K for 12 h and at 1573 K for 2, 6 and 12 h. A systematic APT data reconstruction analysis is currently being conducted for those measurements and the results are intended for a journal publication. Here, we report the preliminary results for the annealed sample at 1573 K for 12 h only. Figure 2 shows the final shape of the sample prepared using a FIB. The apex of the needle is located at a depth of ~200 nm and the APT analytical range is ~200 nm in depth starting from the apex, which covers both the damage peak and Mg profile peak regions.



Figures 3. (a) -3(f) show a sequence of iso-concentration surfaces of Mg at concentrations of 5-50 at.% Mg. The two-dimensional plots are obtained from a 10 nm slice of material in the Mg peak region. With increasing Mg iso-concentration threshold, Mg clusters become smaller, shrinking towards the cluster cores.

At 15 at. % Mg, the clusters are well resolved with a size up to 10 nm or larger. The Mg clusters completely disappear at the iso-concentration value of ~53 at.% Mg in this particular region of implantation. Figure 3(g) shows iso-concentration surfaces of Si at 45 at.% Si, overlapped with 100% of the detected Mg atoms also shown as green dots. The volumes encompassed by the surfaces represent the regions where there is a local Si depletion. As the Si concentration increases, the volume shrinks and diminishes to zero at 38 at.% Si (data not shown). The results suggest formation of a compound containing Mg and Si. From Figure 3(g), there are also regions where Si depletion [or enrichment (data not shown)] is not accompanied by noticeable Mg concentrations. These regions are probably formed due to irradiation-induced structural defects in 3C-SiC. Similarly, some of the C depleted regions shown in Figure 3(h) are also superimposed with Mg clusters, while other locations are not. By comparing Figures 3(g) and 3(h), it is evident that Mg-bearing particles are formed with Si, C or both. Further analysis of Mg to Si and Mg to C concentration ratios (data not shown) suggests that a great majority of the Mg-bearing particles contain both Si and C. Further APT analysis is being performed to visualize three-dimensional dislocation loops, which will be overlapped with Mg cluster maps, similar to a previous report on H⁺ ion irradiated stainless steel [4].



Figure 4. Proximity histograms from (a) 11.8 at.% Mg and (b) 28.2 at.% Mg iso-concentration surfaces of the same particle. (c) Corresponding atom map and iso-concentration surfaces. Error bars represent the standard deviation from counting error.

A representative analysis of a single relatively large Mg cluster is presented in Figure 4. Two different isoconcentration values (11.8 at.% Mg and 28.2 at.% Mg) were used to define the particle and generate proximity histograms. For the lower concentration, the apparent enrichment peaks at ~50 at.% Mg, whereas the higher concentration threshold reveals enrichment in excess of 80 at.% Mg. This suggests that this particle is approaching pure Mg, which is consistent with a previous TEM/EDS observation that appears to indicate that Mg aggregates within the volume of possible voids in 3C-SiC. Further TEM/EDS efforts are needed to verify this result. It should be noted that this particle does not exhibit a strong deviation from the nominal Si to C ratio, which implies that the particle is not approaching either a silicideor carbide-like composition. Estimation of Guinier's radii of Mg clusters has been attempted, which represent the feature size of precipitates in many metal compositions [4-6]. Figure 5 shows the result, indicating that the radius peaks at 0.3 - 0.4 nm with very few clusters larger than 2 nm. This radius distribution is not fully consistent with the TEM observation shown in Figure 1 and may not be representative of the physical cluster size distribution in the Mg⁺ implanted SiC. Conventional cluster analysis [7] of the APT data was unable to determine a clear plateau to establish a d_{max} parameter in the cluster count distribution even using a very large order number (~50). This observation, in concert with the inconsistency with the TEM data, suggests that the conventional cluster size



Figure 5. Guinier's radii of Mg clusters in 3C-SiC implanted to 9.6×10^{16} ²⁵Mg⁺/cm² and annealed at 1573 K for 12 h.

distribution analysis by APT has limitations and does not apply well in this study, probably as a result of the large field evaporation difference between Mg (~21 V/nm) and SiC (>33 V/nm).

An alternative approach for analysis of the cluster distribution has been performed based on the change in the peak height (maximum cluster counts) in the nearest neighbor distribution as order number increases. The optimal order number is chosen at the minimum decrease in the peak height, from which d_{max} is determined. Figure 6(a) shows the cluster fraction profile as a function of the numbers of Mg atoms. The data are binned at a step of 100 atoms. The result shows that clusters containing 200 – 300 Mg atoms are most probable. Some of the clusters can contain 2000 Mg atoms or more. Similarly, for all atoms, including Si, C and Mg, the profile in Figure 6(b) shows similar features with 400 – 500 atoms at the peak. It should be noted that the analysis is parameter-optimized for larger clusters. Smaller clusters may be neglected and not be well reflected in the distributions shown in Figures 6(a) and 6(b). Figure 6(c) shows the composition distribution of the identified clusters. The most abundant clusters in the sample based on the analysis have a composition of ~50% Si, ~37.5% C and ~12.5% Mg.



Figure 6. Distribution of the numbers of (a) Mg and (b) Si, C and Mg atoms in the identified clusters and (c) distribution of the cluster composition in 3C-SiC implanted to 9.6×10^{16} 25 Mg⁺/cm² and annealed at 1573 K for 12 h.

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3.3 ADVANCED CHARACTERIZATION OF IRRADIATION DEFECTS IN SILICON CARBIDE: POSITRON ANNIHILATION SPECTROSCOPY — X. Hu, T. Koyanagi, Y. Katoh (Oak Ridge National Laboratory)

OBJECTIVE

This report describes the advanced characterization of irradiation defects in SiC using positron annihilation spectroscopy for better understanding of the microstructure and material properties in fusion environments.

SUMMARY

Positron annihilation spectroscopy (PAS), i.e., positron annihilation lifetime spectroscopy and coincidence Doppler broadening, was used to characterize the small vacancy clusters in 3C-SiC subject to various neutron irradiation conditions by capturing the dependence of irradiation temperature (380~800°C) and dose (0.01~30dpa). The vacancy cluster distribution obtained from PAS investigation is critically important to complement the current understanding of the microstructural evolution in SiC under the abovementioned neutron irradiation conditions, due to the cluster invisibility in TEM characterization. Subsequently, the vacancy clusters are then linked to the measured swelling behavior to provide insight into the correlation between microstructure and physical properties of SiC.

PROGRESS AND STATUS

Introduction

Silicon carbide (SiC) based-materials are attractive candidates for structural components in fusion reactor due to their superior irradiation tolerance. Swelling and irradiation creep are key properties in assessing the performance of SiC in nuclear service. Correlation between these properties and microstructural evolution has been studied for various irradiation conditions using conventional transmission microscopy (TEM) [1]. However, the irradiation response at the atomic scale is still poorly understood; TEM-visible defects can account for only a small fraction of swelling and irradiation creep [2]. In addition, understanding the elemental composition (chemistry) of the defect clusters is very limited, even for TEM-visible defects.

In this task, we will capture the TEM-invisible (conventionally) defects and characterize elemental composition of the defects in neutron-irradiated SiC using positron annihilation spectroscopy (PAS). PAS is powerful tool to detect atomic-scale vacancy-type defects. Additional experiments using Raman spectroscopy and synchrotron X-ray diffraction are also planned. This study will provide both new approaches to characterizing irradiation defects at the atomic scale, and a more detailed understanding of irradiation response of SiC. This will help guide the building of mechanistic models of the material properties and give a better understanding of a pathway toward to improving the irradiation resistance of SiC materials.

This report describes the system development of positron annihilation spectroscopy in ORNL along with the preliminary results of PAS investigation on neutron irradiated SiC.

Development of positron annihilation spectroscopy system

A PAS system was established within the Low-Activation Materials Development and Analysis (LAMDA) Lab at ORNL for this work, dedicated to investigating radiological materials. The system consists of two sub-techniques: positron annihilation lifetime spectroscopy (PALS) and coincidence Doppler broadening (CDB). A schematic diagram of this system is shown in Figure 1.



Figure 1. Schematic diagram of the PAS system: (a). Positron annihilation lifetime spectroscopy. (b). Coincidence Doppler broadening. The inset in (a) indicates the sample/source packing structure.

Measurement of positron lifetimes of the samples of interest was performed using the system shown in Figure 1 (a), at room temperature, using a conventional sample-source-sample sandwich geometry (The sample packing structure is also shown in Figure 1 (a)). The positron source was made from a ²²NaCl solution directly evaporated onto the surface of the samples with an intensity of 740 kBq. The stack of two identical samples was wrapped by thin aluminum foils to form a sample assembly. The 1.274 MeV gamma ray, indicating a positron emission event, and the two 0.511 MeV annihilation gamma rays were detected using fast scintillators (BaF₂) coupled with photomultiplier tubes (PMTs). Unlike in a traditional experimental setup, a double-stop setup was employed in this work. Pairs of 0.511 MeV gamma rays were detected by two PMTs (PMT 2 and PMT 3) placed face-to-face on the opposite sides of the source-sample assembly. The positron lifetime is defined as the average value of the time intervals between the birth gamma ray and the two annihilation gamma rays for a coincidence event (10 ns). Data were obtained using a LeCroy[®] digital oscilloscope with a calculated system timing resolution of 140 ps. Each recorded lifetime spectrum contained a total of ~1×10⁶ counts and was analyzed by three components, i.e., as a sum of exponentials after deconvolution of the experimental resolution function—usually approximated as a Gaussian function.

Positrons eventually are annihilated by electrons, producing predominantly two gamma rays traveling in approximately opposite directions, as is necessitated by energy-momentum conservation during annihilation. Since there is a net center of mass energy associated with the annihilating positron-electron pair, the total energy does not split equally for the two gamma rays. One gamma ray is upshifted and the other is downshifted. The energy shift of each photon is given by

$$\Delta E = \frac{1}{2} p_L c = \frac{1}{2} \theta_L m_0 c^2 \quad , \tag{1}$$

where ΔE is the photon energy difference from the nominal value, p_L is the corresponding longitudinal momentum shift along the direction of gamma ray emission, in atomic unit (1 a.u.=7.28 mrad× m_0c), θ_L is the angular deviation of the photons from 180°. Since p_L has element-specific spectral distributions that correspond to the momentum distributions of the annihilation electrons, analysis of the orbital electron momentum spectrum (OEMS) provides information on the local chemical environment where the positron annihilates. The OEMS is typically represented as the fraction of annihilations at each momentum interval as a function of p_L , normalized by a standard spectrum. It is more convenient to represent OEMS data in so called S-W plots. The S is a fraction of the low-momentum annihilation defined by the specified p_L region, which in this study is $p_L \le 0.382 a.u$. The W is the corresponding high-momentum annihilation fraction, defined as $1.0 a.u. \le p_L \le 4.0 a.u$. A particular microstructure produces a point on an S-W plot. S-W correlation plots are useful in detecting the change in the nature of the positron trapping defects, since the slope of the plot is a fingerprint of a specific vacancy [3]. The CDB setup is shown in Figure 1 (b). Both annihilation gamma rays are detected in coincidence by using two HPGe detectors facing the source-sample sandwich from opposite sides. The CDB measurement was performed simultaneously with PALS by using the same sample-source assembly. The coincidence events falling within a selected window $2m_0c^2 - 2.0 \ keV < (E_1 + E_2) < 2m_0c^2 + 2.0 \ keV$ were collected for data analysis to obtain a low-background Doppler broadening annihilation spectrum with a peak-to-background ratio of better than 10,000:1.

Evaluation of irradiated SiC materials

High-purity 3C-SiC monoliths were used in this study. Neutron irradiation was performed in the High Flux Isotope Reactor at ORNL. The specimens were irradiated at 380 ~ 800°C to 0.01 ~ 30 dpa. Assuming that 1 dpa in SiC is equivalent to 1×10^{25} n/m² (E > 0.1 MeV), the damage rate for neutron irradiation is ~5×10⁻⁷ dpa/s. The neutron irradiation conditions of the studied specimens are listed in Table 1.

Capsule ID	Irradiation temperature [°C]	Fluence [dpa]	
Reference	Unirradiated	Unirardiated	
T8A1	380	0.01	
T8A2	380	0.11	
TTN01	380	1.5	
TTN03	440	31	
T8B1	540	0.01	
T8B2	540	0.1	
TTN05	500	29	
T8D1	790	0.1	
T8E1	760	1.4	
TTN07	750	29	

Table 1. S	Specimen	matrix for	PAS ex	xperiment
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Results

Positively charged vacancies create a long-range repulsive Coulomb potential, hence have small trapping probability and should not be detected by PAS. Therefore, carbon vacancy in SiC will not be captured in this study. Neutral and negative vacancies (i.e., complexes of Si-C and silicon vacancy), on contrary, can be detected and distinguished. To illustrate directly the influence of neutron irradiation on the measured positron lifetime data, Figure 2 plots the normalized spectra obtained for neutron irradiated SiC. Figures 2 (a), (b), and (c) demonstrate the irradiation dose dependence on the measured positron lifetime spectra at three different irradiation temperatures. The long-lifetime parts of the spectra became more intense with increasing radiation damage level, when comparing T8A1, T8A2, TTN01, and TTN03 (irradiated at 380~440°C). Same conclusions can also be drawn for the specimens irradiated at 500~540°C and 760~800°C. It is noted that the spectra was difficulty to distinct when irradiation dose is less than 1.5 dpa and 30 dpa irradiation leads to more significant long-lifetime tail shift. Figures 2 (d) and (e) show the irradiation temperature dependence on the measured positron lifetime spectra at ~ 0.1 and ~ 30 dpa, respectively. As to the low dose irradiation, the lifetime spectra overlapped, implying the insignificant damage evolution, even at 760~800°C, which is considered as the initial point for vacancy mobility. However, when the damage level reaches 30 dpa, the high temperature irradiation does enhance the long-lifetime parts by driving the formation of larger vacancy clusters, as shown in Figure 2 (e).



Figure 2. Normalized positron lifetime spectra of SiC exposed to various neutron irradiation conditions. (a), (b), and (c) are spectra comparisons at three different irradiation temperatures, indicating the irradiation dose dependence; (d) and (e) are spectra comparisons at two different irradiation doses, indicating the irradiation temperature dependence.

The measured positron lifetime spectra for neutron irradiated SiC were resolved into two lifetime components (one type of vacancy defect was considered). The results are plot in Figure 3. The short lifetime (fixed at 140 ps) indicates the positrons trapped in the SiC matrix. The long lifetime refers to the positrons annihilated in the vacancy defects. For the as-received SiC, the long lifetime of 230 ps indicates the presence of single Si-vacancy. For SiC samples irradiated at 380~440°C, the long lifetime (i.e., the size of the vacancy cluster) increases up to the radiation damage level of 0.11 dpa and then saturates in the damage range from 0.11 to 30 dpa, which implies that the size of the average vacancy cluster keeps constant. The lifetime of 275 ps indicates the presence of $(V_{Si})_3$ or $V_{Si}+V_C+V_{Si}$. On the other hand, the intensity of this long lifetime increases as the dose increases from 0.11 to 30 dpa, implying the increasing number density. The mean lifetime also shows a clearly increasing trend with increasing damage level. For SiC samples irradiated at 500~540°C, the long lifetimes for the two cases of 0.01 and 0.1 dpa are 263 and 265 ps, equivalent to the existence of (V_C+ V_{Si})₂, respectively. This value becomes 287 ps at 30 dpa, implying the existence of (V_{Si})₄ or (V_{Si})₅. Similar to the low temperature irradiation, the mean lifetime increases with increasing irradiation dose and is very close to that of low temperature irradiation. For high temperature irradiation, the long lifetime is greater than 300 ps at 1.4 dpa and 30 dpa, attributed to the existence of ring hexavacancy complex, (V_C+V_{Si})₃-ring, or larger silicon vacancy clusters. The mean lifetime is larger than the other two cases, indicating a more damaged microstructure. The corresponding intensities have a general increasing trend with increasing irradiation dose for all three irradiation temperatures.



Figure 3. Positron lifetimes and the corresponding intensities as a function of radiation damage level for SiC irradiated at three different temperatures.



Figure 4. S-W plot for neutron irradiated SiC at various irradiation conditions. The dashed red line is drawn to guide the eye.

Figure 4 plots the S-W pairs obtained for various neutron irradiated SiC, demonstrating that there is no significant change in the defect nature in terms of defect distributions and types. S-W pairs for T8A2, TTN01, TTN03, T8B2, and TTN05 are quite close to each other, indicating the very similar vacancy clusters contained in these five samples, which is consistent with the positron lifetime analysis.

Future Work

More work is needed to analyze the vacancy cluster obtained from the PAS measurements in more details. The quantification of the vacancy clusters identified by PAS will be performed by applying the classic trapping model. The information of small vacancy clusters will then be linked to the measured swelling behavior of SiC subject to neutron irradiation, therefore, providing insight into the correlation between microstructure and the physical property of SiC.

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4. HIGH HEAT FLUX MATERIALS AND COMPONENT TESTING

4.1 PRELIMINARY PROGRESS IN THE DEVELOPMENT OF DUCTILE-PHASE TOUGHENED TUNGSTEN FOR PLASMA-FACING MATERIALS: DUAL-PHASE FINITE ELEMENT DAMAGE MODELS — C. H. Henager, Jr., B. N Nguyen, R. J. Kurtz (Pacific Northwest National Laboratory)

OBJECTIVE

The objective of this study is to develop a finite element continuum damage model suitable for modeling deformation, cracking, and crack bridging for W-Cu, W-Ni-Fe, and other ductile phase toughened W-composites, or more generally, any multi-phase composite structure where two or more phases undergo cooperative deformation in a composite system.

SUMMARY

A promising approach to increasing fracture toughness and decreasing the DBTT of a W-alloy is by ductile-phase toughening (DPT) [1-3]. In this method, a ductile phase is included in a brittle matrix to prevent fracture propagation by crack bridging or crack deflection. Liquid-phase sintered W-Ni-Fe alloys and hot-pressed and sintered W-Cu composites are two examples of such materials that PNNL and UCSB are investigating. However, there is a need for improved mechanical property models of such composite systems in order to begin to optimize these structural materials with regard to strength and fracture toughness. This report describes such a model that is currently under development at PNNL.

PROGRESS AND STATUS

Background

Tungsten (W) and W-alloys are the solid materials of choice for plasma-facing components (PFCs) of future fusion reactors, such as the International Thermonuclear Experimental Reactor (ITER) and Demonstration Power Plant (DEMO), due to their high melting point, strength at high temperatures, high thermal conductivity, low coefficient of thermal expansion, and low sputtering yield [4-8]. However, W and most W-alloys exhibit low fracture toughness and a high ductile-brittle transition temperature (DBTT) that would render them as brittle materials during reactor operations [4, 6, 9]. The DBTT for unirradiated W-alloys typically ranges from 573K to 1273K (300 to 1000°C) and in a reactor environment radiation hardening would further elevate this range [6, 10, 11]. W-alloys toughened by engineered reinforcement architectures, such as ductile-phase toughening (DPT), are strong candidates for PFCs. In DPT, a ductile phase is included in a brittle matrix to prevent fracture propagation. The principles of DPT are illustrated in Figure 1, which shows an actual and schematic illustration of ductile bridging ligaments stretching across an open crack in a brittle matrix material, such as W [12, 13].



Figure 1. a) SEM image of W-Cu fracture where the ductile phase (Cu) is effectively bridging the crack. b) A steady-state bridging zone shown schematically in 2D [13].

Model Development

The specifics of the finite element continuum damage model (FE-CDM) developed at PNNL have been discussed previously [14, 15]. To understand how deformation proceeds, and how cracks initiate and

propagate in DPT W-composites, finite element analyses of W-composite specimens subjected to bending are being performed using the FE-CDM model for elastic and elastic-plastic materials. The CDM is implemented in the ABAQUS[®] finite element code via user defined subroutines. This CDM model derived from a model developed for long-fiber thermoplastic composites [16] is now being applied at the micron and submicron scale by creating dual-phase FE mesh regions in both 2D and 3D. The constitutive behavior of each phase in the modeling domain is described by the CDM to explore deformation, cracking, and crack bridging in these composite materials. Comparative analyses using an elastoplastic damage model available in ABAQUS are being performed to assess the predictions by this damage model. At this stage, the assessment and further development of the damage model are ongoing.

Summary of Approach

Damage in an elastic-plastic and damageable material can be described by a scalar variable, *D*, that can be related to the level of damage accumulation in the material [17]. Damage affects the material stiffness according to a stiffness reduction law. Using the concepts of thermodynamics of continuous media [17, 18], a thermodynamic potential is defined to derive the constitutive relations and the thermodynamic force associated with the damage variable. This CDM uses the density of the elastic deformation energy as the thermodynamic potential that provides a coupling between damage and elasticity-plasticity. A damage criterion dependent on a damage threshold function is defined and the damage evolution law is obtained. Damage evolves with deformation according to the damage evolution law until a critical (saturation) state at which $D=D_{\rm cr}$ ($0 < D_{\rm cr} < 1$) and failure occurs. In this work, failure at damage saturation ($D=D_{\rm cr}$) leading to crack initiation and propagation is modeled by a vanishing finite element technique [19] that reduces the stiffness and stresses of the failed element to zero.

The FE mesh for these models is created from digital images of actual microstructures by using the public domain software OOF2¹ that creates multiple mesh domains with high-resolution elements at phase boundaries. The software allows the user to specify mechanical properties for each meshed region and outputs an input file for ABAQUS®. Figure 1 is an image of a W-Cu sample microstructure and its associated FE mesh.



(a)

(b)

Figure 2. W-Cu composite with a FE mesh in (a) and the associated digital image in (b) with the phase regions identified. The mesh model contains two separate meshes each with its own set of mechanical properties.

¹ OOF2 was developed at the National Institute of Standards and Technology (NIST).

Figure 3 shows the stress-strain curves obtained from the literature for the two phases, W and Cu. These constitutive relations are applied to each phase as the model is deformed and failure occurs when the strains exceed the ultimate tensile strains. As a test of the model, the FE-CDM is deformed using uniaxial tension along the x-axis for the W-Cu meshed microstructure from Figure 2 as shown in Figure 4.



Figure 3. Constitutive relations for each of the two phases, W and Cu. The W phase is strong and brittle while the Cu phase is softer and much more ductile.



Figure 4. Damage model predictions of deformation in the W-Cu two-phase model. The red regions are failed regions that occur in the Cu phase. Highly stressed regions corresponding to increasing damage are shown in green-yellow-orange and are also found in the Cu phase. These damaged regions surrounded by failed regions would be considered to be ductile bridges in the W-Cu composite.

The FE-CDM approach is being extended to 3D as shown in Figure 5. The original 2D mesh model is extruded into 3D and stressed in uniaxial tension as before. The deformation map in terms of damage accumulation is shown in Figure 6. Note the differences in the amount and type of damage accumulation in the 3D map compared to the 2D map. The relevant overall stress-strain curves for the W-Cu composite is shown in Figure 7 comparing the 2D and 3D results. However, these results are preliminary as noted.



Figure 5. 3D FE mesh created by extruding the original 2D mesh. The blue regions are W and the gold regions are Cu.



Figure 6. (a) 3D damage map under uniaxial tension in the x-direction and (b) is a 2D damage map under the same deformation. The damage accumulation is different in 3D compared to 2D.



Figure 7. Composite stress-strain curves for the W-Cu composite strained in tension along the xdirection. The 3D model results predict a stronger but less ductile material as the loading in the 3D model appears to be shared more with the W phase.

Discussion

These preliminary results indicate the power of the FE-CDM approach in modeling the distributed damage observed in our experimental bend tests of this material. Our dynamic bridging model, while being able to describe the time and temperature dependence of the Cu flow stress with high accuracy was not able to describe the amount of load sharing observed in the bend sample that increased with increasing temperature [20]. Note that multiple cracking occurs naturally in the FE-CDM developed here but we did not yet perform simulations as a function of temperature. We have yet to show agreement with our experimental data except to note the similarities of the distributed cracking and damage in the W-Cu composite that was one of the most significant observations of cracking that we made in our experimental work with this material.

Future Work

Further model development will proceed along with generation of improved 3D mesh models of these W-Cu and W-Ni-Fe materials. We intend to create meshed models that correspond to actual 3D bend bar microstructures and to begin the process of model validation using SENB data.

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4.2 FABRICATION OF FUNCTIONALLY GRADED TUNGSTEN STEEL LAMINATES — L. M. Garrison (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this project is to create a functionally graded tungsten to steel laminate composite for use in plasma facing components in fusion reactors.

SUMMARY

Analysis is underway of the tungsten-steel laminate composites. The composite was fabricated from tungsten foils in thicknesses 250, 100, and 25 μ m and grade 92 steel foils in nominal thicknesses 250, 100, and 76 μ m. The fabrication was by forging and hot rolling at 1000°C. Shear punch tests were completed on the tungsten foils. Tensile and shear punch samples are being machined from the composite.

PROGRESS AND STATUS

Introduction

For the plasma-facing components of fusion reactors, tungsten will be the interface between the plasma and the underlying structural component because tungsten has a low sputtering yield, high melting temperature, and relatively high thermal conductivity. However, because tungsten is brittle and has low fracture toughness, it is impractical to fabricate the entire plasma-facing component out of tungsten. Current divertor designs utilize various methods to bond the tungsten surface layer to the underlying structural part of the component that contains the cooling channels, but for future divertors where the operating temperature will be higher, more robust solutions are needed. Advanced steels are being developed for structural components in future fusion reactors. Unfortunately, tungsten and steel have vastly different coefficients of thermal expansion, so a direct joint would be subjected to intense thermal stresses. A tungsten-steel functionally graded material would ideally both improve the fracture toughness as compared to tungsten alone as well as reduce the thermal stresses between the tungsten and steel parts of the plasma-facing component.

Results

Previously, tensile tests were completed on the individual tungsten and steel foils. Because of the delicate nature of the foils, the results were sensitive to any slight misalignment of the foil in the fixture and any machining defects on the gauge section. This led to a wide scatter in the collected data and a high proportion of the tensile tests being invalid because of premature failure. Additionally, digital image correlation is not well suited to observing tensile tests of the tungsten materials at room temperature because of the limited plastic deformation before failure.

As an alternative to tensile tests, shear punch tests are a way to obtain mechanical property information about the materials. The advantages of the shear punch test are that they do not require a specific sample geometry, are insensitive to sample loading alignment, and are insensitive to edge defects on the material. Shear punch testing was completed on the tungsten foils of thicknesses 250, 100, and 25 μ m. In the shear punch tests, the medium tungsten foil performed the best with more uniform and total elongation than the two other foil thicknesses (Figure 1). It is postulated that the thickest foil had low elongation because it may behave as bulk tungsten would. This is supported by the previous crystallographic texture analysis on the foils that revealed an almost uniform spread of grain orientations in the 250 μ m foil as compared to the highly textured thinner foils (Figure 2). At the other extreme, the 25 μ m foil may have few options for plastic motion because of the small number of grains present through the thickness. The 100 μ m foil may have the benefit of the foil texture and foil effect of dislocations being able to annihilate on the surface, while still having enough grains through the thickness to allow for plastic

deformation.



Figure 1. Shear punch yield stress (YS), ultimate tensile strength (UTS), uniform elongation (UE), and total elongation (TE) for the tungsten foils in thicknesses 250, 100, and 25 μ m.



Figure 2. EBSD analysis of the a) 250 µm thick tungsten foil surface, b) 100 µm thick tungsten foil surface, and c) 25 µm thick tungsten foil surface. Rolling direction is vertical on the page.

The tungsten-steel composite was fabricated using an 80% overall reduction in thickness from the combined forging and rolling. The stresses present in the material during fabrication were more than the 250 µm tungsten foils could withstand, which caused several cracks to form in the tungsten layers (Figure 3). The largest crack had propagated throughout the entire tungsten layer in the composite, such that essentially Section 1 was separated from Sections 2 and 3. The consequence of this crack was that samples could not be fashioned from the whole thickness of the composite material. Instead, tensile samples with their tensile direction aligned to the composite rolling direction and flat face parallel to the foil faces are being fabricated from each of the three sections of the composite. These tensile samples will allow tensile testing followed by shear punch testing using the tab sections.



Figure 3. Cross-section of the tungsten-steel composite fabricated with 80% overall reduction in thickness. The flat planes of the foils are into the page as is the foil and composite rolling direction.

4.3 NEUTRON ENERGY SPECTRUM INFLUENCE ON IRRADIATION HARDENING AND

MICROSTRUCTURAL DEVELOPMENT OF TUNGSTEN — Makoto Fukuda¹, N.A.P. Kiran Kumar², Takaaki Koyanagi², Lauren M. Garrison², Lance L. Snead³, Yutai Katoh², Akira Hasegawa¹, 1- Tohoku University, 2- Oak Ridge National Laboratory, 3- Massachusetts Institute of Technology

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Neutron irradiation to single crystal pure tungsten was performed in the mixed neutron spectrum High Flux Isotope Reactor (HFIR). To investigate the neutron energy spectrum influence, the microstructure development and irradiation hardening was compared to previous data obtained by irradiation in the mixed neutron spectrum Japan Material Testing Reactor (JMTR) and the fast neutron spectrum Joyo reactor. The irradiation temperatures were in the range of ~90 to ~800°C and neutron fluences of 0.02 to 9.00×10^{25} n/m² (E > 0.1 MeV). Post irradiation evaluation included Vickers hardness measurements and TEM observation. Hardness and microstructure changes exhibited a clear dependence on the neutron spectrum. Hardness appeared to increase with increasing thermal neutron dose >1 x 10^{25} n/m² (E>0.1 MeV). Irradiation induced precipitates of χ - and σ -phase were observed in these samples, which were pronounced at high dose and due to the very high thermal neutron flux of HFIR. The result of the precipitates was additional and significant measured hardening of tungsten.

4.4 ANALYSIS OF NEUTRON IRRADIATED TUNGSTEN MICROSTRUCTURES — N.A.P. Kiran Kumar, L. M. Garrison, Y. Katoh (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this project is to analyze the neutron irradiated microstructures of tungsten for evaluating its potential use in plasma facing components in fusion reactors.

SUMMARY

There are two components to neutron irradiation response that change the structure of tungsten: neutron created lattice displacement defects such as interstitials and vacancies, and transmutation products, especially rhenium and osmium. This study is examining the effects of both of these on the tungsten microstructure. Tungsten irradiated to four different doses from 0.7 to 4.5 dpa was examined by transmission electron microscopy, scanning transmission electron microscope, and electron dispersive spectrometry. The tungsten types included single crystal tungsten and as-rolled tungsten foils. The Re and Os transmutation products form needle-shaped precipitates preferentially along the <110> direction. The average precipitate and void sizes increased with increasing dose.

PROGRESS AND STATUS

In our earlier reports microstructure evaluation in tungsten at lower neutron doses were described. The dominate features were dislocation loops at lower temperatures and voids at higher temperatures. This report present the microstructural changes in both polycrystalline and single crystal tungsten specimens exposed to higher neutron doses. The irradiation conditions of examined high dose tungsten specimens are presented in Table 1. A focused ion beam (FIB) system with Ga⁺ ion beam was used to prepare transmission electron microscopy (TEM) specimens. In order to minimize the unwanted damage caused by Ga⁺ ions, very low voltage and current (2 kV and 27 pA) were used on TEM specimens during the final thinning process.

Sample ID	Material	Design Temp	Actual irradiation	Fluence (x10 ²⁵ n/m ²)	dpa
1W17	Single Crystal	500	705	2.2	0.7
1W19	Single Crystal	500	770	9.0	2.9
OW125	Polycrystalline	500	Not available	14.1	4.5
OW158	Polycrystalline	650	Not available	7.4	2.4

Table	1. High	Temperature	-High Dose	Tungsten	specimens	examined under	TEM
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Figure 1 provides the summary of microstructural changes in single crystal and polycrystalline tungsten as a function of irradiation dose and temperature. In order to avoid confusion, henceforth only design temperatures instead of actual exposed temperatures will be shown on all the micrographs and tables.

The TEM micrographs were recorded under two-beam condition with diffraction vectors g = 110 and 110. Line dislocations and loops were seen in 500°C, 0.7 dpa specimens. With increasing dose, considerably fewer loops were seen and the transmuted second phase dominates the microstructure. Both polycrystalline specimens exposed to higher irradiation doses showed heavy precipitation in the microstructures. A dense platelet type structure was observed in all high dose irradiated specimens (see Figure 1). In polycrystalline tungsten, apart from the platelet type structures within the grains, huge pancake type precipitates were also seen at the grain boundaries. The irradiation induced defect sinks such as dislocation loops, voids, which are formed in the early stage of irradiation may have acted as nucleation sites for the second phase precipitates. Therefore a drop in void number density was observed

at higher irradiation doses (Table 2). The size of the precipitates also increased with the irradiation dose and temperature. However the number density of precipitates remained in the same range of about 10^{22} m⁻³, and did not change with the change in irradiation temperature and dose (Table 2).



Figure 1. Micrographs illustrating the damage microstructure in tungsten. All images were recorded at B= [001].

Material	Irradiation Temp (°C)	Fluence (x10 ²⁵ n/m ²)	Mean dislocation loop diameter (nm)	Mean void size (nm)	Void density (m ⁻³)	Precipit ate length (nm)	Precipitate Density (m ⁻³)
Single Crystal	500	2.2	6.37	3.03	1.22X10 ²²	-	-
Single Crystal	500	9.0	-	5.28	7.23X10 ²⁰	20	4.77X10 ²²
Polycrystalline	500	14.1	-	7.40	4.11X10 ²¹	33.5	3.04X10 ²²
Polycrystalline	650	7.4	-	6.40	5.45X10 ²¹	36	1.24X10 ²²

Transmutation

It is widely known that tungsten produces transmutation elements such as rhenium (Re) and osmium (Os) upon neutron irradiation. The compositional change in pure tungsten after exposing to a neutron dose of

1 dpa in HFIR is estimated to be W-9.22%Re-5.02%OS (M.Fukuda et al, Journal of Nuclear Materials, 455, (2014), 460-463). In general, the solubility of Re and Os in pure tungsten is approximately 27 at.% and 5 at.% respectively at room temperature (B. Ralph, D. Brandon, Philosophical magazine, 8, (1963), 919-934 and A. Taylor, B. Kagle, N. Doyle, Journal of Less Common Metals, 3, (1961), 333-347). However during irradiation, Re and Os form precipitates at compositions well below their solubility limits. Figure 2 shows the scanning transmission electron microscope (STEM) images of polycrystalline tungsten irradiated to 2.4 dpa at 650°C with platelet and pancake shaped precipitates within the grains and at the grain boundaries respectively. STEM embedded with Electron Dispersive Spectrometry (EDS) was used to measure the composition of the precipitates. EDS confirms the presence of high concentrations of Re and Os in the platelets, but due to limited width of the platelet type structures the elemental ratio is still unclear. However, the pancake type structures at the grain boundaries showed an average composition of W- 40%Os-24%Re. Figure 3 shows the atomic profile of pancake type precipitates. Further study on these precipitates is ongoing.



Figure 2. STEM micrographs showing the transmuted phase within grains and at the grain boundaries in OW158, 650°C- 2.4 dpa, polycrystalline tungsten a) platelet type precipitates within the grains, b) c) grain boundary precipitates.



Figure 3. Atomic profile of the pancake type grain boundary precipitate.

Voids

Microstructural examination of the irradiated specimens revealed the presence of voids for all four irradiation conditions, Figure 4. The mean size of voids increased with the increasing irradiation dose and temperature (Table 2). Alignment of voids, usually referred to as void lattice formation, in irradiated tungsten is usually observed at doses above 10 dpa (K. Krishan, Radiation Effects, 66, (1982), 121-155). Recently Tanno et al., have report void lattice formation even at lower dpa in JOYO test reactors (T. Tanno et al, Materials Transactions, 48, (2007), 2399-2402). However, such void lattice formation was not observed in current irradiated specimens. Voids were rather randomly distributed in both polycrystalline and single crystal specimens. Void size distribution as a function of irradiation conditions is shown in Figure 5. With the increase in irradiation dose and temperature, the entire distribution moved to larger sizes.



Figure 4. TEM images showing voids in neutron irradiated tungsten.



Figure 5. Void distribution in irradiated tungsten.

4.5 IRRADIATION EFFECTS IN TUNGSTEN-COPPER LAMINATE COMPOSITES — L.M. Garrison^{a*}, Y. Katoh^a, L.L. Snead^{a, b}, T.S. Byun^{a, c}, J. Reiser^d, M. Rieth^d, ^aOak Ridge National Laboratory, ^bPresent affiliation-Massachusetts Institute of Technology, ^cPresent affiliation-Pacific Northwest National Laboratory, ^dKarlsruhe Institute of Technology

Extended abstract of a paper ready for journal submission.

Tungsten alone is not a suitable structural material for a fusion divertor or first wall. Creating a successful plasma-facing component with tungsten requires lowering the ductile to brittle transition temperature (DBTT) and improving the fracture toughness. A tungsten-copper laminate composite was previously tested in tensile, bend, and Charpy impact tests with much improved properties compared to tungsten plate or rod materials. The present study evaluated the tungsten-copper composite after irradiation in the High Flux Isotope Reactor (HFIR) at temperatures between 410 and 780°C to fast neutron fluences of $0.02-9.0 \times 10^{25}$ n/m², E>0.1 MeV (0.0064-2.88 dpa in tungsten). Tensile tests were performed on the composites at room temperature and temperatures up to the irradiation temperatures. The fracture surfaces were analyzed with scanning electron microscopy.

At all irradiation conditions and test temperatures, the copper within the composite failed by ductile knife edge failure, so the determining factor for the composite behavior was the tungsten and the interface behavior. Figure 1 summarizes the different zones of behavior observed by fracture surface analysis in the tungsten-copper laminate composite. The boundaries of the different zones, indicated with dotted lines, are not know precisely but are intended to draw the eye to the different failure modes observed in different regions of the parameter space.



Figure 1. The different fracture modes of the tungsten layers in the tungsten-copper laminate are summarized as they depend on DPA and tensile test temperature.

In the unirradiated state, the composite had 15.5% elongation when tested at 22°C; the tungsten failed by brittle cleavage but the copper had a ductile knife edge failure, indicating that the copper successfully held the composite together after the tungsten layers fractured. In both Zones 1 and 2 in Figure 1, the tungsten layers failed by brittle cleavage. However in Zone 1, up to ~0.1 dpa, the composite as a whole had ductile failure, while after more than ~0.1 dpa, Zone 2, the composite as a whole had brittle failure.

In the unirradiated state, the boundary between brittle cleavage and delamination for the tungsten layers occurs between 22 and 300°C. After irradiation to 0.17 dpa at 420°C and tensile tested at 300°C (SW18, point A in Figure 20) the tungsten layers had mixed mode cleavage and delamination failure, indicating that the irradiation has extended the boundary between cleavage and delamination to a higher temperature. At this irradiation temperature, the primary irradiation defect in the tungsten is expected to be loops and a few voids, which cause the increase in hardness and brittle behavior, while the copper is expected to experience irradiation softening.

The boundary between delamination and ductile failure for the tungsten in the unirradiated state was \sim 500°C. After irradiation, tungsten in composite SW26 at condition B, 0.15 dpa and tensile tested at 650°C, failed by delamination, while in SW14 at condition C, 0.17 dpa and tensile tested at 670°C, the tungsten layers failed in a ductile fashion, so the delamination-ductile boundary was set between points B and C. All composites tested at 670°C and above had ductile tungsten failure and ductile overall composite behavior.

5. MAGNETIC AND DIAGNOSTIC SYSTEM MATERIALS

No contributions this reporting period.

6. FUSION CORROSION AND COMPATIBILITY SCIENCE

6.1 COMPATIBILITY OF AN FeCrAI ALLOY WITH FLOWING Pb-Li IN A THERMAL CONVECTION LOOP — S. J. Pawel and K. A. Unocic (Oak Ridge National Laboratory)

This is the abstract of a manuscript that has been submitted to the Journal of Nuclear Materials.

A mono-metallic thermal convection loop (TCL) fabricated from alloy APMT (Fe21Cr5Al3Mo) tubing and filled with 25 mm long tensile specimens of the same alloy was operated continuously for 1000 h with commercially pure Pb-17at%Li at a peak temperature of 550 ± 1.5 °C and a temperature gradient of ~ 116°C. The resulting Pb-Li flow rate was ~ 0.4 m/min. A 1050°C pre-oxidation treatment (to form an external alumina scale) given to most specimens exposed within the TCL decreased total mass loss by a factor of 3 to 30 compared to adjacent specimens that were not pre-oxidized. However, all specimens exposed above 500°C lost mass suggesting that the alumina scale was not entirely stable in flowing Pb-Li at these temperatures. Post-exposure room temperature tensile tests indicated that the mechanical properties of APMT were substantially influenced by extended exposures in the range of 435-490°C, which caused an increase in yield strength (~65%) and a corresponding decrease in ductility associated with 475°C embrittlement. Specimens annealed in argon at the same temperature exhibited identical changes without exposure to PbLi. Transmission electron microscopy identified Fe- and Cr-clusters in specimens exposed in the low temperature regions of the TCL, indicating the formation of α ' consistent with the mechanism of 475°C embrittlement.

7. MECHANISMS AND ANALYSIS

7.1 EFFECT OF STRAIN FIELD ON THRESHOLD DISPLACEMENT ENERGY OF TUNGSTEN

STUDIED BY MOLECULAR DYNAMICS SIMULATION — D. Wang, N. Gao, (Institute of Modern Physics, Chinese Academy of Sciences) W. Setyawan, R. J. Kurtz (Pacific Northwest National Laboratory), X. Gao, W. H. He (Institute of Modern Physics, Chinese Academy of Sciences)

OBJECTIVE

The objective of this research is to support the interpretation of irradiation damage properties of bulk tungsten-based materials using computational methods. In particular, to provide quantitative information on the directional and strain dependencies of the point defect and threshold displacement energies in bulk tungsten.

SUMMARY

The influence of hydrostatic strain on point defect formation energy and threshold displacement energy (E_d) in body-centered cubic (BCC) tungsten was studied with molecular dynamics simulations. Two different tungsten potentials (Fikar and Juslin) were used. The minimum E_d direction calculated with the Fikar-potential was <100>, but with the Juslin-potential it was <111>. The most stable self-interstitial (SIA) configuration was a <111>-crowdion for both potentials. The stable SIA configuration did not change with applied strain. Varying the strain from compression to tension increased the vacancy formation energy but decreased the SIA formation energy. The SIA formation energy changed more significantly than for a vacancy such that E_d decreased with applied strain from compression to tension.

CONDENSATION OF A PAPER SUBMITTED FOR PUBLICATION¹

Methods

The potentials fitted by Juslin and Wirth [1] and Fikar and Schaublin [2] were used in the present work. In the following text, the notation Juslin-potential and Fikar-potential represent these two potentials, respectively. Both potentials are modifications of the Ackland-Thetford (AT) potential [3]. The Juslin-potential gives properties for SIA defects closer to densify functional theory (DFT) results [4,5] than the Fikar-potential. The potentials differ mainly in their treatment of the connection between the Ziegler-Biersack-Littmark (ZBL) potential [6] and the AT potential. Molecular dynamics (MD) simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code [7]. Periodic boundary conditions were applied in all directions. The effect of an applied hydrostatic strain on various point defect formation energies and E_d was studied. Six configurations of a point defect were explored; 1) vacancy, 2) <111>-crowdion (crowd111), 3) <100>-dumbbell (db100), 4) <110>-dumbbell (db110), 5) octahedral (oct) interstitial, and 6) tetrahedral (tetra) interstitial.

Threshold displacement energies were determined by constructing simulation cells designed to keep the displacement cascade near the cell center. A $30\times30\times30$ BCC lattice containing 54000 tungsten atoms was used for <100> and <110> directions, and a $40\times40\times40$ BCC lattice containing 128000 tungsten atoms for the <111> direction. The simulation cell was divided into two regions by fixing two atomic layers adjacent to the cell surface, denoted as Region-I, and the remaining volume was designated as Region-II, as shown in Figure 1. During the simulation, NVT and NVE ensembles were used for these two regions, respectively. Periodic boundary conditions were applied in all directions. For each direction, six different primary knock-on atoms (PKAs) were selected to calculate the average E_d value. Small hydrostatic strains ranging from -2% to 2% were applied to the simulation cell along the principal directions. The cell was first relaxed under the preset strain by setting T=10 K using an NVT ensemble. After this relaxation, a displacement cascade was created in Region-II with an NVE ensemble while keeping T=10K in Region-I with NVT. In each case, the total simulation time was about 6 ps. If a Frenkel pair existed after 6 ps, then it was regarded as a stable defect. The Wigner-Seitz cell and common-

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neighbor analysis methods were used to analyze the various defect configurations and found to give the same results for E_d .



Figure 1. Schematic of the simulation cell used in the present work. Region-I is the border region, which contains 2 atomic layers from each of the box boundaries. Region-II is the active region. NVT and NVE ensembles are used in Region-I and II, respectively.

Results

Defect formation energy

The formation energies of the six point defects without strain were computed as a reference case. The results are listed in Table 1. Both potentials show that the most stable SIA configuration is a <111>- crowdion, which is also found by DFT [4,5] and the AT [3] potential. For a vacancy, both potentials give the same formation energy, which is approximately equal to DFT values [4,5,8]. The interstitial formation energies obtained from the Fikar-potential are close to AT potential results, while the values calculated with the Juslin-potential are close to DFT values, even though the Juslin-potential is derived from the AT potential.

When strain is applied, both potentials show that the <111>-crowdion is still the most stable SIA, as shown in Figure 2. In Figure 2, negative values represent a compressive strain. Under a compressive strain the octahedral and tetrahedral interstitials are unstable. The octahedral interstitial transforms to a <100>-dumbbell, and the tetrahedral interstitial transforms to an imperfect octahedral configuration when the magnitude of the strain is greater than about 1.0% in both cases. Vacancy and interstitial defects respond differently to applied strain as shown in Figure 2. The vacancy formation energy increases slowly as the strain changes from compressive to tensile. Under a compressive strain the local tensile stress around the vacant site decreases making vacancy formation easier. A tensile strain does the opposite, but only to a smaller degree. At 2% tensile strain, the vacancy formation energy increased only about 3%. For SIAs, the formation energy decreases rapidly with strain state from compression to tension. An interstitial induces local compressive stresses, which increases the potential energy of the system. Thus, a tensile strain reduces these stresses, decreasing the interstitial formation energy.

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E _f , eV	DFT	AT-Potential	Fikar-Potential	Juslin-Potential
vac	3.68 [8] 3.56 [4,5]	-	3.63	3.63
oct	11.68 [4,5]	-	9.98	10.41
tetra	11.05 [4,5]	-	9.97	10.46
crowd111	9.55 [4,5]	8.88 [3]	8.87	9.54
db100	11.49 [4,5]	9.82 [3]	9.79	10.28
db110	9.84 [4,5]	9.64 [3]	9.62	10.18

Table 1.	The formation energy	ies, E _f , of point defects	in tungsten calc	ulated with the F	ikar-potential and
	the Juslin-potential.	Results obtained from	DFT and the AT	potential are als	o listed.



Figure 2. Strain dependence of the formation energies of point defects E_f in W calculated with (a) the Fikar-potential and (b) the Juslin-potential. A negative value represents a compressive strain.

Threshold displacement energy

Threshold displacement energies were determined along the <100>, <110> and <111> directions. The results at zero strain are listed in Table 2. Other simulation results and experimental measurements are also given. Since the <111>-crowdion is the most stable SIA configuration, the majority of defects produced in a displacement cascade should be <111>-crowdions and vacancies, and the minimum E_d should be along a <111> direction. However, results obtained with the Fikar-potential show that the minimum E_d is about 64 eV along a <100> direction. In contrast, the minimum E_d for the Juslin-potential is along a <111> direction, at about 43 eV, even though the <100> direction E_d is very close to the Fikar-potential result. Simulations done by Stuart [9] gave a minimum E_d of 65.6 eV along a <100> direction, in agreement with our Fikar-potential results. The electron irradiation experimental result reported by Maury [10] also found the minimum E_d direction to be <100>. Interestingly, the experimental data show only a small difference between <100> and <111> E_d values, unlike the computed results.

Table 2. The displacement threshold energy, E_d, values for the <100>, <111> and <110> directions intungsten calculated with the Fikar-potential and the Juslin-potential. Electron irradiation results by Maury[10] and computer simulation results by Stuart [9] are presented for comparison.

E _d , eV	<100>	<111>	<110>
Fikar-potential	64 ± 1	70 ± 1	209 ± 7
Juslin-potential	63 ± 1	43 ± 1	164 ± 22
Maury [10]	42 ± 2	44 ± 1	75 ± 5
Stuart [9]	65.6 ± 0.1	~250	~100

When strain is applied, the threshold displacement energies are considerably affected, as presented in Figure 3. The results show that E_d decreases with strain from compression to tension for both potentials. The trend is the same for all three directions and the minimum E_d direction did not change with strain. The results suggest that when tungsten is loaded in hydrostatic compression, more energy will be needed to create a stable Frenkel pair, that is, a pre-compressive stress might increase radiation damage resistance in tungsten, assuming the pre-stress does not rapidly relax at service temperatures.



Figure 3. Strain dependence of the E_d values for the <100>, <111> and <110> directions in tungsten simulated with (a) the Fikar-potential and (b) the Juslin-potential.

Conclusions

Molecular dynamic simulations were used to compute the effect of strain on point defect formation and threshold displacement energies in tungsten. The most stable SIA point defect is a <111>-crowdion with or without an applied hydrostatic strain. The formation energies of SIAs decreased rapidly, while the vacancy formation energy increased slowly with the applied strain increasing from 2% compression to 2% tension. The E_d values for <100>, <110>, and <111> directions decreased over the same strain range. The direction of the minimum E_d depended on the choice of interatomic potential. The Fikar-potential gave the minimum E_d along a <100> direction, while the Juslin-potential indicated the minimum E_d is along a <111> direction. When strain is applied, the minimum E_d direction did not change.

Acknowledgements

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7.2 DAMAGE MECHANISM INTERACTIONS AT THE PLASMA-MATERIALS INTERFACE (An Early

Career Award Project) — C. M. Parish (Oak Ridge National Laboratory)

OBJECTIVE

This work intends to develop the fundamental scientific basis for modelling and predicting the behavior of helium bubbles in refractory materials, to provide support for the science and engineering of the tokamak plasma-facing-material environment.

SUMMARY

This first reporting period of the five-year project has emphasized experimental technique developments as the necessary foundation for all later work, and has begun several valuable collaborations with other institutions. Specifically, tungsten high-purity sheet stock has been obtained and characterized to act as a constant and known baseline for further experiments. Focused ion beam (FIB) methods to prepare samples for transmission electron microscopy (TEM) of plasma-exposed tungsten have been refined. This includes tall (>1000 nm) "nanofuzz" tendrils, which is a significant experimental challenge. A non-FIB technique for nanotendrils has also been developed. Collaborations thus far include UCSD PISCES laboratory, and Dr. D. Donovan, UT-Knoxville.

PROGRESS AND STATUS

Introduction

As the choice for the ITER divertor, and present leading candidate for subsequent tokamak systems, tungsten metal is the current focus for high-flux, high-fluence, high-temperature plasma-materials interactions (PMI) studies. Unfortunately, the fundamental scientific basis for explaining observed PMI behaviors (e.g., nanofuzz growth) and predicting long-term behaviors (e.g., PMI response in a nuclear environment) is lacking. In this reporting period, we have begun examining defect-defect interactions in tungsten metal that has been subjected to plasma exposure.

Experimental Procedure

In this summary, data from two separate sets of specimens are presented. First is a lower-flux exposed ALMT ITER-grade tungsten blank (Sandia-California system, ~1300 K, 75 eV ion energy, ~ 2×10^{19} ions/m²sec, ~ 3×10^{24} ions/m² total), the second a high-flux nanotendril coated specimen (UCSD-PISCES, ~1200 K, 50 eV ion energy, ~ 10^{23} ions/m²sec, ~ 4×10^{26} ions/m² total).

FIB sample preparation has been generally successful using standard methods; the ORNL LAMDA lab FEI Versa DualBeam instrument was used for all results in this report. Samples were milled with 30, 16, 8, and 5 keV Ga⁺ beams. Most samples were cleaned post-FIB using the Fishione Nanomill, 900 eV Ar⁺ beam, for several minutes on each side to remove Ga contamination and reduce the injected black-spot contrast arising from FIB damage. Samples were also typically cleaned using a 25O₂-75Ar plasma to reduce carbonaceous contamination in-TEM.

Significant artifacts are introduced in FIB preparation of nanotendrils, such as coating the tendrils with a C-Ga-Pt layer from FIB preparation, so a method to extract individual nanotentrils for TEM was developed. Specifically, 3 mm copper-mesh TEM grids, with either lacy or continuous carbon films, are wet with methanol, grasped with tweezers, and the swabbed across the tendril-coated surface (also wet lightly with methanol). This extracts both bundles of nanotendrils and isolated nanotendrils suitable for individual TEM examination.

Results

The most important PMI-modified microstructural parameter in terms of influence on properties (fuel retention, thermal conductivity, etc.) is the density and size of helium bubbles. Three sample regions are shown in Figure 1; Figure 1a, the low-flux sample's near-surface region; Figure 1b, the nanotendril-coated sample's substrate region (near the substrate/tendril interface); and Figure 1c, the nanotendrils themselves.



Figure 1. (a) low-flux ALMT-ITER grade specimen, near-surface region. (b) PISCES nanotendril-coated sample, substrate region. (c) PISCES nanotendril-coated sample, tendril region. All three images from FIB-prepared regions.

Analysis of these (and similar) images indicates much larger bubbles in the low-flux, low-fluence specimen compared to nanotendril sample's two regions. Specifically, Figure 1a show mean bubble diameter 16.5 nm with a range from 5-100 nm; Figure 1b, a mean of 7.3 nm with a range of 2-40 nm; and Figure 1c (the tendrils), a mean of 5.9 nm with a range of 3-12 nm.

Although the higher flux and fluence needed to form tendrils might lead to the hypothesis that the bubbles should be larger, this was not observed. One possible mechanism is that as the surface is consumed in order to lengthen the tendrils, the near-surface bubble population is also consumed and new bubbles must be continuously formed, leading to smaller sizes due to shorter lifetimes. Regardless, flux-resolved and interrupted experiments are planned for the near future to begin addressing these questions.

Isolated tendrils, prepared by the method developed recently, are shown in Figure 2a. This new and reliable sample preparation method will allow us to address questions such as grain-boundary character in the tendrils, and might allow EELS-based measurement of the helium content in the bubbles. A convergent-beam electron diffraction pattern is shown in Figure 2b, obtained from the arrowed point in Figure 2a. By analyzing multiple patterns, we intend to determine the grain-to-grain orientation relationships in the tendrils. This should allow inference of growth mechanics (i.e., high-vs-low angle grain boundaries requiring different nucleation energies), as well as providing insight into the energetics of near-boundary bubbles (i.e., Figure 2c). Figure 2d is an EELS low-loss log-ratio thickness map; further technique development for EELS mapping of the energy region of interest to He is underway, in order to gauge the feasibility of direct measurements of He in W.



Figure 2. (a) HAADF-STEM image of suspended nanotendrils. (b) Diffraction pattern from arrowed point in (a). (c) High-resolution TEM image of bubbles near boundaries in isolated tendrils. (d) EELS thickness map of a single tendril on the carbon support film. Dashed circles indicate larger bubbles.

The work in this reporting period illustrates a strong basis for ongoing experiments in upcoming reporting periods. With the plasma-exposure experiments planned at collaborator laboratories, flux-resolved and energy-resolved tests of tungsten under helium bombardment will be performed and detailed microstructural parameters will be determined by the methods described here.

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7.3 A CODE FOR AUTOMATED DERIVATION OF POST NECKING TRUE STRESS-TRUE STRAIN CONSTITUTIVE LAWS FROM STANDARD TENSILE TEST ENGINEERING STRESS STRAIN CURVES — Shuangyu Li, Takuya Yamamoto, G. Robert Odette (UCSB)

OBJECTIVES

Objectives of this study are to automate derivation of true stress-true stain constitutive [$\sigma(\epsilon)$] beyond the strain range (necking) that standard uniaxial tensile tests can normally provide, especially in irradiated alloys that almost immediately neck.

SUMMARY

We previously developed a self-consistent approach to derive true stress-stain constitutive $[\sigma(\epsilon)]$ laws from measured tensile test engineering stress-strain $s(e)_m$ data based on finite element method (FEM) simulations. The simulated $s(e)_s$ were based on trial input $\sigma(\epsilon)_n$ that were adjusted in an iterative fashion until convergence at $s(e)_s \approx s(e)_m$. The adjustments between $\sigma(\epsilon)_n$ and $\sigma(\epsilon)_{n+1}$ were based on experience and judgment but in some cases convergence required many time consuming iterations. Here we report an automated iterative process that is much more efficient and less time consuming for the researcher.

PROGRESS AND STATUS

Introduction

Deformation controlled failure of a structure is mediated by the interaction of a number of intrinsic properties, including constitutive properties and plasticity laws, as well as extrinsic factors, such as geometry and loading conditions. Standard techniques, such as the uniaxial tensile test, cannot provide all of the information relevant to predicting deformation and failure, especially for irradiated materials where low ductility limits the strain range that can be probed. Accordingly, we report progress in developing advanced methods to predict local deformation limits for fusion structures in terms of structural stress-strain [$\sigma(\epsilon)$] or load-displacement (P- Δ) behavior, accounting for both intrinsic and extrinsic factors. The first step requires developing a self-consistent set of constitutive and plasticity laws for materials of interest, both unirradiated and irradiated.

In previous studies we developed self-consistent approach to derive $\sigma(\epsilon)$ laws, that were successfully applied to 8-12Cr tempered martensitic steels and 14Cr oxide dispersion strengthened alloy irradiated in the Advanced Test Reactor (ATR). The approach is based on simultaneous measurements and finite element method (FEM) simulations of engineering stress-strain s(e) curves, which are consistent for a unique $\sigma(\epsilon)$ law. Finding the unique $\sigma(\epsilon)$ generally requires a few to many of iterations involving: (i) modifying input or previous iteration $\sigma(\epsilon)$; (ii) re-running the FEM simulation; (iii) comparing simulated and experimental s(e) curves. In this report we use a MATLAB based code to automate the s(e) fitting.

Approach

The general approach is to measure P- Δ or engineering stress-strain [s(e)] curves and characterize and, in some cases, quantify large geometry changes (LGC) and deformation-flow (micro to macro) patterns of strain distributions (SD) for a wide variety of test geometries to access high stains and bound key structural conditions. Examples are shown in Figure1. The experimental information is combined with finite element modeling (FEM) of the corresponding specimen(s) during testing to simulate LGC behavior, P- Δ /s(e) and SD. The true-stress/strain constitutive equation $\sigma(\epsilon)$ used in the finite element analysis is varied, and the computed values of P- Δ /s(e), LGC and SD compared to the measured values. Differences are used to adjust the $\sigma(\epsilon)$, and the process proceeds iteratively to obtain a best fit maximum self-consistency.



Figure 1. Examples of mechanical tests that can probe high strain behavior of structural materials coupled with FEM simulations to derive a self-consistent $\sigma(\varepsilon)$.

Automated Derivation of $\sigma(\varepsilon)$

Previous manual process consisted of the following components:

- (i) Create an input $\sigma(\epsilon)$ model, starting with the $s(e)_m$ converted to $\sigma(\epsilon)$ up to the necking strain. The experimental $\sigma(\epsilon)$ is then fit and extrapolated to higher strains by a 4 parameter dislocation theory based model that provides for strain hardening, softening and perfectly plastic behavior.
- (ii) Use the current generation $\sigma(\epsilon)$ as input to the FEM ABAQUS to predict the corresponding $s(e)_s$.
- (iii) Parametrically adjust $\sigma(\varepsilon)$ based on a visual comparison the predicted and experimental $s(e)_m$ curves, iterating to self-consistent $s(e)_s \approx s(e)_m$ convergence.

In the semi-automated procedure, the iteration to find the best $\sigma(\epsilon)$ model is controlled by a general MATLAB code "optGUI.m" which incorporates "optimizeFun.m" to manage an optimized fit. The workflow in the management code and its coupling to Excel and ABAQUS software is shown in Figure 2.Essential parameters are first defined in a graphical user interface (GUI) shown in Figure 3.



Figure 2. Schematic diagram of the optimization workflow.

1. In the optimizeFun.m MATLAB code, a *genetic* algorithm is used to randomly generate sets of $\sigma(\epsilon)$ model parameters within a pre-defined space. The term *genetic* refers to a parameter optimization algorithm that mimics natural evolution process and is suitable for highly non-linear problems.

- Each set of parameters are given to Excel spreadsheet "mybook.xlsx", that calculates the input σ(ε) model in a form of true stress versus plastic strain table that is directly used as an input file for Abaqus.
- 3. After the Abaqus FEM simulation, the getData.py code reads the s(e)_s results from the output database (ODB) file.
- 4. OptimizeFun.m plots experimental and FEM simulated engineering s(e) curves in one figure, and calculates the predicted versus measured s(e) difference for a specified set of strains.
- Finally, optimizeFun.m best fits (optimizes) all the input parameters models with the genetic algorithm by repeating all the steps above until s(e)_s ≈ s(e)_m.

The quality of the FEM results, in terms of a defined "Fitness" is shown in Eq. 1. As the sum of the square root of stress variances for each of the specified set of evaluation strains up to the onset of rapid stress decrease indicating the development of internal damage, the individual variances are weighted by a factor that decreases with increasing strain, indicting higher uncertainty and the possibility of internal damage prior to the rapid stress drop-off.

fitness =
$$\sum_{e=0.01,0.02...} \sqrt{\{|s_{FEM} - s_{Exp}|(1-\varepsilon)\}^2}$$
 (1)

Since the procedure is based on a general MATLAB algorithm that can deal with highly non-linear phenomena, which may have a number of local good fit minima, the algorithm is intended to mimic evolution by "natural selection". Fitness is the sum of the absolute predicted minus measured s(e) and is not a classical standard deviation. Indeed the fitness, with units of MPa, is much larger than the standard deviation. Initially, typically, 30 model parameter sets are selected randomly within a defined space. After each iteration, a subset of the models, including those that yield the best fit model are used to define a reduced parameter space, with a new selected set of 27 random model parameters added to the 3 best fit models. The average fitness is for all the models in one generation, while the best fitness is for the top 3 best models that are carried into the next generation. Thus the average model fit decreases with each generation due to the shrinking parameter space. The best fitness model average may also decrease, although typically to a much lesser extent. This so-called "natural selection" is intended to avoid the fitting becoming stuck in a local minimum.

Results

Figure 4 shows an example for the first individuals in the first generation s(e) curves for Eurofer 97 irradiated to 6.5 dpa in ATR at 295°C, that gives a relatively good initial fitness value of \approx 437 since the parameter space was well known and narrowly defined in this case. The best and mean fitness values after 15 generations are 27 and 24MPa respectively in Figure 4(b) for ATR irradiated Eurofer97. However, such a good initial fitness is generally not observed. Figure 5 shows another example for a 14YWT alloy where the initial best and average fitness values are more than 300 and 1000 MPa, respectively. As the generations progress, the mean value decreases rapidly, as more low quality models are excluded in the shrinking parameter space. The single best parameter set is chosen as the final model when the Best fitness average falls below a specified value, like 200 MPa, in this example. The best and mean fitness values are 174 and 195 MPa respectively in Figure 5. Figure 6 shows the corresponding final optimized s(e)s and the s(e)m curves for the irradiated Eurofer 97 along with the control specimen. The classical standard deviation is 9.6 MPa for the irradiated condition and 12.7 MPa for the unirradiated control. Typically, optimization takes 60 iterations for unirradiated, and 150 iterations for irradiated conditions, respectively. Figures 7 and 8 summarize the corresponding results for the irradiated and the unirradiated conditions of F82H IEA with standard deviations of 3.2 and 3.4MPa, respectively, and for NF616 with corresponding standard deviations of 7.2 and 3.4 MPa. Figure 9 summarizes the corresponding results of 14YWT alloy in LT orientation tested at 800°C with standard deviations of 4.0 MPa,

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Name of Inp file	ER04 inp	Decay constant range	0 0	
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poplation in one generation	30	Fracture strain	0.1	
Run				

Figure 3. Graphical user interfaces to assign optimization data and iteration conditions



Figure 4. The first simulation in the first generation for ATR irradiated Eurofer 97(ER04).


Figure 5. The first simulation in the first generation for 14YWT alloy (SSJ2_LT8_800c) and an example evolution of the mean and best fitness values as a function of generation.



Figure 6. Comparison of experimental (EXP) and FEM simulated engineering s(e) curves along with the best optimized $\sigma(\epsilon)$ model for (a) ATR irradiated Eurofer 97 (ER04) specimen and (b) the control specimen (ER07).



Figure 7. Comparison of experimental (EXP) and FEM simulated engineering s(e) curves along with the best optimized $\sigma(\varepsilon)$ model for (a) ATR irradiated F82H IEA (HA07) specimen and (b) the control specimen (HA16).



Figure 8. Comparison of experimental (EXP) and FEM simulated engineering s(e) curves along with the best optimized $\sigma(\epsilon)$ model for (a) ATR irradiated NF616 (NF06) specimen and (b) the control specimen (NF09).



Figure 9. Comparison of experimental (EXP) and FEM simulated engineering s(e) curves along with the best optimized $\sigma(\epsilon)$ model for a 14YWT alloy in LT orientation tested at 800°C.

Finally, we note that the difference between $s(e)_s$ and $s(e)_m$ at high strains in the rapid drop-off region is a measure of the development of load shedding internal damage. The opportunity to use this information to develop a better understanding of damage mechanics, including the effect of irradiation, will be exploited in the future.

Acknowledgements

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8. MODELING PROCESSES IN FUSION SYSTEM MATERIALS

8.1 OBJECT KINETIC MONTE CARLO SIMULATIONS OF RADIATION DAMAGE IN TUNGSTEN SUBJECTED TO NEUTRON FLUX WITH PKA SPECTRUM CORRESPONDING TO HFIR — G. Nandipati, W. Setyawan, H. L. Heinisch, K. J. Roche, R. J. Kurtz (Pacific Northwest National Laboratory) and B. D. Wirth (University of Tennessee)

OBJECTIVE

The objective of this work is to study the damage accumulation in pure tungsten (W) subjected to a neutron flux with a primary knock-on atom (PKA) spectrum corresponding to the high flux isotope reactor (HFIR), using the object kinetic Monte Carlo (OKMC) method.

SUMMARY

We used our recently developed lattice based object kinetic Monte Carlo (OKMC) code, *KSOME* [1], to carry out simulations of radiation damage in bulk W. In this report, we present preliminary results of our study of, the effect of the maximum size of self-interstitial atom (SIA) clusters allowed to rotate on the defect accumulation in bulk tungsten with 1µm grain size when subjected to neutron flux having PKA spectrum corresponding to HFIR at 1025 K for the dose rates in the range 0.17 x 10⁻⁴ to 0.17 x 10⁻⁸ dpa/s.

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Results

A complete description of the simulation parameters used and how the present simulations are preformed is available in Ref. [2]. Figure 1 (a-f) shows a comparison of the number density of vacancies and vacancy clusters, and average vacancy cluster diameters as a function of dose at dose rates of 0.17 x 10⁻⁴ to 0.17 x 10⁻⁸ dpa/s, when SIA clusters up to size 5 (Case1, left column) and up to size 10 (Case 2, right column) are allowed to rotate. Figure 2 shows a comparison of the vacancy microstructures at various dose rates at 1.0 dpa for both cases. Due to lack of space, only the order of the magnitude of the dose rates is shown in both figures, while the factor of 0.17 is omitted, a value of 10⁻⁴ dpa/s in a figure represents a dose rate of 0.17 x 10⁻⁴ dpa/s. Note that in these simulations the effect of both intragranular defects and transmutation are ignored.

As expected the number density of vacancies and vacancy clusters, and the average size of vacancy clusters decrease when the maximum allowed size of the rotation of SIA clusters is increased, and this is due to the increase in the number of recombinations. The general behavior of the number density of vacancies and their clusters, and the average vacancy cluster size with dose rates in both cases remains the same, but the behavior is different as a function of dose, especially, at the dose rates of 0.17 x 10^{-4} and 0.17 x 10^{-5} dpa/s for *case-II*. In the latter case, the vacancy cluster size appears to have saturated at 1.05 nm, while the number density of vacancies and vacancy clusters increases very slowly with dose. For lower dose rates, although the number density of vacancies increases much more slowly in *case-II*, it shows similar behavior with dose for both the cases.

In both cases void lattice formation was observed for dose rates from 0.17×10^{-6} to 0.17×10^{-8} dpa/s (See Figure 2 (e-h)), while for the dose rates of 0.17×10^{-4} and 0.17×10^{-5} dpa/s void lattice formation was observed for case-I but not for *case-II*. At these dose rates, even though the density of vacancy clusters is higher than at lower dose rates, the spatial distribution of vacancy clusters appears to be random. This could be due to the fact that the sizes of the vacancy clusters are very small and they appear to have saturated at 1.05 nm (see Figure 1(f)). This suggests that for the dose rates of 0.17×10^{-4} and 0.17×10^{-5} dpa/s for *case-II*, either the formation of large vacancy clusters is very slow or they do not survive long enough to grow beyond an average size of 1.05 nm.



Figure 1. Comparison of (a-b) vacancy number density and (c-d) vacancy cluster density and (e-f) average vacancy clusters size at various dose rate when SIA clusters are allowed to rotate up to size of 5 (left column) and 10 (right column).



Figure 2. Snap shots of vacancy cluster microstructure at a dose of 1dpa when SIA clusters up to size (a-e) 10 (g-k) 5 at dose rates of (a, g) 10^{-4} (b, h) 10^{-5} (c, i) 10^{-6} (d, j) 10^{-7} (e, k) 10^{-8} dpa/s.

Future Work

We will carry out further analysis of available data and also carry out additional simulations to understand defect accumulation at various dose rates, PKA energies, temperatures, simulation cell and grain size, and also at different PKA spectrums.

Acknowledgement

All computations were performed partly on HOPPER at National Energy Research Scientific Computing Center (NERSC) and PNNL's institutional computing (PIC) systems.

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8.2 STABILITY OF SMALL SELF-INTERSTITIAL CLUSTERS IN TUNGSTEN — W. Setyawan, G. Nandipati, and R. J. Kurtz (Pacific Northwest National Laboratory)

OBJECTIVE

The objective of this research is to explore the structures of small clusters of interstitials in W. These structures will serve as representative configurations that will be used to calculate the binding of such clusters to transmutation products in W. The results will be used to inform kinetic Monte Carlo simulations of radiation damage accumulation containing transmutation products, in particular Re and Os.

SUMMARY

Density functional theory was employed to explore the stability of interstitial clusters in W up to size seven. For each cluster size, the most stable configuration consists of parallel dumbbells. For clusters larger than size three, parallel dumbbells prefer to form in a multilayer fashion, instead of a planar structure. For size-7 clusters, the most stable configuration is a complete octahedron. The binding energy of a [111] dumbbell to the most stable cluster increases with cluster size, namely 2.49, 3.68, 4.76, 4.82, 5.47, and 6.85 eV for clusters of size 1, 2, 3, 4, 5, and 6, respectively. For a size-2 cluster, collinear dumbbells are still repulsive at the maximum allowable distance of 13.8 Å (the fifth neighbor along [111]). On the other hand, parallel dumbbells are strongly bound together. Two parallel dumbbells in which the axis-to-axis distance is within a cylindrical radius of 5.2 Å still exhibit a considerable binding of 0.28 eV. The most stable cluster in each size will be used to explore interactions with transmutation products.

PROGRESS AND STATUS

Method

VASP [1, 2] software was used to perform the quantum calculations within the density functional theory (DFT) framework. Core electrons are modeled with accurate projector-augmented-wave pseudopotentials [2]. Electrons in 6s and 5d states are treated as valence electrons. Perdew-Burke-Ernzerhof formulations [3] were employed for the exchange-correlation functionals. Defect formation energies were calculated using cubic 5x5x5 supercells of tungsten's bcc unit cell. A Monkhorst-Pack [4] k-points grid of 3x3x3 is sufficient to obtain accurate formation energies. The coordinates of atoms and box volume are optimized while maintaining cubic symmetry. In relaxed configurations, the forces are < 0.025 eV/Å and the external pressure < 0.5 kbar. At the end of the relaxations, a static calculation was performed to eliminate errors due to basis incompleteness associated with changes in the simulation cell. A convergence study of the energy cutoff (ENCUT) for the plane waves up to 350 eV. An energy cutoff of 250 eV was found to be sufficient to converge the formation energies of those dumbbells within 20 meV. Therefore, all subsequent calculations were performed with ENCUT = 250 eV.

Results

Size-2 Clusters

Figure 1a shows a pool of 10 lattice sites used to find unique configurations of size-2 clusters. This pool encompasses up to the fifth nearest-neighbor (nn) distance. A new option (synopsis *-pick*) was developed and added to our in-house utility code *axisvasp* to pick n = 2 site combinations out of the m = 10 sites. Subsequently, non-equivalent combinations are identified based on bond lengths. There are 5 unique 2-site combinations. A new option (synopsis *-dbdb*) was developed to build dumbbells at those sites. Note that the most stable dumbbell in W is a [111] dumbbell. Therefore, we explore clusters of <111> dumbbells. For size-2 clusters, a complete permutation of Miller indices (h = ±1, k = ±1, l = ±1) of the dumbbell's orientation is explored. There are 64 possible configurations out of which 23 are unique and subsequently relaxed. Figure 1b-1f shows the relaxed configuration of the five most stable clusters. The binding energy (E_b) needed to separate the two dumbbells is 2.49, 2.46, 1.99, 1.65, and 1.06 eV,

respectively. The most stable configuration is two [111] dumbbells separated at the third nn distance, with axis-to-axis distance of $a\sqrt{2}/\sqrt{3}$ = 2.60 Å (where a is the lattice constant). We refer the most stable cluster-2 configuration as MSC-2.



Figure 1. a) Lattice sites from which configurations of <111> dumbbells are searched. The five most stable structures of size-2 clusters are shown in b) to f) with binding energy of 2.49, 2.46, 1.99, 1.65, and 1.06 eV, respectively. The orientations are b) both [111], c) both [11-1], d) both [111], e) [111] and [11-1], and f) [111] and [1-11].

Two collinear [111] dumbbells are strongly repulsive. The farthest separation with a 5x5x5 supercell along the diagonal is $(5a\sqrt{3})/2 = 13.8$ Å (the fifth neighbor along [111]). At this distance, two collinear dumbbells still exhibit a binding energy of -1.26 eV. On the contrary, if the axes of the dumbbells are parallel, instead of collinear, the dumbbells are strongly binding (Figure 1b-1d). Note that in Figure 1b-1d, the axis-to-axis distance is always $a\sqrt{2}/\sqrt{3} = 2.60$ Å. With the two [111] dumbbells separated at $2a/\sqrt{2} = 4.51$ Å (the third nn) and axis-to-axis distance of $2a/\sqrt{2} = 4.51$ Å, the binding is still strong, 0.78 eV. At a larger axis-to-axis separation of $2a\sqrt{2}/\sqrt{3} = 5.20$ Å, [111] dumbbells separated at $a\sqrt{3} = 5.52$ Å (the second neighbor along [111]) have a binding energy of 0.28 eV. This indicates that two parallel dumbbells within a cylindrical radius of 5.2 Å still exhibit a considerable binding of 0.28 eV.

Non-parallel <111> dumbbells such as the [111] and [11-1] pair can have significant binding as well, as shown in Figure 1e (E_b = 1.65 eV) and Figure 1f (E_b = 1.06 eV). However, the strongest binding is clearly between parallel <111> dumbbells. Therefore, for larger clusters, we focus on clusters of <111> parallel dumbbells.

Size-3 Clusters

Figure 2a shows the nine lattice sites from which the size-3 clusters are identified. Taking combinations of 3 out of 9 sites results in 84 combinations which reduces to 6 unique ones, namely (1, 65, 17), (1, 65, 18), (1, 65, 22), (1, 17, 18), 1, 17, 22), and (1, 18, 6). Permuting <111> orientations of the dumbbells at those unique sites results in 3,072 configurations, which reduces to 101 unique ones. Considering only the parallel orientations reduces the number to 13 configurations, which are then relaxed. Figure 2b-2f shows the relaxed configuration of the five most stable clusters. The binding energy with respect to a [111] dumbbell and MSC-2 is 3.68, 3.13, 2.56, 1.30, and 0.03 eV, respectively. The most stable cluster-3 (MSC-3) configuration consists of [11-1] dumbbells arranged on the (01-1) plane. From this result, we focus on the exploration of larger clusters created from initial configurations of [11-1] dumbbells on the (01-1) plane.



Figure 2. a) Lattice sites from which configurations of size-3 <111> parallel dumbbells are searched. The five most stable structures of size-3 clusters are shown in b) to f) with binding energy, with respect to a [111] dumbbell and the most stable size-2 cluster, of 3.68, 3.13, 2.56, 1.30, and 0.03 eV, respectively.

Size-4 Clusters

Figure 3a shows the 12 lattice sites from which the size-4 clusters are identified. Taking combinations of 4 out of 12 sites results in 495 combinations, which reduces to 90 unique ones. Then, [11-1] parallel dumbbells are placed at those 90 unique combinations of sites and the structures are relaxed. Figure 3b-3f shows the relaxed configuration of the five most stable clusters. The binding energy with respect to a [111] dumbbell and MSC-3 is 4.76, 4.67, 3.40, 2.76, and 2.74 eV, respectively. Figure 3b shows the most stable cluster-4 (MSC-4) configuration. Interestingly, even though all initial configurations are constructed with [11-1] dumbbells on (01-1) plane, i.e. planar configurations, the final structure of MSC-4 shows [11-1]

dumbbells arranged on 2 layers of the (10-1) plane. Arrows in Figure 3b indicate the projected location of three of the dumbbells onto one of the (10-1) layers.



Figure 3. a) Lattice sites from which configurations of size-4 <111> parallel dumbbells are searched. The five most stable structures of size-4 clusters are shown in b) to f) with binding energy, with respect to a [111] dumbbell and the most stable size-3 cluster, of 4.76, 4.67, 3.40, 2.76, and 2.74 eV, respectively. Arrows indicate the projected location of dumbbells on to the shaded plane.

Size-5 Clusters

Size-5 clusters were found from the same 12 lattice sites as size-4 clusters. Taking combinations of 5 out of 12 sites results in 792 combinations, which reduces to 181 unique ones. Then, [11-1] parallel dumbbells are placed at those 181 unique combinations of sites and the structures are relaxed. Figure 4b-4f shows the relaxed configuration of five most stable clusters. The binding energy with respect to a [111] dumbbell and MSC-4 is 4.82, 3.89, 3.87, 3.47, and 3.42 eV, respectively. Figure 4b shows the most stable cluster-5 (MSC-5) configuration. Similar to MSC-4, the final structure of MSC-5 shows [11-1] dumbbells arranged on 2 layers of the (01-1) plane.



Figure 4. a) Lattice sites from which configurations of size-5 <111> parallel dumbbells are searched. The five most stable structures of size-5 clusters are shown in b) to f) with binding energy, with respect to a [111] dumbbell and the most stable size-4 cluster, of 4.82, 3.89, 3.87, 3.47, and 3.42 eV, respectively. Arrows indicate the projected location of dumbbells on to the shaded plane.

Size-6 Clusters

Size-6 clusters are found from the same 12 lattice sites as size-4 clusters. Taking combinations of 6 out of 12 sites results in 924 combinations, which reduces to 259 unique ones. Then, [11-1] parallel dumbbells are placed at these 259 unique combinations of sites and the structures are relaxed. Figure 5b-5f shows the relaxed configuration of five most stable clusters. The binding energy with respect to a [111] dumbbell and MSC-5 is 5.47, 5.13, 4.97, 4.97, and 4.92 eV, respectively. Figure 5b shows the most stable cluster-6 (MSC-6) configuration. The final structure of MSC-6 shows [11-1] dumbbells arranged on 2 layers of the (110) plane.



Figure 5. a) Lattice sites from which configurations of size-6 <111> parallel dumbbells are searched. The five most stable structures of size-6 clusters are shown in b) to f) with binding energy, with respect to a [111] dumbbell and the most stable size-5 cluster, of 5.47, 5.13, 4.97, 4.97, and 4.92 eV, respectively. Arrows indicate the projected location of dumbbells on to the shaded plane.

Size-7 Clusters

Size-7 clusters are identified from the same 12 lattice sites as size-4 clusters. Taking combinations of 7 out of 12 sites results in 792 combinations, which reduces to 269 unique ones. Then, [11-1] parallel dumbbells are placed at these 269 unique combinations of sites and the structures are relaxed. Figure 6b-6f shows the relaxed configuration of five most stable clusters. The binding energy with respect to a [111] dumbbell and MSC-6 is 6.85, 5.30, 5.27, 4.29, and 4.18 eV, respectively. Figure 6b shows the most stable cluster-7 (MSC-7) configuration. The final structure of MSC-7 shows [11-1] dumbbells forming a complete octahedron.



Figure 6. a) Lattice sites from which configurations of size-7 <111> parallel dumbbells are searched. The five most stable structures of size-7 clusters are shown in b) to f) with binding energy, with respect to a [111] dumbbell and the most stable size-6 cluster, of 6.85, 5.30, 5.27, 4.29, and 4.18, respectively. Arrows indicate the projected location of dumbbells on to the shaded plane.

The stability of interstitial clusters up to size seven has been obtained. The results show that the binding of a [111] dumbbell to interstitial clusters increases with the size of the clusters. For each cluster size, the most stable configuration has been obtained and will be used to explore the interaction of such clusters with transmutation products such as Re and Os.

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8.3 A GENERALIZED ISING MODEL FOR STUDYING ALLOY EVOLUTION UNDER IRRADIATION AND ITS USE IN KINETIC MONTE CARLO SIMULATIONS — Chen-Hsi Huang and Jaime Marian (University of California Los Angeles)

SUMMARY

We provide an Ising Hamiltonian for kinetic simulations involving interstitial and vacancy defects in binary alloys. Our model, which we term `ABVI', integrates solute transport by both interstitial defects and vacancies, and thus represents a generalization to the widely- used ABV model for alloy evolution simulations. The Hamiltonian captures the three possible interstitial configurations in a binary alloy: A-A, A-B, and B-B, which makes it useful for irradiation damage simulations. We implement the ABVI Hamiltonian in kinetic Monte Carlo simulations and perform a verification exercise by comparing our results to published irradiation damage simulations in simple binary systems with Frenkel pair defect production and several microstructural scenarios, with matching agreement found. (*This is the abstract of a paper submitted to: J. Phys.: Condensed Matter*)

1.0 Introduction

Stochastic modeling of microstructural evolution in substitutional binary alloys using Monte Carlo methods is a relatively mature field, where alloy configurations are generated randomly, typically by direct atom exchange (the so-called `Kawasaki' dynamics) [1-5], or by (local) vacancy-mediated solute transport [3-13]. The time scale is recovered by using physical jump frequencies that depend on the energies of the configuration before and after the exchange in such a way that detailed balancing holds. These energies are calculated using a suitable Hamiltonian function, which - in most cases - depends only on the chemical nature of the species participating in an exchange, as well as on their separation distance. Such methods, aptly called `AB' or `ABV' - in reference to the atomic species involved -, generally write the Hamiltonian as a cluster expansion truncated to first or second nearest neighbor distances [3-5, 7, 8, 11, 12, 14]. The order of the cluster expansion is variable, although it is generally restricted by computational considerations to second order [3-6, 8, 12-14]. However, it is often advantageous to express the cluster expansion Hamiltonian in terms of an Ising model where the site occupancy variables reflect the different species involved. This is because of the extensive mathematical and computational infrastructure associated with the Ising system, which is one of the most widely studied, and whose behavior is best understood, models in computational physics [3-5, 8, 14-17].

The ABV models are also of interest in irradiated materials, to study non-equilibrium phenomena such as radiation enhanced diffusion and segregation, and indeed have been applied on numerous times in irradiation damage scenarios [11, 18-21]. However, by their very nature, ABV simulations obviate the existence of self-interstitial atoms (SIA), which are companion to vacancies during their production in the primary damage phase [22]. Neglecting SIA (as well as mixed interstitial) involvement in solute transport can often be justified when interstitial diffusion is orders of magnitude faster than that of vacancies, and - more importantly - occurs in a (quasi) one-dimensional manner. This results in a point defect imbalance when SIAs reach defect sinks on time scales that are much shorter than those associated with vacancy motion, leaving vacancies as the sole facilitators of atomic transport [18, 23]. However, in certain cases interstitials play an important role in mediating solute diffusion, and their effect can no longer be dismissed when formulating global energy models for solute transport. A case in point is the recent discovery of solute drag by so-called `bridge' interstitial configurations in W-Re/Os alloys [24], although several other examples exist [25-27]. In such cases, the ABV Hamiltonian is insufficient to capture the contribution of SIAs to microstructural evolution. This has prompted the development of cluster expansion Hamiltonians that include interstitials as well as vacancies as defect species [28-33]. To date, however, an extension of such Hamiltonians to the Ising framework has not been attempted. That is the central objective of this paper.

Here, we propose a generalization of the Ising model to ABVI systems of binary alloys subjected to irradiation. The paper is organized as follows: after this introduction, we describe our methodology in

detail in Section 2, providing a recipe to perform the ABV->ABVI extension. Subsequently, in Section 3 we provide three different verification exercises in increasing order of complexity using published works. We finalize with a brief discussion and the conclusions in Section 4.

2.0 Theory and Numerical Methods

2.1 Cluster expansion Hamiltonians for binary alloys

The most common approach to study the energetics of substitutional systems is the cluster expansion method, in which the energies of the different crystal configurations are defined by specifying the occupation of each of the N sites of a fixed crystal lattice by a number of distinct chemical species (which may include solvent and solute atoms, defects, etc.). This problem can become easily intractable, given the combinatorial nature of arranging N distinguishable atomic sites, and a number of approaches have been proposed to reduce the dimensional complexity of the problem [34-36]. A common simplification is to assume that the Hamiltonian *H* of the system can be calculated as the sum of all possible pair interactions, defined by their *bond energies*:

$$H = \sum_{\alpha,\beta} n_{\alpha-\beta} \varepsilon_{\alpha-\beta}$$
(1)

where α and β refer to a pair of lattice sites, *n* is the total number of different bond types, and ε is the energy coefficients.

Further, a binary system containing two types of atoms (matrix) A and (solute) B, as well as vacancy defects is termed the `ABV' system, for which the pairwise cluster expansion Hamiltonian (1) can be expressed as an Ising Hamiltonian of the following form [3-5, 37]:

$$H = H_0 + K \sum_{\langle i,j \rangle}^{nn} \sigma_i^2 \sigma_j^2 + U \sum_{\langle i,j \rangle}^{nn} (\sigma_i^2 \sigma_j + \sigma_j^2 \sigma_i)$$
(2)

where $\langle i,j \rangle$ refers to a pair of lattice sites i and j, and σ are the occupancy variables:

$$\sigma = \begin{cases} 1 & A \text{ (matrix)} \\ 0 & V(\text{vacancy}) \\ -1 & B(\text{solute atom}) \end{cases}$$
(3)

 H_0 in eq. (2) is a constant independent of the configuration of lattice sites. The three coefficients *K*, *U*, and *J* are:

$$K=1/4(\varepsilon_{A-A}+\varepsilon_{B-B}+2\varepsilon_{A-B})+(\varepsilon_{V-V}-\varepsilon_{A-V}-\varepsilon_{B-V})$$
$$U=1/4(\varepsilon_{A-A}-\varepsilon_{B-B})-1/2(\varepsilon_{A-V}-\varepsilon_{B-V})$$
$$J=1/4(\varepsilon_{A-A}+\varepsilon_{B-B}+2\varepsilon_{A-B})+(\varepsilon_{V-V}-\varepsilon_{A-V}-\varepsilon_{B-V})$$

These constants give an idea about the kinetic behavior of the ABV system. The second term in the r.h.s. of eq. (2) gives the relative importance of vacancies in the system. A large value of K implies low vacancy concentrations, which in the limit of one single vacancy in the crystal converges to a constant value of K'z (N/2-1), where K' = 1/4 ($\epsilon_{A-A} + \epsilon_{B-B} + 2\epsilon_{A-B}$) - ($\epsilon_{A-V} + \epsilon_{B-V}$), and z is the coordination number [5]. The asymmetry factor U determines whether there is more affinity between A atoms and vacancies or B atoms and vacancies. U > 0 indicates a preference of A-V pairs. J determines the thermodynamics of the system, with J > 0 leading to an ordered solid solution, J < 0 to a phase-separated system, and J = 0 results in an ideal solid solution. The Hamiltonian can be extended from 1st nearest neighbors (nn) to higher nn by summing over all contributions:

nn

$$H = H_{1\text{st-nn}} + H_{2\text{nd-nn}} + \dots \tag{4}$$

2.2 Generalization of the ABV Ising Hamiltonian to systems with interstitial atoms

Next, we expand eq. (2) to a system containing A and B atoms, vacancies, and interstitial atoms, which we term `ABVI'. Interstitial atoms can be of one of three distinct types, but in all cases two (otherwise substitutional) atoms share a single lattice position: AA denotes a self-interstitial atom (SIA), AB represents a mixed interstitial, and BB is a pure solute interstitial. Adding these extra species to the cluster expansion Hamiltonian results in six total species, which results in the following expression:

$$H = \sum_{\langle i,j \rangle}^{\min} \sum_{\alpha,\beta} \varepsilon_{\alpha-\beta} \lambda_i^{\alpha} \lambda_j^{\beta}$$
(5)

where α , β = A, B, V, AA, AB, BB and the occupancy variable λ_i^{α} =1 if lattice site i is occupied by type α and zero otherwise. The total number of independent terms in eq. (5) is 36. However, assuming that a pair vacancy-interstitial is unstable up to several nearest neighbor distances, we can eliminate all the _V-I_V_I (where I= AA, AB, BB) terms in the equation, thus reducing the total number of terms to 30.

In the spirit of the ABV Ising model, we assign spin variables of different types to each of the species of the Hamiltonian:

$$\sigma = \begin{cases} 2 & AA (self-interstitial atom) \\ 1 & A (matrix atom) \\ 0 & V (vacancy) and AB (mixed interstitial) \\ -1 & B (solute atom) \\ -2 & BB (solute-solute interstitial) \end{cases}$$
(6)

Although the set of spin variables for the ABVI model is not unique, the one chosen above uses the lowest-order integer possible and preserves the *magnetization* of the Ising model, *i.e.* the excess amount of solvent after the solute has been subtracted out. The convenience of choosing a zero spin variable for both the V and AB species brings about some complications in the Hamiltonian, however, which will be dealt with in Section 2.2.1.

From their definition in eq. (5), the six independent λ^{α} variables can be written in terms of the spin variables furnished in eq. (6):

$$\lambda^{AA} = \frac{1}{24} (\sigma^{4} + 2\sigma^{3} - \sigma^{2} - 2\sigma)$$

$$\lambda^{A} = \frac{1}{6} (-\sigma^{4} - \sigma^{3} + 4\sigma^{2} + 4\sigma)$$

$$\lambda^{V} = \lambda^{AB} = \frac{1}{4} (\sigma^{4} - 5\sigma^{2} + 4)$$

$$\lambda^{B} = \frac{1}{6} (-\sigma^{4} + \sigma^{3} + 4\sigma^{2} - 4\sigma)$$

$$\lambda^{AA} = \frac{1}{24} (\sigma^{4} - 2\sigma^{3} - \sigma^{2} + 2\sigma)$$
(7)

Inserting the above expressions into eq. (5) and operating, the cluster expansion Hamiltonian is transformed into a generalized Ising system with integer spins:

$$H = \sum_{\langle i,j \rangle} [C_{44}\sigma_{i}^{4}\sigma_{j}^{4} + C_{43}(\sigma_{i}^{4}\sigma_{j}^{3} + \sigma_{i}^{3}\sigma_{j}^{4}) + C_{42}(\sigma_{i}^{4}\sigma_{j}^{2} + \sigma_{i}^{2}\sigma_{j}^{4}) + C_{41}(\sigma_{i}^{4}\sigma_{j} + \sigma_{i}\sigma_{j}^{4}) + C_{33}\sigma_{i}^{3}\sigma_{j}^{3} + C_{32}(\sigma_{i}^{3}\sigma_{j}^{2} + \sigma_{i}^{2}\sigma_{j}^{3}) + C_{31}(\sigma_{i}^{3}\sigma_{j} + \sigma_{i}\sigma_{j}^{3}) + C_{22}\sigma_{i}^{2}\sigma_{j}^{2} + C_{21}(\sigma_{i}^{2}\sigma_{j} + \sigma_{i}\sigma_{j}^{2}) + C_{11}\sigma_{i}\sigma_{j} + C_{40}(\sigma_{i}^{4} + \sigma_{j}^{4}) + C_{30}(\sigma_{i}^{3} + \sigma_{j}^{3}) + C_{20}(\sigma_{i}^{2} + \sigma_{j}^{2}) + C_{10}(\sigma_{i} + \sigma_{j}) + C_{00}$$
(8)

where C_{mn} are the coefficients of the cluster expansion.

2.2.1 Corrections to the Hamiltonian to separate V and AB contributions

By construction, both vacancies and AB interstitials share $\sigma = 0$ in eq. (8), which in turn makes $\lambda_V = \lambda_{AB} = 1$ leading to miscounting of both contributions. Corrections must therefore be adopted to recover the correct energy from the Hamiltonian. These corrections can simply be subtracted from the uncorrected Hamiltonian in eq. (8) as:

$$H_{\text{corrected}} = H_{\text{uncorrected}} - [\text{correction terms}]$$
(9)

The correction terms can be readily identified on inspection of eq. (1):

$$[\text{correction terms}] = \varepsilon_{V-V} n_{AB-AB} + \varepsilon_{AB-AB} n_{V-V} + \varepsilon_{A-V} n_{A-AB} + \varepsilon_{V-B} n_{AB-B} + \varepsilon_{A-AB} n_{A-V} + \varepsilon_{AB-B} n_{V-B}$$
(10)

where n is numbers of bonds. Tracking the number of bonds in simulations takes extra computational effort, and also implies deviating from a purely Ising treatment. It is thus desirable to express n_{AB-AB} , n_{V-V} , n_{A-AB} , n_{AB-B} , n_{A-V} , and n_{V-B} as summations of powers of the spin variables, as in eq. (8). In this fashion, the correction terms do not add any additional cost to the evaluation of the Hamiltonian but, instead, only alter the value of the coefficients in eq. (8). First, however, we must obtain expressions for all $n_{\alpha-\beta}$ in terms of the spin variable σ .

After discounting the n_{V-I} terms (with I=AA, AB, BB), there are 18 $n_{\alpha-\beta}$ and therefore 18 independent equations are needed. 10 of them can be obtained from the summations of σ -polynomials:

$$\sum \sigma_i \sigma_j = 4n_{AA-AA} + 2n_{AA-A} - 2n_{AA-B} - 4n_{AA-BB} + n_{A-A} - n_{A-B} - 2n_{A-BB} + n_{B-B} + 2n_{B-BB} + 4n_{BB-BB}$$
(11)

$$\sum \sigma_i^2 \sigma_j + \sigma_i \sigma_j^2 = 16n_{AA-AA} + 6n_{AA-A} - 2n_{AA-B} + 2n_{AA-BB} + 2n_{A-A} + 2n_{A-BB}$$

$$-2n_{B-B} - 6n_{B-BB} - 16n_{BB-BB}$$
(12)

$$\sum \sigma_i^2 \sigma_j^2 = 16n_{AA-AA} + 4n_{AA-A} + 4n_{AA-B} + 16n_{AA-BB} + n_{A-A} + n_{A-B} + 4n_{A-BB} + n_{B-B} + 4n_{B-BB} + 16n_{BB-BB}$$
(13)

$$\sum \sigma_i^3 \sigma_j + \sigma_i \sigma_j^3 = 32n_{AA-AA} + 10n_{AA-A} - 10n_{AA-B} - 32n_{AA-BB} + 2n_{A-A} - 2n_{A-B} + 10n_{A-BB} + 2n_{B-B} + 10n_{B-BB} + 32n_{BB-BB}$$
(14)

$$\sum \sigma_i^3 \sigma_j^2 + \sigma_i^2 \sigma_j^3 = 64n_{AA-AA} + 12n_{AA-A} + 4n_{AA-B} + 2n_{A-A} + -4n_{A-BB} - 2n_{B-B} - 12n_{B-BB} - 64n_{BB-BB}$$
(15)

$$\sum \sigma_i^3 \sigma_j^3 = 64n_{AA-AA} + 8n_{AA-A} - 8n_{AA-B} - 64n_{AA-BB} + n_{A-A} - n_{A-B} - 8n_{A-BB} + n_{B-B} - 8n_{B-BB} + 64n_{BB-BB}$$
(16)

$$\sum \sigma_i^4 \sigma_j + \sigma_i \sigma_j^4 = 64n_{AA-AA} + 18n_{AA-A} - 14n_{AA-B} + 2n_{A-A} + 14n_{A-BB} - 2n_{B-B} - 18n_{B-BB} - 64n_{BB-BB}$$
(17)

$$\sum \sigma_i^4 \sigma_j^2 + \sigma_i^2 \sigma_j^4 = 128n_{AA-AA} + 20n_{AA-A} + 20n_{AA-B} + 128n_{AA-BB} + 2n_{A-A} + 2n_{A-B} + 20n_{A-BB} + 2n_{B-B} + 20n_{B-BB} + 128n_{BB-BB}$$
(18)

$$\sum \sigma_i^4 \sigma_j^3 + \sigma_i^3 \sigma_j^4 = 256n_{AA-AA} + 24n_{AA-A} - 8n_{AA-B} + 2n_{A-A} + 8n_{A-BB} - 2n_{B-B} - 24n_{B-BB} - 256n_{BB-BB}$$
(19)

$$\sum \sigma_i^4 \sigma_j^4 + \sigma_i^4 \sigma_j^4 = 256n_{AA-AA} + 16n_{AA-A} + 16n_{AA-B} + 256n_{AA-BB} + n_{A-A} + n_{A-B} + 16n_{A-BB} + n_{B-B} + 16n_{B-BB} + 256n_{BB-BB}$$
(20)

However, the above equations do not contain any $n_{\alpha-\beta}$ with α or β = V, AB. Six more equations that do contain these terms can be obtained by counting numbers of six species N_{α} :

$zN_{AA} = 2n_{AA-AA} + n_{AA-A} + n_{AA-AB} + n_{AA-B} + n_{AA-BB}$	(21)
$zN_A = n_{AA-A} + 2n_{A-A} + n_{A-V} + n_{A-AB} + n_{A-B} + n_{A-BB}$	(22)
$zN_{\rm V} = n_{\rm A-V} + 2n_{\rm V-V} + n_{\rm V-B}$	(23)
$zN_{AB} = n_{AA-AB} + n_{A-AB} + 2n_{AB-AB} + n_{AB-B} + n_{AB-BB}$	(24)
$zN_B = n_{AA\text{-}B} + n_{A\text{-}B} + n_{V\text{-}B} + n_{AB\text{-}B} + 2n_{B\text{-}B} + n_{B\text{-}BB}$	(25)
$\mathcal{Z}N_{BB} = n_{AA-BB} + n_{A-BB} + n_{AB-BB} + n_{B-BB} + 2n_{BB-BB}$	(26)

where z is the coordination number. Combining eqs. (11) through (26), we have 16 equations with 18 unknowns. In order to solve the system, we express everything parametrically in terms of two bond numbers, nAB-A and nAB-B^{*}, and solve for the rest of the $n_{\alpha-\beta}$. n_{AB-A} and n_{AB-B} are then the only bond numbers that must be calculated on the fly in the kMC simulations.

2.2.2 The corrected Ising Hamiltonian

After solving for all $n_{\alpha-\beta}$, the corrected Hamiltonian can be obtained by substituting eq. (10) into eq. (9). Except for an additional term C₀, the final expression of the corrected Hamiltonian is the same as the uncorrected one in eq. (8). However, the coefficients Cmn are now `corrected' to account for the AB/V

conflict. Based on the physical characteristics of each coefficient, each term in the Hamiltonian of the ABVI system can be grouped into three different configurational classes and one non-configurational group:

* This choice is justified both by the fact that neither A-AB nor AB-B bonds are very likely to appear in the simulations, and because - as will pointed out below - AB interstitially jumps are the likeliest to change the global concentration of species, which results in the need to update the non-configurational constants in the ABVI Hamiltonian (cf. eq. (27)).

$$\begin{split} H_{\text{corrected}} &= \sum_{\langle i,j \rangle}^{nn} \left[C_{44} \sigma_{i}^{4} \sigma_{j}^{4} + C_{42} \left(\sigma_{i}^{4} \sigma_{j}^{2} + \sigma_{i}^{2} \sigma_{j}^{4} \right) + C_{22} \sigma_{i}^{2} \sigma_{j}^{2} \right] + \quad (\text{class 1}) \\ &+ \sum_{\langle i,j \rangle}^{nn} \left[C_{43} \left(\sigma_{i}^{4} \sigma_{j}^{3} + \sigma_{i}^{3} \sigma_{j}^{4} \right) + C_{41} \left(\sigma_{i}^{4} \sigma_{j} + \sigma_{i} \sigma_{j}^{4} \right) + C_{32} \left(\sigma_{i}^{3} \sigma_{j}^{2} + \sigma_{i}^{2} \sigma_{j}^{3} \right) \right. \\ &+ C_{21} \left(\sigma_{i}^{2} \sigma_{j} + \sigma_{i} \sigma_{j}^{2} \right) \right] + \qquad (\text{class 2}) \\ &+ \sum_{\langle i,j \rangle}^{nn} \left[C_{33} \sigma_{i}^{3} \sigma_{j}^{3} + C_{31} \left(\sigma_{i}^{3} \sigma_{j} + \sigma_{i} \sigma_{j}^{3} \right) + C_{11} \sigma_{i} \sigma_{j} \right] + \qquad (\text{class 3}) \\ &+ \sum_{\langle i,j \rangle}^{nn} \left[C_{40} \left(\sigma_{i}^{4} + \sigma_{j}^{4} \right) + C_{30} \left(\sigma_{i}^{3} + \sigma_{j}^{3} \right) + C_{20} \left(\sigma_{i}^{2} + \sigma_{j}^{2} \right) + C_{10} \left(\sigma_{i} + \sigma_{j} \right) + C_{00} \right] \\ &+ C_{0} \qquad (\text{Non - configurational}) \qquad (27) \end{split}$$

Where the coefficients C_{mn} are:

Class 1

$$\begin{aligned} C_{44} &= \{(\epsilon_{AA-AA} - 8\epsilon_{AA-A} - 8\epsilon_{AA-B} + 2\epsilon_{AA-BB} - 8\epsilon_{A-BB} - 8\epsilon_{B-BB} + \epsilon_{BB-BB}) + (12\epsilon_{AA-AB} - 12\epsilon_{AB-AB} + 12\epsilon_{AB-BB}) + (-48\epsilon_{A-V} + 48\epsilon_{V-V} - 48\epsilon_{V-B}) + (16\epsilon_{A-A} + 32\epsilon_{A-B} + 16\epsilon_{B-B})\}/576 \\ C_{42} &= \{(-\epsilon_{AA-AA} + 20\epsilon_{AA-A} + 20\epsilon_{AA-B} - 2\epsilon_{AA-BB} - 20\epsilon_{A-BB} + 20\epsilon_{B-BB} - \epsilon_{BB-BB}) + (-36\epsilon_{AA-AB} + 36\epsilon_{AB-AB} - 36\epsilon_{AB-BB}) + (216\epsilon_{A-V} - 216\epsilon_{V-V} + 216\epsilon_{V-B}) + (-64\epsilon_{A-A} - 128\epsilon_{A-B} - 64\epsilon_{B-B})\}/576 \\ C_{22} &= \{(\epsilon_{AA-AA} - 32\epsilon_{AA-A} - 32\epsilon_{AA-B} + 2\epsilon_{AA-BB} - 32\epsilon_{A-BB} - 32\epsilon_{B-BB} + \epsilon_{BB-BB}) + (60\epsilon_{AA-AB} - 60\epsilon_{AB-AB}) + (-960\epsilon_{A-V} + 960\epsilon_{V-V} - 960\epsilon_{V-B}) + (256\epsilon_{A-A} + 512\epsilon_{A-B} + 256\epsilon_{B-B})\}/576 \\ C_{1ass} 2 \\ C_{43} &= \{(\epsilon_{AA-AA} - 6\epsilon_{AA-A} - 2\epsilon_{AA-B} + 2\epsilon_{A-BB} + 6\epsilon_{B-BB} - \epsilon_{BB-BB}) + (6\epsilon_{AA-AB} - 6\epsilon_{AB-BB}) + (-12\epsilon_{A-V} + 12\epsilon_{V-B}) + (8\epsilon_{A-A} - 8\epsilon_{B-B})\}/288 \\ C_{41} &= \{(-\epsilon_{AA-AA} + 12\epsilon_{AA-A} - 4\epsilon_{AA-B} + 4\epsilon_{A-BB} - 12\epsilon_{B-BB} + \epsilon_{BB-BB}) + (-6\epsilon_{AA-AB} + 6\epsilon_{AB-BB}) + (-30\epsilon_{AA-AB} + 30\epsilon_{AB-AB}) + (-32\epsilon_{AA-A} + 14\epsilon_{AA-A} - 14\epsilon_{A-B} - 14\epsilon_{A-BB} - 18\epsilon_{B-BB}) + (-30\epsilon_{AA-AB} + 4\epsilon_{A-AB} + 4\epsilon_{A-BB} - 12\epsilon_{B-BB} + \epsilon_{BB-BB}) + (-30\epsilon_{AA-AB} + 4\epsilon_{A-AB} + 32\epsilon_{B-B})\}/288 \\ C_{32} &= \{(-\epsilon_{AA-AA} + 18\epsilon_{AA-A} + 14\epsilon_{AA-B} - 14\epsilon_{A-BB} - 18\epsilon_{B-BB} + \epsilon_{BB-BB}) + (-30\epsilon_{AA-AB} + 6\epsilon_{AB-AB}) + (-30\epsilon_{AA-AB} + 32\epsilon_{B-B})\}/288 \\ C_{32} &= \{(-\epsilon_{AA-AA} + 18\epsilon_{AA-A} + 14\epsilon_{AA-B} - 14\epsilon_{A-BB} - 18\epsilon_{B-BB} + \epsilon_{BB-BB}) + (-30\epsilon_{AA-AB} + 6\epsilon_{AB-AB}) + (-30\epsilon_{AA-AB} + 32\epsilon_{B-B})\}/288 \\ \end{array}$$

 $C_{21} = \{ (\epsilon_{AA-AA} - 24\epsilon_{AA-A} - 8\epsilon_{AA-B} + 8\epsilon_{A-BB} + 24\epsilon_{B-BB} - \epsilon_{BB-BB}) + (30\epsilon_{AA-AB} - 30\epsilon_{AB-BB}) + (-240\epsilon_{A-V} + 240\epsilon_{V-B}) + (128\epsilon_{A-A} - 128\epsilon_{B-B}) \} / 288$

Class 3

 $C_{33} = \{(\epsilon_{AA-AA} - 4\epsilon_{AA-A} + 4\epsilon_{AA-B} - 2\epsilon_{AA-BB} + 4\epsilon_{A-BB} - 4\epsilon_{B-BB} + \epsilon_{BB-BB}) + (4\epsilon_{A-A} - 8\epsilon_{A-B} + 4\epsilon_{B-B})\}/144$

 $C_{31} = \{(-\epsilon_{AA-AA} + 10\epsilon_{AA-A} - 10\epsilon_{AA-B} + 2\epsilon_{AA-BB} - 10\epsilon_{A-BB} + 10\epsilon_{B-BB} - \epsilon_{BB-BB}) + (-16\epsilon_{A-A} + 32\epsilon_{A-B} - 16\epsilon_{B-B})\}/144$

 $C_{33} = \{(\epsilon_{AA-AA} - 16\epsilon_{AA-A} + 16\epsilon_{AA-B} - 2\epsilon_{AA-BB} + 16\epsilon_{A-BB} - 16\epsilon_{B-BB} + \epsilon_{BB-BB}) + (64\epsilon_{A-A} - 128\epsilon_{A-B} + 64\epsilon_{B-B})\}/144$

Non-Configurational

$$\begin{split} &C_{40} = \{(\epsilon_{AA-AB} + \epsilon_{AB-BB}) + (-4\epsilon_{A-AB} + 6\epsilon_{AB-AB} - 4\epsilon_{AB-B}) + (-4\epsilon_{A-V} + 6\epsilon_{V-V} - 4\epsilon_{V-B}) \} / 24 \\ &C_{30} = \{(\epsilon_{AA-AB} - \epsilon_{AB-BB}) + (-2\epsilon_{A-AB} + 2\epsilon_{AB-B}) + (-2\epsilon_{A-V} + 2\epsilon_{V-B}) \} / 12 \\ &C_{20} = \{(-\epsilon_{AA-AB} - \epsilon_{AB-BB}) + (16\epsilon_{A-AB} - 30\epsilon_{AB-AB} + 16\epsilon_{AB-B}) + (16\epsilon_{A-V} - 30\epsilon_{V-V} + 16\epsilon_{V-B}) \} / 24 \\ &C_{10} = \{(-\epsilon_{AA-AB} + \epsilon_{AB-BB}) + (8\epsilon_{A-AB} - 8\epsilon_{AB-B}) + (8\epsilon_{A-V} - 8\epsilon_{V-B}) \} / 12 \\ &C_{00} = (\epsilon_{AB-AB} + \epsilon_{V-V}) \\ &C_{0} = n_{AB-B} / 2(-\epsilon_{AB-AB} + 2\epsilon_{A-AB} - 2\epsilon_{A-V} + \epsilon_{V-V}) + n_{AB-B} / 2(-\epsilon_{AB-AB} + 2\epsilon_{AB-B} - 2\epsilon_{V-B} + \epsilon_{V-V}) \\ &+ Z / 2[N_A(\epsilon_{AB-AB} - 2\epsilon_{A-AB}) + N_B(\epsilon_{AB-AB} - 2\epsilon_{AB-B})] - Z / 2[N_V \epsilon_{AB-AB} + N_{AA} \epsilon_{V-V} - N_{AB} \epsilon_{V-V} + N_{BB} \epsilon_{V-V}] \end{split}$$

This way of grouping the Cmn is not unique. We have chosen the three classes above to represent a given physical behavior along the lines of the coefficients K, U, J of the ABV Ising model. Loosely speaking, the physical meanings of each of the three classes are as follows:

- Class 1 (even-even power terms) gives the relative importance of interactions between point defects (vacancies and interstitials).
- Class 2 (even-odd power terms) gives the Annity between atoms and point defects.
- Class 3 (odd-odd power terms) determines the equilibrium phase diagram.

In the standard ABV model, defect (vacancy) hops do not change the global species concentrations. That means that the non-configurational class of terms in the Hamiltonian (27) does not change merely by vacancy jumps. However, the ABVI model now allows for defect transitions that change the global balance of species and in our case, there are two types of transitions that affect the species concentrations when they occur. The first one involves vacancy-interstitial re-combinations:

 $AA+V \rightarrow A + A$ $AB+V \rightarrow A + B$ $BB+V \rightarrow B + B$

The second type is related to the interstitially mechanism, by which an interstitial atom displaces an atom from an adjacent lattice position so that it becomes the interstitial in its turn, able to displace another atom. This mechanism includes four and the most obvious one being a vacancy-interstitial recombination.

Reactions:

 $AA + B \rightarrow A + AB$ $AB + A \rightarrow B + AA$ $AB + B \rightarrow A + BB$ $BB + A \rightarrow B + AB$

Except when one of the above reactions occurs, the incremental energy formulation used to compute energy differences between the initial and final states allows us to discard the C_0 during calculations. In order to truly represent a generalized Hamiltonian, the ABVI model Hamiltonian must reduce to the AV and ABV models in their respective limits (AV: no solute, vacancies; ABV: solute plus vacancies). Indeed, we have conducted verification tests of both particular cases and we have found matching results. This is the subject of Sec. 3, where we have simulated the time evolution of ABV and ABVI systems using the generalized Hamiltonian presented above. Our method of choice is kinetic Monte Carlo (kMC), which we describe in detail in the following section.

2.3 Kinetic Monte Carlo Simulation

In this section we discuss relevant details of the kMC simulation method in relation to our extended ABVI model. All simulations are conducted on a rigid lattice generated from monoclinic representations of face-centered cubic (FCC) and body-centered cubic (BCC) crystals. 2x2x2 unite cells for FCC and BCC crystal structures are provided in Figure 1. The simulations are generally conducted in the grand canonical ensemble, to allow for irradiation damage simulations when required. All kinetic transitions are assumed to be due to defect hops. In particular, we consider the vacancy and interstitially mechanisms to enable atomic transport. After every transition, the configuration of the system is updated and a new transition is considered.



Figure 1: Crystal 2x2x2 cells for (a) FCC and (b) BCC lattices employed here. The vectors a1, a2, and a3 are primitive basis of crystal.

2.3.1 Residence-time algorithm

We use the residence-time algorithm (RTA) [38] to track the kinetic evolution of the system through a series of thermally activated transitions. The transition rates R_{ij} connecting an initial state i to a final state j are calculated as:

$$r_{ij} = v \exp\left(-\frac{\Delta E_{ij}}{k_{\rm B}T}\right) \tag{28}$$

where $\Delta E_{ij} > 0$ is an activation energy that will be discussed below, v is the attempt frequency, and 1=kBT is the reciprocal temperature. With the system in configuration i, an event is randomly chosen with a probability proportional to its rate, and the time advanced per kMC step is on average $\delta t_i = (\Sigma_j r_{ij})^{-1}$. In addition to thermally activated transitions such as those represented by eq. (28), we consider spontaneous events - for which, formally, ΔE_{ij} may be negative - such as recombination between vacancies and interstitials, absorption at sinks, etc. These events occur instantaneously with $\delta t = 0$.

2.3.2 Activation energy models

There are several models proposed to describe the activation energy, which are based on different interpretations of the atomic migration process (see for e.g., [32] for a recent review). The first model is the so-called saddle-point energy model (also known as `cut-bond' model in [11]) [10,18,39]. The activation energy is given by:

$$\Delta E_{ij} = E_{XY}^{SP} - \sum_{n} \varepsilon_{X-n} - \sum_{p \neq X} \varepsilon_{Y-p}$$
(29)

where Y refers to the defect (e.g. a vacancy), and X to the atom exchanging positions with Y. The later two summations are the bonding energies between X, Y and the adjacent neighbor sites n and p. In this model, the energy barrier is calculated as the difference between the energy of the system at the saddle point and that of the initial state, symbolized by the two summations in the r.h.s. of eq. (29). These summations can be computed using the ABVI Ising Hamiltonian formulas described in Section 2.1. The saddle-point energy ESP XY is generally taken to be a constant [18], or is computed as a especial sum of bond energies of the jumping atom at the saddle point: $E_{XY}^{SP} = \sum_{q} \epsilon_{Xa}^{SP,Y}$ [10, 39].

The second model is the so-called kinetic Ising model [12,40] (or final-initial system energy, as is referred to by Vincent et al. [11]). In this model, the activation energy is dependent on the energy difference of the system Δ Hij between the initial i and final states j, as well as a migration energy E_m, which is a constant determined by the type of defect-atom exchange. Two different forms of activation energy are proposed within this model. The first form is given by [12]:

$$\Delta E_{ij} = \begin{cases} E_m + \Delta H_{ij}, & \text{if } \Delta H_{ij} > 0\\ E_m, & \text{if } \Delta H_{ij} < 0 \end{cases}$$
(30)

This form assumes that the energy barrier of transitions from higher to lower energy states is the migration energy E_m , and $E_m + \Delta H_{ij}$ otherwise. An alternative, which is used in this work, is given by [11, 40]:

$$\Delta E_{ij} = E_m + \frac{\Delta H_{ij}}{2} \tag{31}$$

In this case, the migration energy is considered to be the energy difference between the saddle point and the average energy between states i and j, $Em = E^{SP} - (H_i + H_j)/2$. This definition of E_m results in an expression for ΔE_{ij} that does not depend of the final state energy H_j . The schematic diagram of the activation energy models is shown in Figure 2. It can be shown that all the three activation energy models satisfy the detailed balance condition, i.e.:

$$\frac{r_{ij}}{r_{ji}} = \exp\left(-\frac{\Delta H_{ij}}{k_{\rm B}T}\right) \tag{32}$$

The different characteristics of each of these models have been discussed in detail by Soisson et al. [32]. In the saddle-point energy model, the height of the energy barrier is not dependent on the energy of the final state, which agrees with the theory of thermally- activated processes. Also, the energy barrier dependence on configurations can be fitted directly from empirical potentials or ab initio calculations. For its part, the kinetic Ising model assumes that the migration energy depends on the average of the energy difference between the initial and final states. This approach links the energy barrier to the local chemical environment, with the advantage that no knowledge of the saddle-point energy is required. In this case, the dependence of energy barrier can be easily fitted to more than just 1st-nn (which is the extent of the broken-bond model). It is also possible to evaluate energy barrier of events other than defect jumps such as recombination and surface reactions (defect annihilation and vacancy creation), described below in Sec. 2.3.4.



Figure 2: The three different models of activation energy.

2.3.3 Computing bond energies from electronic-structure calculations

Bond energies to parameterize eq. (27) and associated constants C_{mn} can be calculated using a suitable atomistic force fields such as semi-empirical potentials, density-functional theory (DFT, etc. Considering 2nd-nn interactions, the following parameters can be used to write a set of equations from which to calculate the bond energies:

• The cohesive energy of the pure metal A or B can be written as:

$$E_{A}^{\alpha} = -\frac{z_{1}}{2}\varepsilon_{A-A}^{(1)} - \frac{z_{2}}{2}\varepsilon_{A-A}^{(2)}$$
(33)

$$E_{\rm B}^{\alpha} = -\frac{z_1}{2} \varepsilon_{\rm B-B}^{(1)} - \frac{z_2}{2} \varepsilon_{\rm B-B}^{(2)}$$
(34)

where z_1 and z_2 are coordination numbers of the first and second nearest neighbor shells, and the super index ⁽ⁱ⁾ refers to the nn shell. Care must be exercised when computing each cohesive energy to ensure that the crystal lattice corresponds to the equilibrium crystal lattice at the desired temperature.

 The pair interactions between an A atom and a B atom ε_{A-B} can be obtained from the enthalpy of mixing:

$$E_{\rm mix} = -\frac{z_1}{2} (\epsilon_{\rm A-A}^{(1)} + \epsilon_{\rm B-B}^{(1)} - 2\epsilon_{\rm A-B}^{(1)}) - \frac{z_2}{2} (\epsilon_{\rm A-A}^{(2)} + \epsilon_{\rm B-B}^{(2)} - 2\epsilon_{\rm A-B}^{(2)})$$
(35)

 The formation energy of vacancy is calculated by removing an atom from a perfect lattice position and placing it at the physical limits of the system. For a vacancy in a perfect A-atom matrix containing N lattice sites:

$$E_{f}^{V} = NE_{coh}^{A} - (N-1)E_{coh}^{A} - z_{1}\varepsilon_{A-V}^{(1)} - z_{2}\varepsilon_{A-V}^{(2)}$$
(36)

• Similarly, the formation energy of an interstitial pair in an A-atom matrix can be written as:

$$E_{f}^{I} = E_{coh}^{A} - z_{1} \varepsilon_{A-I}^{(1)} - z_{2} \varepsilon_{A-I}^{(2)}$$
(37)

where I= AA, AB, BB.

2.3.4 Events

In kMC the kinetic evolution is determined by a series of independent events that represent state transitions. Within the ABVI model, we consider events mediated by point defect mechanisms, In this work, we consider five distinct types of events, which we discuss below.

(i) Defect jumps: vacancies move by exchanging positions with one of the $z_1 1^{st}$ nn atoms:

$$V + a -> a + V$$

where a=A, B. Interstitials, for the part, move via the interstitially mechanism introduced above. Interstitials are assumed to be of the dumbbell or crowdion structure, i.e. two atoms sharing one lattice site:

$$I(a_1-a_2) + a_1 -> a_1 + I(a_2-a_1)$$

where an interstitial composed of two atoms a1 and a2 (a_1 , $a_2=A,B$) jumps into a neighboring lattice site occupied by atom a1, giving rise to a new interstitial composed of atoms a_2 and a_1 .

(ii) Recombination: when a vacancy and an interstitial within a distance less than a critical distance r_c , a recombination event occurs. The generic reaction is:

$$I(a_1-a_2) + V \rightarrow a_1 + a_2$$

Re-combinations events occur spontaneously, with $\delta t = 0$.

(iii) Annihilation at defect sinks: in this work two types of defect sinks are used. The first one is a perfect, artificial defect sink, as suggested by Soisson [29]. A thin slab of the simulation box is designated to act as a perfect defect sink (a simple model of grain boundary). When a defect jumps into a lattice position belonging to the slab, it instantly disappears. To preserve the alloy composition, a `reservoir' is used such that when a vacancy is absorbed at the sink, an atom is randomly chosen from the reservoir and placed at the sink site; for interstitials, one of the two atoms is randomly chosen and stored in the reservoir; the other atom remains on the sink site. Another inexhaustible sink is a free surface. The lattice beyond the free surface is considered to be part of a `vacuum' such that atoms adjacent to vacuum lattice sites are defined as `surface atoms'. When a vacancy jumps onto a site occupied by a surface atom, it first switches its position with the atom, and then the vacancy becomes a vacuum site:

$$V + a_s \rightarrow a_s + v$$

where a_s refers to a surface atom, and v is a vacuum site. The mechanism for interstitial annihilation is more complex. When an interstitial jumps onto a surface atom site, an instantaneous recombination between the interstitial and the vacuum site occurs (vacuum sites are a special class of vacancies). The reaction can be described as:

 $I(a_1-a_2) + v \rightarrow a_1 + a_2$

(iv) Thermal vacancy emission: when surfaces, grain boundaries, dislocations, etc., are present they can act as thermal sources of defects. Due to the relatively high energy of interstitial defects compared to vacancies, interstitial emission is often considered negligible. A thermal emission can be regarded as the inverse of a vacancy annihilation event. For a free surface, a vacancy is created just below the surface by having a vacuum site exchange positions with a surface atom:

$$v + a_s -> a_s + V$$

The rate of vacancy emission can become sizable at high temperature, and should not be discarded as an efficient vacancy generation mechanism with a strong effect on the system kinetics.

(v) Frenkel pair generation: when considering irradiation with light particles (e.g., electrons), V-I pairs are generated in the lattice. As implemented in our method, when a Frenkel pair insertion occurs, two lattice sites are randomly chosen, one becomes a vacancy and the other becomes an interstitial formed by the two atoms involved:

$$a_1 + a_2 \rightarrow V + I(a_1 - a_2)$$

Frenkel pairs are introduced at a rate consistent with the imposed irradiation dose rate (usually measured in displacements per atom per second, or dpa/s). A compilation of all the reactions and events discussed in this section is provided in Table 1.

Table 1: Event reactions considered in this work. V: vacancy, A: matrix atom, B: solute atom, AA: selfinterstitial, AB: mixed interstitial, BB: pure solute interstitial, v: vacuum atom, As: surface matrix atom,Bs: surface solute atom.

Vacancy jumps	Interstitial jumps	Recombinations	Frenkel pair generation
V+A->A+V	AA+A->A+AA	AA+V->A+A	A+A->AA+V
V+B->A+B	AA+B->B+AA	AB+V->A+B	A+B->AB+V
	BB+A->B+AB	BB+V->B+B	B+B->BB+V
	BB+B->B+BB		
	$AB + A \rightarrow \begin{cases} A + AB \\ B + AA \end{cases}$		
	$AB + B \rightarrow \begin{cases} A + BB \\ B + AB \end{cases}$		

Defect an	Thermal emission		
Ideal sink	Surface	Thermal emission	
V->A	$V+A_s->A_s+v$	$v + A_s - >A_s + V$	
V->B	$V+B_s->B_s+\nu$	$\nu + B_s - > B_s + V$	
AA->A	$AA+v \rightarrow A+A_s$		
BB->B	$BB+\nu \rightarrow B+B_s$		
$AB \rightarrow \begin{cases} A \\ B \end{cases}$	$AB + v \rightarrow \begin{cases} A + B_s \\ B + A_s \end{cases}$		

3.0 Results

This section consists of various verification checks undertaken to ensure the correctness of our approach. The first tests are designed to check the `downward' consistency of our model, i.e. comparing against AV and ABV models with reduced complexity w.r.t. the ABVI Hamiltonian*. Subsequently, we compare our method with KMC simulations of three different ABVI systems published in the literature. In all simulations, atoms are initially assigned randomly to lattice sites so as to achieve a perfect solid solution as a starting configuration.

*The AV case – as studied by Reina et al. [12] – was trivially reproduced by our method, and for brevity we omit any further discussion on it.

3.1 ABV system: Precipitation of Fe-Cu alloys

First we simulate the system considered by Vincent et al. [11]: a Fe-0.6% at. Cu alloy occupying a periodic BCC lattice arranged into a rhombic computational box with 80x80x80 primitive cells containing 512000 atoms and a single vacancy, which has similar box size of Vincent et al. work. The Hamiltonian includes 2nd-nn interactions with energy coefficients given in Table 2. The energies of mixing for 1st and 2nd-nn are 0.26 and 0.24 eV, which suggest a strong tendency toward phase separation [41]. The temperature is fixed at 773 K. During the simulations, the vacancy may become trapped in solute precipitates, which does not lead to any further microstructural evolution and stalls the simulations. To correct for this, Vincent et al. proposed to increment the kMC time only when the vacancy is surrounded by at most one solute atom. As well, to account for an unrealistically high vacancy concentration, the kMC time step was rescaled according to:

$$\delta t = \frac{C_V^0}{C_V^{kMC}} \delta t_{kMC}$$
(38)

where $C_V^0 = \exp(-E_f^V/k_BT)$ is the thermodynamic vacancy concentration. However,

Vincent et al. adjust their kMC time by comparing the kinetic evolution directly with experiments. By way of example, they matched a cluster mean radius of 0.9 nm in their to a time of 7200 s. For consistency, we adopt the same approach here. The initial and final configurations are shown in Figure 3. The kinetic evolution of precipitation is quantified by calculating the cluster mean radius of solute atoms as a function of time. It is assumed that a B atom belongs to a cluster if one of its 1st-nn is also a B atom of the cluster. The cluster size is computed from the expression [9]:

$$\overline{R} = a_0 \left(\frac{3N}{8\pi}\right)^{\frac{1}{3}}$$
(39)

which assumes a spherical cluster shape, and where \bar{R} is the cluster mean radius, N is the number of solute atoms in the cluster, and a0 is the lattice constant of the BCC lattice. As in ref. [11], clusters containing three or less atoms are not counted towards the calculation of \bar{R} . Figure 4 shows our data compared to those of Vincent et al. At about 10^5 s, a transition in \bar{R} occurs, where the cluster size grows abruptly before leveling off at longer times. Although our model captures the timescale of \bar{R} , a factor of 1.6 was found among our data and theirs. This may be due to different cluster mean radius calculation methods or an unspecified shift in the results in order to fit the experimental data.

 Table 2. Bond energies for the Fe-Cu ABV system. A represents Fe atoms, B Cu atoms, and V is the vacancy.

	ot					
1 st -nn interactions (eV)				Migration e	energy (eV)	
$\mathcal{E}_{A-A}^{(1)}$	$\mathcal{E}_{A-B}^{(1)}$	$arepsilon_{B-B}^{(1)}$	$\varepsilon_{A-V}^{(1)}$	$arepsilon_{B-V}^{(1)}$	E_m^{V-A}	E_m^{V-B}
-0.611	-0.480	-0.414	-0.163	-0.102	0.62	0.54
2 nd -nn interactions (eV)			Jump freq	uency (s^{-1})		
$\varepsilon_{A-A}^{(2)}$	$\varepsilon_{A-B}^{(2)}$	$\varepsilon_{B-B}^{(2)}$	$\varepsilon_{A-V}^{(2)}$	$\varepsilon_{B-V}^{(2)}$	ν_A^V	$ u_B^V $
-0.611	-0.571	-0.611	-0.163	-0.180	$6 \ge 10^{12}$	$6 \ge 10^{12}$



Figure 3. Initial (a), t = 0, and final (b), t = 28368 s alloy configurations. The red dots represent solute atoms (B atoms). Solvent atoms and the vacancy are omitted for clarity.



Figure 4. The cluster mean radius of the ABV Fe-Cu system. The red line represents the results in this work; the black filled squares are the data from Vincent et al. [11]

3.2 ABVI system: Solute segregation at sinks

In this test, we reproduce the work of Soisson et al. [29]. The system consists of a BCC 256x64x64 rhombic crystal lattice containing an A-5%B alloy, vacancies and interstitials defects. A perfect planar defect sink is placed in the middle of the crystal and kMC simulations of (radiation-induced) segregation at the defect sink are performed. Frenkel pairs are generated at a rate of $G = 10^{-6}$ dpa/s following the mechanism described in Sec. 2.3.4.

Segregation at the sinks is governed by the onset of solute fluxes in the system. These fluxes are mediated by defect migration to and absorption at the sink. The solute flux can be controlled by setting the defect migration energies such that exchanges with B atoms are preferred over exchanges with A atoms (or vice versa), resulting in enrichment or depletion of solute at the defect sink. While Soisson et al. use a saddle-point model to obtain the activation energy (cf. Sec. 2.3.2), here we employ a kinetic Ising model, and so in order to make our model as close to theirs as possible, we use their bond energies directly and adjust the migration energies E_m so as to match the kinetic evolution. The parameters used are shown in Table 3. There are four sets of parameters. The first two, ABVI-1 and ABVI-2, correspond to a system with relatively low energy of mixing ($E_{mix} = 0.216 \text{ eV}$), representing under saturated solid solutions with high solubility limits. The other two, ABVI-3 and ABVI-4 correspond to a system with E_{mix} = 0.680 eV leading to supersaturated solid solutions. Systems ABVI-1 and ABVI-3 E_m are set to have a net flux of B atoms accumulating at the sink ($E_m^{V-A} < E_m^{V-B}$; ($E_m^{I-A} >$ E^{I-B}_m), whereas ABVI-2 and ABVI-4 result in solute depletion at the sink – known as inverse Kirkendall effect –($E_m^{V-A} > E_m^{V-B}$; ($E_m^{I-A} < E_m^{I-B}$). For simplicity, migration energies of vacancies and interstitials are set to produce the same segregation tendency for each set of parameters. Other details considered by Soisson et al., such as recombination radii, event sampling, etc., are also followed here[#]. The spatial solute concentration profiles are shown in Figure 5.

Table 3. Parameters for the ABVI system (after Soisson et al. [29]). `A' and `B' denote solvent andsolute atoms, respectively. `V' represents vacancies and `I' all types of interstitial defects. All energiesgiven in eV. Attempt frequencies given in Hz.

	ABVI-1	ABVI-2	ABVI-3	ABVI-4
Kinetic parameters	high solubility		low solubility	
	enrichment	depletion	enrichment	depletion
$\nu_A^V = \nu_A^V = \nu_A^V = \nu_A^V$	5×10^{15}	5×10^{15}	5×10^{15}	5×10^{15}
$\varepsilon_{A-A} = \varepsilon_{B-B}$	-1.07	-1.07	-1.07	-1.07
ε _{A-B}	-1.043	-1.043	-0.985	-0.985
$\varepsilon_{A-V} = \varepsilon_{B-V}$	-0.3	-0.3	-0.3	-0.3
$\varepsilon_{A-I} = \varepsilon_{B-I}$	0	0	0	0
E ^{V-A}	0.95	1.1	0.8	1.05
E ^{V-B}	1.05	0.9	1.2	0.95
E _m ^{I-A}	0.5	0.35	0.55	0.2
E _m ^{I-B}	0.5	0.65	0.45	0.8

#With one exception: the Frenkel pair distance is not set in this work.



Figure 5. Spatial solute concentration profiles at different doses for the under saturated alloy for the (a) solute enrichment and (b) solute depletion cases at T = 800 K. The supersaturate case for (c) solute enrichment and (d) solute depletion at the same temperature are also shown. The nominal solute concentration of the alloy is $C_B = 0.05$ and the dose rate is 10^{-6} dpa/s.

In the under saturated alloy, no precipitation in the bulk is observed. As the dose increases, the concentration of B atoms near the sink is enhanced (reduced) for the enrichment (depletion) parameter set. For the enrichment case ABVI-1, a solute concentration drop at the center of the system is observed. This can rationalized in terms of interstitially jumps. After the solute concentration rises near the sink, interstitials must traverse a solute-rich region in order to reach the sink. As interstitials penetrate the near-sink region, they will increasingly become of the AB type. Because $\epsilon_{A-B} > \epsilon_{B-B}$, A atoms located in this solute-rich region are energetically unfavorable. Therefore, interstitials jumps favor the avoidance of A-B bonds, which results in enhanced matrix atom transport to the sink. This phenomenon was not observed in Soisson's work because they used a saddle-point energy model that gives a nonlocal activation energy (does not depend on the atomic environment of the jumping atom). Increasing the driving force for solute transport toward the sink (e.g., by setting E_m^{I-A} =0.6; E_m^{I-B} = 0.4), the drop at the sink disappears. Snapshots for ABVI-1 and ABVI-4 at three different doses are shown in Figure 6.



Figure 6. Snapshots of ABVI-1 system (under saturated, enrichment) at (a) 2.56x10⁻³ (b) 2.01x10⁻² and (c) 2.01 dpa. For the ABVI-4 case (supersaturated, depletion), configurations are shown at (d) 8.78x10⁻⁴ (e) 2.63x10⁻² and (f) 0.258 dpa. Only solute atoms are shown.

For the low solubility alloy, on the other hand, bulk precipitation does occur, as one would expect given the low marginal difference between bulk and sink segregation driving forces. As Figure 5 shows, the solute spatial profiles are much more fluctuative than their high solubility counterparts, especially for depletion case (ABVI-2 vs. ABVI-4). This of course is a manifestation of the formation of precipitates in bulk. In the depletion case, the mean free path for solute diffusion is quite low, due to a high number density of precipitates acting as trapping sites. Therefore, the depletion dynamics is slow. Soisson et al. observed a less intense bulk precipitation than shown here, possibly also due to the different in activation energy models employed. In any case, the global qualitative features of the alloy evolution kinetics are matched by both methods.

33. ABVI system: Radiation-induced segregation at surfaces

The last verification example that we tackle in this paper is that of a finite system containing a binary alloy under irradiation. This mimics the case considered by Dubey and El-Azab, which studied binary Au-Cu alloy under irradiation using a two-dimensional continuum reaction-diffusion model bounded by a free surface [42]. These authors use effective rate theory to solve the ordinary differential equation system representing defect kinetics with spatial resolution. As such, our method differs fundamentally in that it is substantiated in a discrete lattice description, and so the comparison between both approaches must account for this distinction. Our lattice system, however, is constructed so as to create two free surfaces along one of the dimensions of the computational cell, with periodic boundary condition used for the other two. Adjacent to the free surfaces, several layers of `vacuum' atoms are introduced (cf. Sec. 2.3.4 for the mechanisms involving these vacuum atoms). In this fashion, the surface is always univocally defined as the interface between atomic lattice sites and vacuum sites, which provides a convenient way to study the surface roughness as simulations progress. Due to the high formation energy difference between interstitials and vacancies, we disregard the possibility of thermal SIA emission from the surface and focus only on vacancies.

Considering free surfaces introduces both a defect sink and a source. In addition to Frenkel-pair generation by irradiation, point defects can also be emitted thermally from the surface. Following Dubey and El-Azab, Frenkel-pair generation rate is set at 1.0 dpa/s. Regarding thermal vacancy emission from the surface, we allow vacancies to be created at all surface sites. In each step, the rates of all the possible creation paths, i.e. all 1st-nn jumps from surface sites towards the interior of the box, are calculated and added to the global kMC event list [+].

[+] Vacancy emission can occur from any surface site. Given the large number of such sites, we precompute all the thermal emission rates at the beginning, and then simply update the list when the local chemical environment around the surface site changes during the kMC simulation.

The annihilation of defects at surfaces is also considered, as described in Sec. 2.3.4. After Dubey and El-Azab, we study a face-centered cubic binary Au-Cu alloy using the energetics provided in Table 4 based on a study by Hashimoto et al. [43]. The computational box dimensions are 660x270x4 primitive cells, with a vacuum buffer of 20 atomic layers on either side of the free surface, along the x-direction. The atomic bulk size in x and y-dimension is similar to system in Dubey and El-Azab's work. The setup in z-dimension is designed to mimic 2D conditions as used in ref. [42]. Contrary to Soisson et al. (cf. Sec. 3.2), jumps of mixed interstitials are calculated considering both directional possibilities, e.g. AB+A->B+AA, or AB+A->AB+A (cf. Table 1), with their total rate weighted by a factor of 1/2 to preserve the correct sampling statistics.

Bond energies (eV)					
ϵ_{X-Y}	ϵ_{V-X}	ϵ_{AA-X}	ϵ_{AB-X}	ϵ_{BB-X}	
-0.1425	-0.01625	0.24625	0.12875	0.14625	
Migration energies (eV)					
E _m V-A	E _m ^{V-B}	E _m ^{I-AA}	E _m ^{I-AB}	E _m ^{I-BB}	
0.88	0.76	0.3	0.377	0.12	
Conversion energies (eV)					
E _c ^{AA→AB}	E _c ^{AB→AA}	E _c ^{BB→AB}	E _c ^{AB→BB}		
0.3	0.5	0.12	0.32		

Table 4. The parameters for the Au-Cu ABVI system. `A' are Cu atoms, `B' are Au atoms. X, Y= A, B;
Z= A, B, V, <i>v</i> .

In this work, we set the vacuum energy level as the zero reference, i.e. $\varepsilon_{v-X} = 0$ (where X= A, B, V, v), and the energies of atoms on the surface are simply tallied in terms of the number of missing surface bonds. The defect bond energy parameters then can be obtained from formation energies of vacancy and interstitials using the formulas described in Sec. 2.3.3. The surface energy per area and formation energies are acquired from Dubey and El-Azab's paper. In addition, following the work of Hashimoto et al., a conversion energy is applied when interstitial defects change their type after a diffusive jump. On some occasions, the activation energy for interstitially jumps can become negative, which we simply interpret as a spontaneous event within the kMC cycle.

Our kMC simulations are run up to a maximum dose of 0.04 dpa. The spatial solute concentration profiles along the x-dimension at 650 K as a function of dose are shown in Figure 7. From the figure, the enrichment of solute atoms near the surfaces can be clearly appreciated, which is accompanied by local depletion in the subsurface region. Segregation near the surfaces increases with dose, in agreement with Dubey and El-Azab's work. These authors also studied the degree of segregation as a function of time M(t), defined as:

1

$$M(t) = \int_{0}^{t_{s}} (C(x,t) - \bar{C}) dx$$
(40)

where I_s is an arbitrary segregation distance, C(x, t) is the instantaneous solute concentration profile, and C is the average solute concentration of the whole system. Here, we replace the integral by a discrete sum over lattice positions, with Is defined as the distance from the surface at which the local concentration is within 10% of the background global concentration. To avoid noise due to lattice fluctuations, we apply a Savitzky-Golay smoothing filter [44] prior to the determination of Is. The evolution of M as a function of dose and temperature is shown in Figure 8. Our results are in agreement with those of Dubey and El-Azab, with M increasing with dose monotonically in all cases. However, the evolution with temperature shows two distinct trends. First, M increases with temperature up to a critical value of approximately 650 K. Then, it gradually decreases until, at T = 900 K, the degree of segregation is practically zero. The causes behind this behavior are well understood [45]. Essentially, at low temperatures, vacancy mobility is limited, leading to high excess vacancy concentration and high recombination rates. As a consequence, segregation is low due to small defect fluxes to surfaces. At higher temperatures, vacancy and interstitial diffusion are activated resulting in net solute segregation. However, above 650 K, significant numbers of vacancies start to be emitted from the surfaces, leading to high back diffusion rates and again high recombination rates. The two effects result in a reduced solute segregation to the surfaces. Therefore, the maximum degree of segregation occurs at intermediate temperatures, consistent also with Dubey and El-Azab's findings.



Figure 7. Solute concentration profile at 650 K for different doses.



Figure 8. Evolution of the degree of segregation at different temperatures.

The KMC simulations are capable of providing morphological features that continuum methods cannot furnish. For example, our method can be used to study the evolution of roughness of the surfaces. Snapshots of the surface of the system with 660x32x32 primitive cells at 500 K at different doses can be seen in Figure 9, revealing a clear surface morphology evolution as a function of dose. Also, it can be seen that the concentration of solute atoms at the surface increases evidently, as explained above.



Figure 9. Snapshots of surface roughness at (a) t = 0, and (b), t = 0.02 s for a 660x32x32 alloy at 500 K. Red dots represent solvent (A) atoms, while solute atoms (B) are represented as green dots.

4.0 Conclusions

We have proposed an extension of the standard ABV Hamiltonian to discrete binary systems containing interstitial defects. The chosen framework for this extension is the Ising model, where three new values for the spin variables are considered: `+2', Huang & Marian 24 representing pure self-interstitials (A-A), `-2', representing pure solute interstitials (B-B), and `0', for mixed interstitials (A-B). The reason for choosing these values is to preserve one of the essential magnitudes of the Ising model, the magnetization N⁻¹ $\Sigma_i\sigma_i$, or, in the ABVI context, the excess solute concentration. The main
advantage behind expressing a cluster expansion Hamiltonian as an Ising Hamiltonian is that thermodynamic information about the system can more easily be construed in the Ising framework. For example, the values of the constants of class 3 identified in eq. (27) uniquely determine the thermodynamic phase diagram of the ABVI model (much like constant J in eq. (2) determines the structure of the ABV system). Indeed, one of the aspects of greatest interest associated with the ABVI model is to study how the presence of interstitials alters the behavior of substitutional binary alloys.

However, we leave this thermodynamic analysis for a specific binary system with well characterized bond energetics for a future study, and, instead, in this paper we have focused on verification by comparing against a number of selected published studies. The main tests that we have conducted include discrete lattice ABV and ABVI for dilute Fe- Cu alloys, as well as comparison against a spatially-resolved mean-field study of solute segregation at free surfaces in irradiated Au-Cu alloys. In all cases, basic metrics related to the timescale and/or some governing kinetic parameters were reproduced with good agreement. In terms of computational cost, our Ising ABVI model scales in a similar manner as second-order cluster expansion Hamiltonians with similar cutoff radius – as it should,– given that no advantage is lost by simply recasting a cluster expansion Hamiltonian into the Ising form.

Thus, in conclusion, we present an ABVI Hamiltonian, cast as an Ising model Hamiltonian, for discrete event simulations that can be considered a generalization of ABV models. Our model has been verified against existing parameterizations of cluster expansion Hamiltonians using kinetic Monte Carlo simulations, with good agreement observed. We will study the thermodynamic behavior of our Hamiltonian in a future publication.

Acknowledgments

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9. FUSION SYSTEM DESIGN

No contributions this reporting period.

10. IRRADIATION METHODS, EXPERIMENTS AND SCHEDULES

10.1 FUSION MATERIALS IRRADIATION TEST STATION (FMITS) AT SNS — Mark Wendel, Phil Ferguson (Oak Ridge National Laboratory)

OBJECTIVE

The Fusion Materials Irradiation Test Station (FMITS) is a plan for an irradiation facility at the Spallation Neutron Source (SNS). The FY16 effort follows through on FY15 objectives to address comments by the reviewers of the 2014 feasibility study and to reduce the technical risks to a potential project by analysis and by building and testing hardware mockups. The 2014 effort produced a Feasibility Study Report, 30% Design Review, and a Preliminary Safety Assessment. The 2014 estimate for implementation of the FMITS at SNS was \$13.4 M including a 25% contingency.

SUMMARY

The FMITS is a design concept for installation at the SNS Facility. The project received funding from OFES during FY15 for (1) performing a mockup test on an FMITS-type target seal, (2) augmenting the safety assessment based on the 2014 technical review, (3) analyzing thermal-hydraulic off-normal transients with a full 3D model to assess the performance of the FMITS sensor array, and (4) remote-handling electrical connector operational mock-up, which was successfully completed in FY15. The work was continued in FY16 using residual funding. The main goals of the effort are to remove the project technical risks and prepare for a potential future project.

PROGRESS

Seal Mockup

The FMITS-type (double-pillow) seal hardware (Figure 1) was received last year along with a test report from the vendor that shows it successfully tested to 2.9×10^{-6} torr-liter/s. This seal is a prototype of the assembly that could be used between the target module and the core vessel flange for an FMITS harness. It would replace the single-sided version currently in use at SNS. Hardware has also been designed that would modify the inflatable seal test tank at SNS to confirm that the new seal operates to required specifications, and to show robust and repeatable performance. The hardware has not yet been ordered to perform the tests at ORNL, but the testing tank is now ready.



Figure 1. Double-inflatable seal ring received at ORNL from KSM Corporation. Outside diameter is 0.65 meters.

Safety Assessment

Deterministic analysis does not seem feasible that can rule out possible FMITS test-section tube rupture severe consequences. It is likely that the FMITS plan will have to keep the engineering control safeguard of a calibrated containment tube with directional failure bias. To that end, a sub-contract was placed with Fike Company (the same company that designed, tested, and supplied HFIR rupture disks) to design and test FMITS tubes that would hold at least 300 psig water pressure, and then fail consistently and without fragmentation in a direction away from the SNS target and moderators. Fike completed the fabrication and testing of 20 tubes with a positive result: The burst pressures ranged from 400 – 800 psig and each tube failed in the pre-determined direction. Also, three of the tubes were precisely weighed before and after rupture, showing that there was no detectable fragmentation. These tests confirm that a rupture tube concept could reliably avert safety issues in an FMITS coolant flow blockage event.

Another concern raised by the 2014 Feasibility Study Review Committee is the reaction with tungsten and water at high temperature leading to deflagration or detonation in the SNS core vessel. An evaluation of the tungsten-steam interaction was previously performed to support the Los Alamos FSAD for a solid tungsten target. The present analysis strategy is based on that Los Alamos approach. Even with extremely conservative assumptions, if the tungsten packing fraction is limited to 50% or less (545 grams) there is insufficient hydrogen production to support deflagration or detonation within the core vessel. This finding alleviates the safety concern raised by the committee.

Assessing FMITS Thermal-hydraulics in the Test Section

A full 3D model of a representative FMITS capsule has been developed and meshed for finite element analysis. A loss-of-flow transient was completed for which the FMITS capsule experiences a sudden

blockage leading to a 50% flow reduction. Within 5 s of the flow blockage event, the hottest thermocouples indicate a 10°C temperature rise. This type of results will be useful in formulating the strategy and timing for machine protection at SNS.

In addition to the simulation of the thermal response of the test-section, a sensor has been developed that could verify that actual operational temperatures are managed in FMITS. The instrumentation described in the FMITS feasibility study includes both thermocouples and an RTD-based flow sensor to ensure cooling of the FMITS test section. The compact flow sensor was not currently available for water in 2014, but is now being developed. A sub-contract is in place with Delta M Corporation to test and deliver a prototype water flow sensor that would stand up to the harsh radioactive environment of the FMITS seal ring. The water sensor is scheduled for delivery to ORNL near the beginning of calendar year 2016.

10.2 A HIGH ENERGY SELF-ION IRRADIATION STUDY OF METALLIC REACTOR MATERIALS AT THE LLNL CENTER FOR ACCELERATOR MASS SPECTROMETRY (CAMS) — N. Almirall, T.

Yamamoto, D. Gragg, K. Fields, N. Cunningham, P. Wells, G. R. Odette (University of California, Santa Barbara), S. Tumey, T. Brown (Lawrence Livermore National Laboratory)

OBJECTIVE

The objective of the Lawrence Livermore National Laboratory (LLNL) Center for Mass Spectrometry (CAMS) experiment is to characterize the combined effects of charged particle ion versus neutron irradiations, including the effects of dpa and dpa rate, on an extensive matrix of materials for various reactor applications.

SUMMARY

The LLNL CAMS accelerator experiment was designed to irradiate a range of reactor materials (~80 samples per condition) with 70 MeV Fe⁺⁹ ions to a dose of 3 dpa at two dpa rates that differ by a factor of 10. The experiment also explores ion versus neutron irradiation effects by cross-comparing the CAMS results with previous neutron and charged particle irradiation (CPI) data for the same alloy. Following a prototype test on 10/8/15, the actual CAMS irradiation was successfully conducted beginning on 12/3/2015. Extensive PIE is planned for the FeCr alloys, NFA, TMS and other fusion reactor relevant alloys, including W. One objective is to explore the concept of using precipitation as a damage meter to evaluate the relative effects of neutron irradiations versus CPI; and to isolate the effects of dpa rate from that of the irradiating particle. Here some preliminary ion versus neutron results are reported.

PROGRESS AND STATUS

Introduction

The CAMS facility of LLNL houses a tandem accelerator that can be used for high-energy ion irradiations. The 70 MeV Fe⁺⁹ ions used in this study have a peak dpa range of $\approx 6.4 \,\mu$ m, as illustrated in Figure 1a, that is based on the SRIM code. In this case the total ion current produced a peak K&P dose of 3 dpa. However, the dpa varies widely over the ion range due to an increasing fraction of nuclear versus electronic ion energy loss rates. Thus a single irradiation can explore almost an entire dose (dpa)-response (hardening, loop formation, segregation, solute clustering and precipitation) behavior space. However, direct interpretation of such data is confounded by the simultaneous variation in the dose rate. Thus the initial experiment was conducted at two different dpa rates that vary by a factor of 10 as illustrated in Figure 1b.



Figure 1. a) The dpa-depth profile in steel for 70MeV Fe ion calculated using SRIM 2008 with $E_d = 40$ eV and the KP model; b) two dose rate regimes that vary by a factor of 10.

Experimental Procedure

CAMS Irradiations

Ion beam irradiations are expensive (but trivial compared to neutrons), so maximizing the number of specimens is very important. Thus we developed and implemented a new target design to irradiate a large numbers of specimens while improving both the mechanical durability and heat transfer performance of the targets. The design is illustrated in Figures 2a and b. The holder contains 80 2x0.5x8 mm bars clamped by plates loaded by setscrews in a thermally conductive and highly rigid bundle of specimens in a pocket in the copper target assembly. The top surfaces of the specimens are polished together to finished amenable to FIB lift-outs for APT and TEM. The sides of the bars can also be polished without loss of irradiated material and used for measuring nano-hardness profiles. The specimens can also be used for EBSD as well as grazing incidence SAXS and XRD.

а



Figure 2. Sample holders used in CAMS experiment: a) Polished specimen array with ~80 4x0.5x8mm sample bars; b) a rendering of the bolt on copper target assembly developed by UCSB for use in the CAMS experiment

A prototype irradiation was successfully carried out on 10/8/15 to test the CAMS ion beam capabilities wand the new sample holder. Target irradiation conditions were achieved, at different dpa rates that varied by a factor of 10. The actual irradiations were carried out at 3 and 30 hours to reach a peak dose of 3 dpa on two identical targets starting on 12/3/15. LLNL scientists (S. Tumey, T. Brown) ran the irradiation with the help of a UCSB graduate student (N. Almirall), including calibrating the heaters, thermocouples, infared camera and ion beam distribution on target. The temperature of the sample was

held at $295\pm5^{\circ}$ C provided by three cartridge heaters and controlled by an active air cooling system under a high vacuum of 10^{-7} torr. An infared camera was used to monitor the temperature and temperature fluctuations on the specimen surface over the entire experiment. Thermocouples were attached to the back of the target holder as well as in direct contact with the specimen bundle. There were no significant variations in temperature or vacuum over the entire irradiation.

The 70MeV ion beam using Fe⁺⁹ ions was aligned on target and tuned to obtain the desired gaussian beam envelope with a FWHM of 8 mm. The dpa profile was calculated using SRIM code for a peak K&P dose of 3 dpa There was a maximum of $\approx 5^{\circ}$ C of beam heating, that was accounted for by the active cooling system. The total beam current and current spatial distrubtion was measured in front of the target by a multi-pin channel array faraday cup that will be translated to detailed dose and dose rate distributions on all individual samples. Based on these readings, relatively minor adjustments were carried out during the experiment.

Materials and Characterization Method

The alloy matrix consists of NFA/ODS, TMS, Fe-3 to 18Cr binary, RPV and maraging Fe-based alloys, tungsten and nickel alloys. CAMS alloys directly relevant to fusion materials, include: TMS Eur97, F82H IEA and M3, HT9 and NF616; NFA/ODS PM2, NFA-1, US and French MA957, MA956, PM2000; tungsten; and, model Fe 3-18%Cr binaries. FIB lift outs at selected depths were used for APT to characterize the high Ni alloy precipitates.

Results

A preliminary APT study of high Ni (3.5wt%) low alloy steels irradiated at the higher CPI dose rate found no precipitation at a depth of 1.3 µm, and a volume fractions (f_{ppt}) of $f_{ppt} \approx 0.51\%$ and 1.3% of a Mn-Ni-Si intermetallic G-phase type precipitates at 3.3 and 5.5 µm, respectively. This alloy had previously been CPI under generally similar conditions in the DuET facility to 4.5 dpa at 290°C, that produced fppt \approx 4.6% of precipitation. A similar alloy was irradiated in ATR-2 to ≈ 0.2 dpa producing $f_{ppt} \approx 2.6\%$ precipitation. Correcting f_{ppt} to 2.1% to account for a lower Si content in this alloy yields an $f_{ppt} \approx 2.1\%$. Assigning crude and very preliminary dpa estimates for the CAMS irradiation, that will be refined in the near future, leads to the plot of f versus \sqrt{dpa} shown in Figure 3. These results suggest that the CPI dpa are ≈ 8.1 times less efficient in producing precipitation, primarily by radiation-enhanced diffusion, than fission reactor neutrons. This result is generally consistent with previous observations suggesting that an effective dpa (dpa_e) dose can be simply defined based on scaling dpa with relative dpa rates (dpa') as dpa_e = dpa(dpa'_r/dpa')^p where dpa'_r is an arbitrary reference dpa rate. The p ≈ 0.23 observed in this preliminary, is consistent with previous estimates of p = 0.15 to 0.25.

Future Work

The PIE on FeCr alloys, NFA and other fusion alloys is planned in the near future. This microstructural characterization will be carried out primarily using APT, TEM and SAXS/XRD. Nanohardness as a function of depth, or dpa, profiles will be carried out at UC Berkeley.



Figure 3. A comparison of the volume fraction (f_{ppt}) of Mn-Ni-Si precipitates formed under neutron (blue diamond) and CPI (red circles) irradiations of a 3.5%Ni low alloy steel as a function of \sqrt{dpa} .

Acknowledgments

We gratefully acknowledge the contributions of the DOE NE National Scientific Users Facilities Program for the UCSB ATR-2 neutron irradiation. The UCSB funding for the CAMS irradiation was provided by the DOE Offices of Nuclear Energy and Office of Fusion Energy Sciences. Support for the PIE is being provided by the DOE NEUP and LWR Sustainability Program, Rolls Royce and the Basic Energy Sciences Office of Fusion Energy Sciences.

10.3 METHOD FOR ANALYZING PASSIVE SILICON CARBIDE THERMOMETRY WITH A CONTINUOUS DILATOMETER TO DETERMINE IRRADIATION TEMPERATURE — Anne A. Campbell (ORNL), Wallace D. Porter (ORNL), Yutai Katoh (ORNL), Lance L. Snead (MIT)

This is the abstract of a paper published in Nuclear Instruments and Methods in Physics Research B, 370, (2016) 49-58.

OBJECTIVE

Develop a technique to analyze SiC temperature monitors with a dilatometer, and develop a computer software code to analyze results.

SUMMARY

Silicon carbide is used as a passive post-irradiation temperature monitor because the irradiation defects will anneal out above the irradiation temperature. The irradiation temperature is determined by measuring a property change after isochronal annealing, i.e., lattice spacing, dimensions, electrical resistivity, thermal diffusivity, or bulk density. However, such methods are time-consuming since the steps involved must be performed in a serial manner. This work presents the use of thermal expansion from continuous dilatometry to calculate the SiC irradiation temperature, which is an automated process requiring minimal setup time. Analysis software was written that performs the calculations to obtain the irradiation temperature and removes possible user-introduced error while standardizing the analysis. This method has been compared to an electrical resistivity and isochronal annealing investigation, and the results revealed agreement of the calculated temperatures. These results show that dilatometry is a reliable and less time-intensive process for determining irradiation temperature from passive SiC thermometry.

10.4 IRRADIATION STUDY OF ADVANCED CERAMICS: STATUS OF IRRADIATION EXPERIMENTS — T. Koyanagi, C.M. Petrie, N.O. Cetiner, Y. Katoh (Oak Ridge National Laboratory)

OBJECTIVE

This report describes the technical planning and progress of neutron irradiation experiments on advanced ceramics materials for potential use in fusion structural components.

SUMMARY

HFIR Rabbit capsules were designed for irradiation of various advanced ceramics. The materials include isotopically-controlled ultra-high temperature ceramics such as TiB_2 and ZrB_2 , MAX phases such as Ti_2AIC , Ti_3AIC_2 , and Ti_3SiC_2 , SiC with various qualities, AIN, TiC, YAG, glassy carbon, and Si. The first phase of the irradiation has been completed.

PROGRESS AND STATUS

Introduction

The novel high-temperature ceramics including ultra-high-temperature ceramics (UHTCs) and a family of layered ternary compounds (MAX phases) are recently recognized as attractive materials for use in nuclear fusion applications [1]. UHTCs are generally capable of surviving temperatures of ~2000°C because of their extremely high melting temperatures (above ~3000°C). There are potential fusion applications for these materials including tokamak divertor and plasma facing materials [1]. MAX ($M_{n+1}AX_n$) phase materials, where M is an early transition metal, A is an A-group element, and X is either C or N, exhibit interesting mechanical properties. More than a few percent of failure strain was achieved for a Ti₃SiC₂ material at 1200°C [2], which is significantly larger than common ceramics and beneficial for structural applications. Though UHTCs and MAX phase materials are attractive materials used in extreme environments, the major concern for nuclear fusion applications is irradiation effects on the mechanical and physical properties. Very limited information regarding neutron irradiation effects on these materials is available.

The aim of this task is understanding radiation resistance of the advanced ceramics. The materials investigated are UHTCs such as TiB₂ and ZrB₂, MAX phases such as Ti₂AlC, Ti₃AlC₂, and Ti₃SiC₂, and additional high-temperature ceramics including SiC with various qualities, AlN, TiC, YAG, glassy carbon, and silicon. Note that the diboride samples were isotopically controlled; >99 wt% purity of ¹¹B powder was used for fabrication instead of ¹⁰B powder to avoid producing transmutant helium during irradiation. Irradiation experiments using rabbit capsules will be conducted. This report presents the capsule design, the current status of HFIR irradiation, and plans for the post-irradiation examination.

Capsule design and test specimens

The overall capsule assembly is shown in Figure 1. This rabbit has 32 disk specimens that are nominally 0.5 mm thick and 6.0 mm diameter. There are two sets of 16 specimens located on either side of the center retainer spring. Each set has 2 layers of 8 specimens stacked between SiC thermometry pieces. The arrangement of the disk specimens changes from one capsule to another. Although the loading order is unique for each capsule, the total volume that the specimens occupy is the same for all capsules. There are SiC thermometry bars and SiC retainer specimens pressed against the disk specimens. Thermometry and specimens are pushed to the inside surfaces of the holder with SiC springs. There are insulator discs at the top and bottom of the assembly to reduce axial heat loss.

A summary of the irradiation conditions and test materials is given in Table 1. A total of 8 rabbit capsules are to be irradiated. The target irradiation temperatures range from 200 to 1000°C. The number of HFIR cycles is up to 5, and the neutron fluence will be up to $\sim 1 \times 10^{26}$ (n/m², E > 0.1 MeV).



Figure 1. Exploded view of the rabbit capsule assembly. The table shows the explanation of each capsule part.

Capsule ID	Target Irradiation Temperature [°C]	Number of HFIR Cycles	Materials Investigated
IMR 3	200	1	SX 3C SiC, SX 6H SiC, Faulted SiC, Si, AlN, YAG, TiC,
IMR 4	200	1	TiB ₂ , ZrB ₂ , Ti ₃ SiC ₂ , Ti ₃ AlC ₂ , Ti ₂ AlC, Sintered SiC, Glassy carbon
IMR 6	600	1	TiB ₂ , ZrB ₂ , Ti ₃ SiC ₂ , Ti ₃ AlC ₂ , Ti ₂ AlC, Sintered SiC, Glassy carbon, Si, AlN, YAG, TiC
IMR 7	600	3	TiB ₂ , ZrB ₂ , Ti ₃ SiC ₂ , Ti ₃ AlC ₂ , Ti ₂ AlC, Sintered SiC, Glassy carbon, YAG, TiC
IMR 8	600	5	TiB ₂ , ZrB ₂ , Ti ₃ SiC ₂ , Ti ₃ AlC ₂ , Ti ₂ AlC, Sintered SiC, Glassy carbon, Si, YAG, TiC
IMR 9	1000	1	Ti ₃ SiC ₂ , Ti ₃ AlC ₂ , Ti ₂ AlC, Sintered SiC, Glassy carbon, AlN, YAG, TiC
IMR 10	1000	5	Ti ₃ SiC ₂ , Ti ₃ AlC ₂ , Ti ₂ AlC, Sintered SiC, Glassy carbon, YAG, TiC
IMR 11	1000	5	TiB ₂ , ZrB ₂ , Sintered SiC

Table 1. Inaulation and specimen matrix	Table 1.	Irradiation	and s	specimen	matrix.
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Simulation of irradiation temperatures

Irradiation capsules were designed to control the specimen temperatures using three-dimensional thermal analysis performed with the ANSYS software package. The simulations consider the arrangement of the specimens and the influence of <1at% of B¹⁰ content in the diborides on heat generation in the capsules. A calculation showed that the heat generation of the diborides changes significantly during irradiation, indicating changes in specimen temperatures [3]. At the initial stage, high heat generation is due to neutron absorbance by B¹⁰. After ~13 days of irradiation, all the B¹⁰ burns out, and the heating rate largely drops by \geq 70%. Figures 2A & B shows the simulation results for the irradiation are generally within 50-60°C of the design temperature for all design cases, and they are within ~30°C of the 200°C design case. In addition, the temperature differences at the beginning and the end of irradiations are as large ~300°C for the diborides and ~50–~150°C for the other materials in the capsules containing diborides specimens. The magnitude of these temperature differences depends on the specific design (capsule materials, fill gas, etc.), specimen matrix, and specimen location within the capsule. The actual irradiation temperatures of the specimens will be experimentally investigated by dilatometry of 8 SiC temperature monitors which are designed to be in contact with the disc specimens.



Figure 2A. Calculated temperature distributions expected at end of irradiation for ceramic irradiation capsules designed for 200C (IMR 3 & 4) or 600C (IMR 6 & 7).



Figure 2B. Calculated temperature distributions expected at end of irradiation for ceramic irradiation capsules designed for 600C (IMR 8) or 1000C (IMR 9, 10 & 11).

Plan for post irradiation experiments

Disk specimens with 6 mm diameter and 0.5 mm thickness will be used. Post-irradiation examination will include investigations of swelling, thermal properties, electrical properties, equibiaxial flexural strength at room temperature and high temperature, microstructure, and positron annihilation lifetime. In addition, dilatometry of SiC samples placed in the irradiation capsules will be conducted to measure actual irradiation temperatures.

Progress of irradiation and future work

The irradiation of the IMR3 capsule has been completed and the other capsules are under fabrication for the irradiation. The next step is characterization of unirradiated specimens to obtain reference information to compare with results obtained from the irradiated materials.

References

[1] W.E. Lee, M. Gilbert, S.T. Murphy, and R.W. Grimes, J. Am. Ceram. Soc., 96 [7] (2013) 2005–2030. [2] M.W. Barsoum and M. Radovic, Annual review of materials research 41 (2011) 195–227.

[3] ORNL internal document, C-HFIR-2014-022 Rev.1

10.5 HFIR IRRADIATION EXPERIMENTS – J.P. Robertson, Y. Katoh and J. McDuffee (Oak Ridge National Laboratory)

Summary of recent, current and planned Fusion Materials Program experiments.

Status of the Reactor

HFIR completed 3.2 cycles during the second half of 2015. Cycle 460C (July 6 – July 11, 2015) added 406 MWdays to complete this cycle. Cycle 460 started on June 9, 2015, but there was a manual shutdown on June 13, 2015, in response to a reactor setback. The cycle was restarted on June 15, but the reactor was again forced to shut down due to abnormal fluctuations in the primary temperature. Cycles 461 (July 21 – August 15), 462 (October 6 – October 31), and 463 (November 17 – December 11) were completed without incident.

Summary of Recent, Current and Planned Fusion Materials Program HFIR Experiments

Experiment Designation	Primary Materials	Specimen Types*	Irradiation Temperature (°C)	Max Exposure (dpa)	Number of Reactor Cycles	Irradiation Period (month/year)					
Beryllium reflector (RB) irradiation positions											
RB-15J	F82H	T, F, FT	300, 400	6	10	6/08	_	12/09			
RB-19J	W alloys and F82H	various	250/300C, 500C, 800C, 1200C	1.5	6	6/16		6/17			
Target zone full-length capsules											
JP-25	F82H	T, FT	300, 500	20	10	2/99	_	1/01			
JP-26	F82H	T, FT	300,400,500	9	5	12/03	_	11/04			
JP-27	F82H	T, FT	300, 400	21	13	12/03	_	1/08			
JP-28	F82H	T, FT	300,400,500	80	46	4/05	_	7/13			
JP-29	F82H	T, FT	300,400,500	80	46	1/05	_	7/13			
12-DCT	F82H	DCT	50	1.6	1	8/11	_	8/11			
JP-30	F82H	T, FT	300,400,650	20	~10	11/11	_	8/13			
JP-31	F82H	T, FT	300,400,650	20	~10	11/11	_	8/13			
Target zone rabbit capsules (DOE-JAEA)											
F8A1	F82H	T, FT	300	50	29	2/09	_	7/13			
F8A2	"	"	"	"	**	"	_	"			
F8B1	"	"	"	"	**	"	_	"			
F8B2	"	"	"	"	**	"	_	"			
JCR-1	SiC/SiC	Bend bars	800	30	15	10/04	_	1/09			
JCR-2	"	"	"	"	"	"	-	"			
JCR-3	"	"	"	"	"	"	-	"			
JCR-4	"	"	"	"	"	"	-	"			
JCR-5	"	"	"	>50	>25	10/04	_	2/11			

Experiment Designation	Primary Materials	Specimen Types*	Irradiation Temperature (°C)	Max Exposure (dpa)	Number of Reactor Cycles	Irradiation Period (month/year)				
Target zone rabbit capsules (DOE-JAEA) (Continued)										
JCR-6	"	"	"	"	"	"	_	"		
JCR-7	"	"	"	"	"	"	-	"		
JCR-8	"	"	"	"	"	"	-	"		
JCR-9	"	"	500	30	15	10/04	_	1/09		
JCR-10	"	"	"	"	"	"	_	"		
JCR-11	"	"	"	"	"	"	-	"		
JCR-12	"	"	"	"	"	"	_	"		
F11A3	F82H	T, FT	300	20	12	5/11	-	2/13		
F11A4	"	"	"	"	"	"	_	"		
F11B3	"	"	"	"	"	"	_	"		
M4-TEN	F82H	DCT	50	1.6	1	8/11	_	8/11		
JCR11-01	SiC/SiC	Bend bars	950	50	25	11/12	-			
JCR11-02	SiC/SiC	Bend bars	950	10	5	10/12	-	8/13		
JCR11-03	SiC/SiC	Bend bars	950	30	15	5/13	-	8/15		
JCR11-04	SiC/SiC	Bend bars	950	30	15	5/13	-	8/15		
JCR11-05	SiC/SiC	Bend bars	950	50	25	10/12	_			
JCR11-06	SiC/SiC	Bend bars	950	10	5	10/12	-	7/13		
JCR11-07	SiC/SiC	Bend bars	950	100	50	10/12	_			
JCR11-08	SiC/SiC	Bend bars	950	100	50	10/12	-			
JCR11-09	SiC/SiC	UDMC	950	4	2	6/13	-	11/13		
JCR11-10	SiC/SiC	UDMC	950	10	8	6/13	-	8/14		
JCR11-11	SiC/SiC	UDMC	950	30	15	6/13	-	8/15		
JCR11-12	SiC/SiC	UDMC	950	100	50	6/13	-			
F13A5	F82H	T, FT	300	10	9	1/14	-	3/15		
F13A6	F82H	T, FT	300	20	18	1/14	-			
F13B4	F82H	T, FT	300	10	9	1/14	-	3/15		
F13B5	F82H	T, FT	300	20	18	1/14	-			
SCF6	SiC/SiC	Bend bars	600	10	6	11/14	_	10/15		
SCF7	SiC/SiC	Bend bars	600	30	14	11/14	_			
SCF8	SiC/SiC	Bend bars	600	100	45	11/14				
SCF9	SiC/SiC	Bend bars	600	200	90	11/14	_			
SCF10	SiC/SiC	Bend bars	950	10	5	1/15	_	10/15		
SCF11	SiC/SiC	Bend bars	950	30	14	1/15	_			
SCF12	SiC/SiC	Bend bars	950	100	45	1/15	-			
Target zone rabbit capsules (DOE-NIFS)										
T8A1	SiC	BSR	300	0.01	HT**	10/09	_	10/09		
T8A2	SiC	BSR	300	0.1	HT	10/09	_	10/09		
T8B1	SiC	BSR	500	0.01	HT	10/09	_	10/09		
T8B2	SiC	BSR	500	0.1	HT	10/09	_	10/09		
T8C1	SiC	BSR	500	~1	1	5/09	_	6/09		
T8D1	SiC	BSR	800	0.1	HT	3/11	_	10/09		
T8E1	SiC	BSR	800	~1	1	8/09	-	8/09		

Experiment Designation	Primary Materials	Specimen Types*	Irradiation Temperature (°C)	Max Exposure (dpa)	Number of Reactor Cycles	Irradiation Period (month/year)				
Target zone rabbit capsules (DOE-NIFS) (Continued)										
T8F1	SiC	BSR	1200	~1	1	8/09	-	8/09		
T9A1	W, Ni	Discs	90	0.1	HT	1/09	-	10/09		
T9A2	W, Ni	Discs	90	1.2	1	1/09	_	1/09		
T9C1	Steels	T, MC	500	5.5	3	11/09	-	2/10		
T9C2	Steels	T, MC	500	9.6	5	11/09	-	6/10		
T9G1	Steels	T, MC	300	1.2	1	6/09	-	8/09		
T9G2	Steels	T, MC	300	9.6	8	6/09	_	8/11		
MTTN01	Steels	T, MC	300	4.8	4	1/12		8/11		
300-LD-1	Steels	SSJ, MC	300	2	1	5/12		6/12		
300-HD-1	Steels	SSJ, MC	300	12	6	5/12	_	2/13		
500-LD-1	Steels	SSJ, MC	500	2	1	5/12	_	6/12		
500-HD-1	Steels	SSJ, MC	500	12	6	5/12	_	2/13		
500-HD-2	Steels	SSJ, MC	500	12	6	5/12	_	2/13		
500-HD-3	Steels	SSJ, MC	500	12	6	5/12	_	2/13		
650-LD-1	Steels	SSJ, MC	650	2	1	5/12	_	6/12		
650-LD-2	Steels	SSJ, MC	650	2	1	5/12	_	6/12		
650-HD-1	Steels	SSJ, MC	650	12	6	5/12		2/13		
650-HD-2	Steels	SSJ, MC	650	12	6	5/12	_	2/13		
300-LD-2	Steels, W	SSJ, MC	300	2	2	7/12	_	8/12		
300-MD-1	Steels, W	SSJ, MC	300	7	4	7/12	_	2/13		
500-LD-2	Steels, W	SSJ, MC	500	2	2	1/13	_	7/13		
300-LD-3	Steels, W	SSJ, MC	300	2	2	7/12	_	11/12		
300-HD-2	Steels, W	SSJ, MC	300	12	8	7/12	_	2/14		
500-LD-3	Steels, W	SSJ, MC	500	2	1	7/12		8/12		
500-HD-4	Steels, W	SSJ, MC	500	12	6	7/12		7/13		
650-LD-3	Steels, W	SSJ, MC	650	2	2	10/12	_	7/13		
650-HD-3	Steels, W	SSJ, MC	650	12	8	7/12	_	11/13		
PC1	Various	SSJ, MC	80/100	0.02	HT	6/12		6/12		
PC1A	Various	SSJ, MC	80/100	0.02	HT	6/12		6/12		
PC2	Various	SSJ, MC	80/100	0.1	HT	6/12		6/12		
PC2A	Various	SSJ, MC	80/100	0.1	HT	6/12		6/12		
PC3	Various	SSJ, MC	80/100	0.5	HT	6/12		7/12		
PC3A	Various	SSJ, MC	80/100	0.5	HT	6/12		7/12		
PC4	Various	SSJ, MC	80/100	2	1	6/12		7/12		
PC4A	Various	SSJ, MC	80/100	2	1	6/12	_	//12		
PC5	Various	SSJ, MC	80/100	20	9	6/12	_	11/13		
TB-300-1	Steels, W	SSJ, MC	300	0.02		8/12		8/12		
TB-300-2	Steels, W	SSJ, MC	300	0.1		8/12	_	8/12		
TB-300-3	Steels, W	SSJ, MC	300	0.5	ні	8/12		8/12		
1B-300-4	Steels, W	SSJ, MC	300	(5	//12	-	6/13		
IB-500-1	Steels, W	SSJ, MC	500	0.1		8/12		8/12		
1B-500-2	Steels, W	SSJ, MC	500	0.5	HI	8/12	-	8/12		
IB-500-3	Steels, W	SSJ, MC	500	(4	//12		2/13		
IB-650-1	Steels, W	SSJ, MC	650	0.1	HT	8/12		8/12		

Experiment Designation	Primary Materials	Specimen Types*	Irradiation Temperature (°C)	Max Exposure (dpa)	Number of Reactor Cycles	Irradiation Period (month/year)				
Target zone rabbit capsules (DOE-NIFS) (Continued)										
TB-650-2	Steels. W	SSJ. MC	650	0.5	HT	8/12	_	8/12		
TB-650-3	Steels, W	SSJ. MC	650	7	5	7/12	_	6/13		
TB-650-4	Steels, W	SSJ. MC	650	20	11	7/12	_	7/14		
TTN09	SiC	Joint	500	3.4	2	8/11	_	11/11		
TTN10	SiC	Joint	500	4.1	2	8/11	_	11/11		
TTN11	SiC	Joint	800	4	2	3/12	_	5/12		
TTN01	SiC	BSR	300	1	1	2/11	_	3/11		
TTN02	SiC	BSR	300	10	6	2/11	_	12/11		
TTN03	SiC	BSR	300	20	11	2/11	_	8/13		
TTN04	SiC	BSR	500	10	6	5/11	_	4/12		
TTN05	SiC	BSR	500	20	11	5/11	_	8/13		
TTN06	SiC	BSR	800	10	6	5/11	_	4/12		
TTN07	SiC	BSR	800	20	11	5/11	_	8/13		
TTN08	SiC	BSR	1200	10	6	5/11	_	8/12		
TTN16	SiC	Fiber BSR	500	1	1	11/11	_	12/11		
TTN17	SiC	Fiber BSR	500	10	6	8/11	_	6/12		
TTN18	SiC	Fiber BSR	500	20	11	8/11	_	8/13		
TTN19	SiC	Fiber BSR	1200	1	1	3/12	_	4/12		
TTN20	SiC	Fiber BSR	1200	10	6	3/12	_	11/12		
PXW1	W	Discs	800	2	1	0/12	_	,		
PXW2	Ŵ	Discs	800	2	1	1/15	_	2/15		
PXW3	Ŵ	Discs	800	6	3		_	2/10		
PXW4	Ŵ	Discs	1100	2	1		_			
PXW5	Ŵ	Discs	1100	2	1	1/15	_	2/15		
PXW8	Ŵ	Discs	1100	6	3		_	_,		
		21000	1100	Ŭ	Ŭ					
		Target zone	rabbit capsules	s (US-NIFS-J	AEA)					
			ſ	r	1		,			
T11-01J	V-4Cr-4Ti	BTC	425	2	1	11/12	_	12/12		
T11-02J	V-4Cr-4Ti	BTC	425	6	3	1/13	_	7/13		
T11-03J	V-4Cr-4Ti	BTC	425	2	1	11/12	-	12/12		
T11-04J	V-4Cr-4Ti	BTC	425	6	3	1/13	_	7/13		
T11-05J	SiC	BTC	600	2	1	11/12	_	12/12		
T11-06J	SiC	BTC	600	6	3	1/13	_	7/13		
T11-08J	SiC	BTC	600	6	3	1/13	_	7/13		
T11-09J	SiC	BTC	600	2	1	11/12	_	12/12		
T11-11J	SiC	BTC	600	2	1	11/12	_	12/12		
T11-13J	Graphite	BTC	600	2	1	11/12	_	12/12		
T11-14J	Graphite	BTC	600	6	3	1/13	_	7/13		
J12-01	F82H	BTC	300	1.5	1	1/13	_	2/13		
J12-02	F82H	BTC	300	6	3	5/13	_	7/13		
J12-03	F82H	BTC	300	1.5	1	5/13	-	2/13		
J12-04	F82H	BTC	300	6	3	1/13	_	6/13		
J12-05	F82H	BTC	300	1.5	1	1/13	-	2/13		

Experiment Designation	Primary Materials	Specimen Types*	Irradiation Temperature	Max Exposure (dpa)	Number of Reactor	Irradiation Period (month/year)				
			(0)	(upa)	Cycles	(monun/year)				
Target zone rabbit capsules (US-NIFS-JAEA) (Continued)										
J12-06	F82H	BTC	300	6	3	5/13	-	6/13		
Target zone rabbit capsules (US-IMR)										
MX-1	Ceramics	Various	400	2	1	7/13	_	8/13		
MX-2	Ceramics	Various	400	6	3	7/13	_	3/14		
MX-3	Ceramics	Various	400	10	6	7/13	_	7/14		
MX-4	Ceramics	Various	700	2	1	7/13	-	8/13		
MX-5	Ceramics	Various	700	6	3	7/13	-	2/14		
MX-6	Ceramics	Various	700	10	5	7/13	_	5/14		
MX-7	Ceramics	Various	1000	2	1	7/13	_	8/13		
MX-8	Ceramics	Various	1000	6	3	7/13	-	3/14		
MX-9	Ceramics	Various	1000	10	5	7/13	-	5/14		
IMR1	Various	Various	200	2	1	6/15	-	7/15		
IMR2	Various	Various	200	2	1	6/15	-	7/15		
IMR3	Various	Various	200	2	1	6/15	-	7/15		
IMR4	Various	Various	200	2	1		-			
IMR5	Various	Various	200	4	2	6/15	-	2/16		
IMR6	Various	Various	600	2	1		-			
IMR7	Various	Various	600	6	3		-			
IMR8	Various	Various	600	10	5					
IMR9	Various	Various	1000	2	1					
IMR10	Various	Various	1000	6	3					
IMR11	Various	Various	1000	10	5		-			
Target zone rabbit capsules (US)										
SCJ2-10	Ceramics	Joint	500	3	2	5/14	_	7/14		
SCJ2-11	Ceramics	Joint	500	>10	12	5/14	_			
SCJ2-12	Ceramics	Joint	500	3	2	5/14	_	7/14		
SCJ2-16	Ceramics	Joint	1000	3	2	6/14	_	8/14		
SCJ2-17	Ceramics	Joint	1000	3	2	6/14	-	8/14		

*T = Tensile, F = Fatigue, FT = Fracture Toughness, MC = Multipurpose Coupon, BSR = Bend Stress Relaxation Creep, DCT = Disc Compact Tension, BTC: Bellows-loaded Tensile Creep, UDMC: Unidirectional Mini-composite. Most experiments also contain TEM disks, other special purpose specimens, and monitors occupying small spaces.

**Hydraulic tube – fractional cycle exposures.