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FUSION MATERIALS SEMIANNUAL PROGRESS REPORT FOR THE PERIOD ENDING June 30, 2007

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FOREWORD

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

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

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

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

TABLE OF CONTENTS

1.0 VANADIUM ALLOYS

1.1 OPERATION OF A V-4CR-4TI THERMAL CONVECTION LOOP WITH LI AT 700°C— ORNL Loop Team: B. A. Pint, S. J. Pawel, M. Howell, J. L. Moser, G. Garner, M. Santella, P. F. Tortorelli, and J. R. DiStefano (Oak Ridge National Laboratory)

The loop experiment ran for 2,355h from March to June 2007 with a maximum temperature of $700^{\circ}\pm10^{\circ}$ Cand was stopped due to an unplanned power outage. After initial heating, the vacuum system ran at<1x10-5Pa, well below the level where significant oxidation of V-4Cr-4Ti is expected. Temperature control and monitoring was an issue and somewhat unusual temperature gradients were observed. Characterization of the exposed material will be conducted after the loop is drained and the specimens are removed in October 2007.

2.0 CERAMIC COMPOSITE MATERIALS

2.1 SUBCRITICAL CRACK PROPAGATION STUDIES IN HI-NICALON AND HI-NICALON 7 TYPE-S FIBER SIC/SIC COMPOSITES USING COMPACT TENSION SPECIMENS—C. H. Henager, Jr. (Pacific Northwest National Laboratory)

The potential use of SiC composites in fusion energy systems is well documented and studied. One of the main issues for the use of this material, other than radiation stability, is the long term crack growth stability problem or static fatigue issue compounded by environmental interactions. In ceramics this requires environmental crack growth studies under constant load and the properties of composites, while improved relative to monolithic ceramics, are nevertheless known to be strongly time and temperature dependent, especially with regard to crack growth. There are strong environmental interactions but also thermally-induced crack propagation rates are not well known. As fiber types evolve and weave structures are modified some of the basic crack growth data is required to understand failure in these materials and to provide design guidelines. Specimen geometry is critical since much data has been obtained using small specimens such as single-edge notched beams due to high materials costs. SENB bars in bending are attractive from a material conservation viewpoint but may not be attractive when geometrical and stress state effects are raised. The need for larger and more uniformly stressed samples is an important consideration. The use of CT specimens, even subscale, is a perceived improvement over SENB tests. This study is designed to show comparisons between data sets of similar materials tested in both geometries.

3.0 FERRITIC/MARTENSITIC STEELS AND ODS STEELS

3.1 MECHANICAL PROPERTIES OF UNIRRADIATED AND IRRADIATED REDUCED- 12 ACTIVATION MARTENSITIC STEELS WITH AND WITHOUT NICKEL COMPARED TO PROPERTIES OF COMMERCIAL STEELS—R. L. Klueh, M. A. Sokolov, and N. Hashimoto (Oak Ridge National Laboratory)

Tensile and Charpy specimens of four normalized-and-tempered martensitic steels were irradiated to 23-33 dpa at 376–405°C in the Experimental Breeder Reactor (EBR-II). The steels were the ORNL reduced-activation steel 9Cr-2WVTa and that containing 2% Ni (9Cr-2WVTa-2Ni), modified 9Cr-1Mo (9Cr-2WVTa), and Sandvik HT9 (12Cr-1MoVW). Two tempering conditions were used for 9Cr-2WVTa and 9Cr-2WVTa-2Ni: 1 hr at 700°C and 1 h at 750°C. The 9Cr-1MoVNb and 12Cr-1MoVW were tempered 1 h at 760°C. These heat treatments produced tempered-martensite microstructures for all steels except 9Cr-2WVTa-2Ni tempered at 750°C, where, a duplex structure of tempered and untempered martensite

11

6

1

2

formed. Based on changes in tensile and Charpy impact properties, the results demonstrated the superiority in strength and ductility of the 9Cr-2WVTa reduced-activation steel over the commercial steels. Comparison of the mechanical properties after irradiation of 9Cr-2WVTa-2Ni and 9Cr-2WVTa steels indicated a favorable effect of nickel that could lead to development of a heat treatment for improved irradiation resistance.

3.2 THE THERMAL STABILITY OF NANOSTRUCTURED FERRITIC ALLOYS—P. Miao, G. R. **25** Odette, T. Yamamoto, and D. Klingensmith (University of California, Santa Barbara)

The excellent tensile and creep strength and the potential for managing radiation damage make nanostructured ferritic alloys (NFAs) promising candidates for high temperature applications in spallation proton, advanced fission, and fusion neutron environments. The thermal stability of NFAs is critical for such applications, hence, this has been investigated in a series of aging experiments on MA957 at 900°C, 950°C, and 1000°C for times up to 8000 h. Optical and transmission electron microscopy (TEM) studies for 3000 h aged MA957 showed the fine scale grain and dislocation structures are stable up to 1000°C. TEM and small angle neutron scattering (SANS) showed that the nm-scale solute cluster-oxide features (NFs), that are a primary source of the high strength of NFAs, were stable at 900°C and coarsened only slightly at 950°C and 1000°C after 3000 h aging. Porosity that developed during high temperature aging was minimal at 900°C and modest at 950°C, but was much larger after 1000°C. Microhardness for the 3000 h aged MA957 was basically unchanged after the 900°C aging and decreased only slightly (\leq 3%) after aging at 950°C and 1000°C.

4.0	COPPER ALLOYS	34
	No contributions.	
5.0	REFRACTORY METALS AND ALLOYS	35
	No contributions.	
6.0	AUSTENITIC STAINLESS STEELS	36
6.1	INFLUENCE OF SILICON ON SWELLING AND MICROSTRUCTURE IN RUSSIAN AUSTENITIC STAINLESS STEELS IRRADIATED TO HIGH NEUTRON DOSES —S. I. Porollo, S. V. Shulepin, Yu. V. Konobeev (State Scientific Center of Russian Federation, Institute of Physics and Power Engineering), and F. A. Garner (Pacific Northwest National Laboratory)	37
	Void swelling and microstructural development of EI-847 austenitic stainless steel were investigated by destructive examination of fuel pin cladding irradiated in three fast reactors located in either Russia or Kazakhstan. The tendency of yoid swelling to be progressively	

investigated by destructive examination of fuel pin cladding irradiated in three fast reactors located in either Russia or Kazakhstan. The tendency of void swelling to be progressively reduced by increasing silicon concentration appears to be a very general phenomenon, whether observed in simple single-variable experiments on well-defined materials or observed in multivariable, time-dependent irradiations conducted on commercially-produced steels over a wide range of irradiation temperatures, neutron spectra and dpa rates. The role of silicon on microstructural development is expressed both in the solid solution and via its influence on formation of radiation-induced phases that in turn alter the matrix composition.

7.0 MHD INSULATORS, COATINGS, INSULATING CERAMICS, AND OPTICAL 52 MATERIALS

TRANSFORMATION OF Al₂O₃TO LiAIO₂ IN Pb-17Li AT 800°C—B. A. Pint and K. L.
More (Oak Ridge National Laboratory)

A FeCrAl substrate was pre-oxidized at 1000°C to thermally grow an external Al_2O_3 scale and then isothermally exposed to Pb-17Li for 1000h at 800°C to determine if this layer would protect the under lying alloy from dissolution. After exposure, a small mass gain was measured, indicating that the layer did inhibit dissolution. However, characterization of the external layer determined that it had transformed to LiAlO₂ with an increased thickness and a much larger grain size than the original layer. This observation has implications for the use of Al_2O_3 as a tritium diffusion barrier.

8.0 BREEDING MATERIALS

No contributions.

9.0 RADIATION EFFECTS, MECHANISTIC STUDIES, AND EXPERIMENTAL METHODS 59

9.1 PREDICTION OF STRUCTURAL AND ELECTRONIC PROPERTIES OF Y-TI-O 60 COMPLEX OXIDES USING AB-INITIO CALCULATIONS—Y. Jiang, J. R. Smith, and G. R. Odette (University of California, Santa Barbara)

Our objective is to develop a fundamental understanding of the identity and character of nm-scale features (NFs) in nanostructured ferritic alloys (NFAs), especially at the smallest sizes. The NFs' features are believed to be responsible for the very high creep strength and radiation damage resistance of NFAs. Atom probe tomography studies have indicated that the NFs have Ti + Y to O ratios greater than 1 and Ti to Y ratios much greater than 1. These elemental ratios are inconsistent with the known complex oxide phases in the Ti-Y-O system, which include complex cubic pyrochlore $Y_2Ti_2O_7$ and orthorhombic (at lower temperatures) Y₂TiO₅. Both of these phases have been observed in transmission electron microscopy studies of NFAs, but generally in a size range that is larger than the smallest, and very likely, non-equilibrium NFs. There are also a number of other open questions including the basic thermokinetics of NF precipitation and coarsening; and the basic characteristics of NFs, such as elastic properties and interface structures, that mediate their interactions with dislocations. Since it is difficult, if not impossible, to fully address many of these questions with direct experimental measurements, we have developed a multiscale modeling approach that will complement a range of characterization techniques that are needed to obtain reliable answers.

9.2 THE FORMATION AND STABILITY OF HE-VACANCY CLUSTERS WITHIN 67 DISPLACEMENT CASCADES IN α-Fe—F. Gao, H. L. Heinisch and R. J. Kurtz (Pacific Northwest National Laboratory)

Molecular dynamics (MD) methods have been utilized to study the formation of vacancy clusters created by displacement cascades in α -Fe containing concentrations of substitutional He atoms varying from 1-5%. These He concentrations are not necessarily intended to represent specific conditions within a fusion reactor (average end-of-life He concentrations in the first wall are expected to be on the order of 0.15%), but they provide an opportunity to investigate the effects of substantial amounts of He on cascade processes and microstructure development under damage producing conditions.

9.3 MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION—A. Caro, 72 P. Erhart, M. Serrano de Caro, B. Sadigh (Lawrence Livermore National Laboratory), E. Lopasso (Centro Atomico Bariloche, Argentine), D. Farkas (Virginia Polytechnic Institute), S. G. Srinivasan and C. Jiang (Lawrence Livermore National Laboratory)

Atomistic simulations of alloys at the empirical level face the challenge of correctly modeling basic thermodynamic properties. In the periods reported previously we develop a methodology to generalize many-body classic potentials to incorporate complex formation energy curves. Application to Fe-Cr allows us to predict the implications of the ab initio results of formation energy on the phase diagram of this alloy and to get a detailed insight

58

into the processes leading to precipitation of α' phase under irradiation. In particular in this period we report on the consequences of the negative heat of formation at low Cr composition on the short range order SRO existing in the α phase. We elaborate a simple description of SRO on a two-phase alloy and compare the predictions with experiments. We provide a key to rationalize a diversity of experiments on SRO versus annealing time or irradiation dose.

9.4 EFFECT OF MASS OF THE PRIMARY KNOCK-ON ATOM ON DISPLACEMENT CASCADE DEBRIS IN α-IRON—A. F. Calder, D. J. Bacon, A. V. Barashev (The University of Liverpool), and Yu. N. Osetsky (Oak Ridge National Laboratory)

Results are presented from molecular dynamics (MD) simulations of displacement cascades created in α -iron (Fe) by primary knock-on atoms (PKAs) with energy from 5 to 20 keV and mass chosen to represent C, Fe and Bi. Molecular Bi₂ has also been simulated using two Bi PKAs, and PKA-Fe interaction potential has also been varied. Four effects are reported. First, the PKA mass has a major effect on cascade damage while the interaction potential has little if any. Second, the total number of point defects produced in a cascade decreases with increasing PKA mass. This fact is not accounted for in models used conventionally for estimating damage. Third, interstitial loops of $\frac{1}{2}$ <111> type and both vacancy and interstitial loops of <100> type are formed, the latter being observed in MD simulation for the first time. The probability of <100> loop appearance increases with increasing PKA mass as well as energy. Finally, there is a correlation between production of large vacancy and interstitial clusters in the same cascade.

9.5 EFFECT OF SIZE ON THE DESTRUCTION MECHANISMS OF STACKING FAULT 89 TETRAHEDRA INDUCED BY GLIDING DISLOCATIONS IN QUENCHED GOLD—Y. Matsukawa (Argonne National Laboratory), Y. N. Osetsky, R. E. Stoller, and S. J. Zinkle (Oak Ridge National Laboratory)

The destruction processes of stacking fault tetrahedra (SFTs) induced by gliding dislocations were examined by transmission electron microscopy (TEM) in situ straining experiments for SFTs with edge lengths ranging from 10 to 50 nm. At least four distinct SFT destruction processes were identified: (1) consistent with Kimura model for both screw and 60-degree dislocations, (2) stress-induced SFT collapse into a triangular Frank loop, (3) partial annihilation leaving an apex portion, and (4) complete annihilation. Process (4) was observed at room temperature only for small SFTs (~10 nm); however, this process was also frequently observed for larger SFTs (~30 nm) at higher temperature (~853 K). When this process was induced, the dislocation always cross-slipped, indicating only screw dislocations can induce this process.

9.6 A COMPRESSION ANVIL BEAM TEST METHOD TO MEASURE THE ARREST 106 FRACTURE TOUGHNESS OF SEMI-BRITTLE MATERIALS WITH SMALL SPECIMENS— M. Y. He, G. R. Odette, and M. Hribernik (University Of California)

Our goal was to design a specimen and test procedure that allowed the measurement of cleavage arrest (K_{Ia}) fracture toughness in very small oriented iron single crystals (< 10 mm). This was accomplished by incorporating iron single crystal slices into composite specimens. The test method described here is based on compression loaded, double-anvil beam fracture specimen, illustrated in Fig. 1. Conceptually, slow, uniform compression (σ) loading of a beam with a shallow fatigue starter crack (thick black line) in an double anvil fixture (shown in black) results in Poisson stresses normal to the crack faces, and elastic energy is released as the crack (thin black line) propagates. Composite specimens were fabricated by a sequence of diffusion bonding single crystal slices (light grey) to low alloy steel arms (darker grey), followed by a sequence of electro-discharge machining (EDM), fatiguing and final EDM to the pre-cracked bar configuration shown in Fig. 1. The mode I stress intensity factor (SIF), K_{I_1} is a strong function of the crack depth **1**

80

(a/W). The SIF first increases to a maximum at a small a/W, and subsequently decreases very rapidly approaching 0 as a/W goes to 0.9 or less. The test is carried out by gradually increasing σ to the point where the crack initiates at σ_c and propagates until it arrests at a lower SIF K_I = K_{Ia}, terminating a substantial pop-in jump.

9.7 A CHEVRON NOTCHED WEDGE LOADED DOUBLE CANTILEVER BEAM TEST 117 METHOD TO MEASURE THE INITIATION AND ARREST FRACTURE TOUGHNESS OF SEMIBRITTLE MATERIALS WITH SMALL SPECIMENS—G. R. Odette, M. Y. He, and M. L. Hribernik (University of California, Santa Barbara)

Our goal was to design a specimen and test procedure that allowed the initiation and arrest of a crack in very small cleavage oriented iron single crystals (< 10 mm). This was accomplished by incorporating iron single crystal slices into composite specimens. The test method described here is based on a chevron-notched, wedge-loaded, double-cantilever beam specimen. Conceptually, slow insertion of the wedge, to load the beam arms, gradually increases the crack mouth opening displacement (Δ), and the corresponding stress intensity factor (SIF), K₁, up to K_{1c}, thus initiating a propagating cleavage crack. However, due to the combination the wedge loading a double-cantilevered beam and chevron geometry, the K₁ decreases very rapidly with increasing depth (a/W), and the crack arrests at a SIF K₁ = K_{1a}, after a short pop-in jump. Thus the crack can be grown in a series of short, and relatively stable, jumps. The initiation and arrest-re-initiation depths can be seen on the fracture surface.

10.0	DOSIMETRY, DAMAGE PARAMETERS, AND ACTIVATION CALCULATIONS	128
	No contributions.	
11.0	MATERIALS ENGINEERING AND DESIGN REQUIREMENTS	129
	No contributions.	
12.0	IRRADIATION FACILITIES AND TEST MATRICES	130
	No contributions.	

1.0 VANADIUM ALLOYS

OPERATION OF A V-4CR-4TI THERMAL CONVECTION LOOP WITH Li AT 700°C—ORNL Loop Team: B. A. Pint, S. J. Pawel, M. Howell, J. L. Moser, G. Garner, M. Santella, P. F. Tortorelli, and J. R. DiStefano (Oak Ridge National Laboratory)

OBJECTIVE

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

SUMMARY

The loop experiment ran for 2,355h from March to June 2007 with a maximum temperature of $700^{\circ}\pm10^{\circ}$ C and was stopped due to an unplanned power outage. After initial heating, the vacuum system ran at <1x10⁻⁵ Pa, well below the level where significant oxidation of V-4Cr-4Ti is expected. Temperature control and monitoring was an issue and somewhat unusual temperature gradients were observed. Characterization of the exposed material will be conducted after the loop is drained and the specimens are removed in October 2007.

PROGRESS AND STATUS

Introduction

A self-cooled lithium blanket concept is attractive for a fusion reactor because of lithium's tritium breeding capability and excellent heat transfer characteristics. Due to compatibility issues at >500°C, vanadium alloys [1] are the most likely structural materials for this concept. One of the critical issues for this, and any liquid-metal concept, is the need to reduce the pressure drop associated with the magneto hydrodynamic (MHD) force due to the high magnetic field in the reactor. [2,3] One solution to the MHD problem is to apply an electrically insulating coating to decouple the structural wall from the liquid metal.[4] The coating must be thin, durable and have a high electrical resistivity. It also must be almost crack-free to prevent shorting.[5,6] The current focus of the U.S. program on reducing the MHD pressure drop is on durable multi-layer coatings or a flow-channel insert. [7,8] Both of these solutions have been previously proposed;[4,9,10] however, little experimental verification has been conducted. Both concepts rely on excellent compatibility of a relatively thin V or V alloy layer to prevent Li from contacting and degrading the insulating ceramic layer. Initial capsule and in-situ testing of multi-layer coatings has shown some promising results.[11] However, a flowing Li test with a temperature gradient is needed to validate the compatibility of such thin layers. A brief summary of the vanadium-lithium compatibility literature[12] indicated a wide range of results with no systematic study of the effects or relative importance of alloying elements and Li impurities. To examine compatibility in a flowing system, a monometallic V-4Cr-4Ti thermal convection loop with V-4Cr-4Ti specimens was designed, constructed and operated with relatively high purity Li for 2,355h and a maximum operating temperature of ~700°C. A previous report[13] described the construction of the loop and the test specimens, while this report describes the operation. The loop will be drained and opened and the specimens characterized after October 1, 2007.

Results and Discussion

The V-4Cr-4Ti loop and 20 thermocouples (TC) were assembled in the vacuum chamber and the loop and fill tank (containing Li sticks) were evacuated with a roughing pump. The vacuum chamber was then closed and baked out for 48h at 150°C. A base vacuum of $<1x10^{-5}$ Pa was achieved with a vacuum gauge located on the chamber wall opposite the vacuum pump. On February 21, 2007, the furnaces were turned on and slowly heated to maintain the pressure in the $\sim 2x10^{-4}$ Pa range. A W wire with ceramic beads was

used to heat the cold leg to ~250°C. On February 22, 2007, an unsuccessful attempt was made to start flow in the loop. The Li melted in the tank and appeared to fill the loop. However, based on the various TC readings, there was concern that there was insufficient Li in the system or a Li leak. The furnaces were shut down and, after the system had cooled to room temperature, the chamber was opened. No Li leak was detected. An x-ray of the top of the loop showed that the hot leg was not filled to the top of the saddle. (Although with thermal expansion, there may have been sufficient Li to fill the loop at 700°C.) As a precaution, additional liquid Li was added to the tank from a heated secondary pot using pressurized He. The loop and tank were then closed and evacuated. The vacuum chamber was then closed and given a second 48h bake out at 150°C. A base vacuum of $8x10^{-6}$ Pa was achieved.

On March 7, 2007, the furnaces and W wire were again heated to melt the Li and begin operation. During this attempt, the upper and lower hot leg furnaces were heated to 950° and 890°C (60°C higher than the previous attempt) and flow was achieved at 5:40pm. The temperature at the top of the hot leg stabilized at 700°C by 6:15pm. This was considered the start of operation. During heating, the chamber pressure spiked into the 10^{-4} Pa range and a large pressure spike was observed when flow began and the top leg heated to >600°C for the first time. Within 100h of operation, the vacuum chamber pressure was below 1×10^{-4} Pa, Figure 1. Within 400h of operation, the pressure had dropped into the desired 10^{-5} Pa range and remained there for the rest of the operating period.

The temperature difference between the top of the hot leg and the bottoms of the cold leg and hot leg was unexpectedly high, Figure 1. The maximum temperature difference began at ~340°C and increased to almost 400°C during the first ~1250h. There is no apparent reason for the observed cooling of the bottom of the loop. A change in the heat transfer rate in the system does not appear likely. The ~700°C maximum loop temperature was controlled based on the TC in the thermal well at the top of the hot leg. After some initial adjustments of the furnace controller set point, the system operated with no set point changes until ~800h, Figure 2. A hot spot test conducted during this period indicated the Li velocity was ~2cm/s,



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



Figure 2. Comparison of temperature of the control TC in the furnace at the top of the hot leg to the TC temperature in the thermal well above that furnace that was used to control the maximum temperature in the loop.

somewhat slower than the 3-4cm/s measured in the stainless steel test loop at 550°C.[13] However, with the higher temperatures in this loop, it was more difficult to conduct the hot spot test as the hot spot temperature did not significantly increase the normal TC readings, especially in the hot leg. (Also, the hot spot was not moved from the bottom of the loop to the top of the loop where it would have worked more effectively.)

Figure 2 shows that after 800h it was necessary to increase the control point on the top furnace on the hot leg in order to keep the peak hot leg temperature at ~700°C. The furnace temperature was increased from 930°C to 965°C between 800h and 1200h. Between 1247 and 1262h of operation, the system underwent several unexplained excursions in temperature. There is no clear reason for these fluctuations which occurred over a weekend. No external change was evident in the vacuum system or furnaces. At ~1247.5h of operation, the cold leg began increasing in temperature with little change in the peak hot leg temperature, Figure 1. However, at 1260h the peak temperature increased to ~730°C for ~1h before dropping to ~690°C. At this point, the top furnace on the hot leg lost control and could no longer maintain its set point. The furnace control TC varied from 900-915°C during the remainder of the test instead of \pm 1°C observed during the first 1260h of operation, Figure 2. This is the reason why the maximum temperature was not maintained at 700°C during the final ~1100h of operation. It averaged ~688°C during this period. However, it is not clear what caused the furnace control problem. The furnace was still drawing current after the upset and was producing heat. Typical failures of resistively heated furnaces result in complete furnace failures due to element degradation or other problem. The furnace will be inspected when the chamber is opened.

The increase in temperature of the cold leg suggested that the Li velocity increased at this point. However, this could not be confirmed with the hot spot test. With the higher temperatures in the cold leg it was even more difficult to detect the effect of the hot spot on the local temperature. One test indicated that the Li

velocity had decreased to 0.6 cm/s but a lower velocity is not consistent with the observed temperature changes. A possible reason for the change is that the one (or both) of the specimen chains was restricting flow and that it moved, crept or broke during Li exposure. These possibilities cannot be evaluated until the loop is opened. For the remaining ~1100h, the loop operated with a temperature gradient of 215-230°C which is much closer to the expected gradient for this temperature and loop geometry. A thunderstorm caused an interruption in plant-wide power at 9:49pm on June 13, 2007. The system shut down after 2,355.5h of operation and was not restarted.

The two type S TCs did not indicate any degradation in the type K TCs during operation. One pair of S and K TCs located together at the bottom of the hot leg showed a difference of $8\pm1^{\circ}$ C during the entire test. The other pair at the top of the hot leg showed a wider variation but it did not consistently change with time.

One conclusion from the operation of this loop is that the system may have benefited from a third furnace on the loop between the bottom of the cold leg and the bottom of the hot leg. Over this ~30cm segment, the Li was flowing upward ~9cm (compared to 84cm in the hot and cold vertical legs). This uphill segment would represent a slight drag on flow and may be the reason it was difficult to initially start flow in the system. Four TC thermal wells were included in the V-4Cr-4Ti loop based on the poor experience with only one thermal well in the SS loop[13] and they were critical to controlling and monitoring this loop. However, even more TC redundancy would have been beneficial. Extra TCs could have been included to ensure that spurious readings were not due to TC degradation or failure.

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2.0 CERAMIC COMPOSITE MATERIALS

SUBCRITICAL CRACK PROPAGATION STUDIES IN HI-NICALON AND HI-NICALON TYPE-S FIBER SIC/SIC COMPOSITES USING COMPACT TENSION SPECIMENS—C. H. Henager, Jr. (Pacific Northwest National Laboratory)

OBJECTIVE

PNNL has performed subcritical crack growth tests under constant applied load at various elevated temperatures in inert environments using subscale compact tension (CT) specimens of two types of SiC-composite materials. The use of CT specimens is preferred over the usual dingle-edge notched beam (SENB) specimens due to more uniform applied stresses over the crack growth region. This study will compare crack growth data taken between two materials as well as specimen geometry types, CT compared to SENB. Plain weave [0/90] Hi-Nicalon CT specimens were tested in argon atmospheres and compared to similar tests of 5-harness satin weave [0/90] Hi-Nicalon Type-S composites. We report here some of the preliminary fractographic examinations of the two materials and an initial assessment of the crack growth data. Additional information on this study will be presented later and also at the 13th International Conference on Fusion Reactor Materials in December.

SUMMARY

The potential use of SiC composites in fusion energy systems is well documented and studied. One of the main issues for the use of this material, other than radiation stability, is the long term crack growth stability problem or static fatigue issue compounded by environmental interactions. In ceramics this requires environmental crack growth studies under constant load and the properties of composites, while improved relative to monolithic ceramics, are nevertheless known to be strongly time and temperature dependent, especially with regard to crack growth. There are strong environmental interactions but also thermally-induced crack propagation rates are not well known. As fiber types evolve and weave structures are modified some of the basic crack growth data is required to understand failure in these materials and to provide design guidelines. Specimen geometry is critical since much data has been obtained using small specimens such as single-edge notched beams due to high materials costs. SENB bars in bending are attractive from a material conservation viewpoint but may not be attractive when geometrical and stress state effects are raised. The need for larger and more uniformly stressed samples is an important consideration. The use of CT specimens, even subscale, is a perceived improvement over SENB tests. This study is designed to show comparisons between data sets of similar materials tested in both geometries.

PROGRESS AND STATUS

Materials

The SiC/SiC materials that were tested included (1) a 5-harness satin weave, 8-ply, [0/90] Hi-Nicalon Type-S fiber composite t from GE Power Systems¹ and (2) a plain weave, 8-ply, [0/90] Hi-Nicalon fiber composite from Dupont Lanxide Corporation (now GE Power Systems¹). A 150-nm thick pyrocarbon (PyC) interface was applied to the Type-S fibers prior to ICVI processing, while the Hi-Nicalon fibers were coated with 1- μ m PyC and similarly processed. Fiber volume fractions were 40% for each material.

Experimental

Subscale CT specimens of each material [1] were tested in an Instron test machine in a high-temperature furnace in argon at the specified test temperature. The initial notch radius was 0.2-mm and the specimens were tested under constant applied loads calculated to provide an initial stress intensity of 10 MPa \sqrt{m} at the notch root. Crack propagation was monitored using a laser extensometer that measured load-line displacements (COD). A plot showing the time-dependent displacements observed during these

¹http://www.gepower.com



tests for both materials is shown in Fig. 1, where the test temperature is 1373K.

Fig. 1. Load-line crack opening displacements versus time plot of Hi-Nicalon and Hi-Nicalon Type-S fiber composites at 1373K slow crack growth for CT specimens tested in argon.

RESULTS AND DISCUSSION OF ONGOING WORK

One of the main findings has been reported before, namely, that Hi-Nicalon Type-S fiber is more creep resistant than Hi-Nicalon fiber and this is clearly observed in the data shown in Fig. 1. Under identical loading conditions the Type-S fiber has a lower crack growth rate as reflected in the load-line COD data. This is illustrated in Fig. 2 showing displacement-time data for Hi-Nicalon at 1373K compared to that for Type-S at 1473K. The fiber creep data of DiCarlo et al. indicates that Type-S fiber provides about 100K of additional temperature utility compared to Hi-Nicalon fibers [2-4], which the CT data demonstrates.



Fig. 2. Load-line crack opening displacement versus time plot of Hi-Nicalon at 1373K and Hi-Nicalon Type-S fiber composite at 1473K slow crack growth for CT specimens tested in argon.

Compared to an SENB bar, the CT specimen geometry offers much larger crack growth volumes and more uniform stresses during the crack growth test as the crack extends from the notch. For the SENB bars tested previously at PNNL and elsewhere previously [5], the distance from the notch tip to the end of the specimen is 4.5-mm versus 22-mm for the CT specimen. In terms of fiber bundles and weave patterns this translates into approximately 3 fiber weave bundles for the SENB bar compared to 14 for the CT specimen, which is significant difference. However, for the CT specimen once the crack has grown about 10-mm the system becomes unstable with respect to fast fracture and, under constant load, the sample will fail. Thus, the difference in usable crack extension is not as great as indicated above. The SENB bar is stable until the crack reaches the far end. Further work will compare SENB data with CT data in terms of absolute crack velocities and the measure temperature dependence of crack growth in the Type-S fiber composite. Both the CT and SENB specimens are able to sustain stable crack growth over 6 x 10^5 seconds. Figure 3 shows representative curves for CT and SENB tests with the Type-S composite material in each case at 1373K.



Fig. 3. Displacement-time data for Type-S fiber composites tested at 3173K in argon for CT and SENB specimens. The displacement curves cannot be directly compared due to geometry effects. However, the curve shapes are similar and can be fit using log functions as discussed previously [6].

Fractography on the CT specimen has begun and is one aspect of comparing specimen geometry types. Longer crack growth distances and larger interaction volumes provide more crack-fiber interactions for study. Figure 4 is a composite image spanning about 1.2-mm in distance from the notch tip showing the cracking pattern present in the CT specimen tested at 1373K in argon. Broken fibers near the tip of the notch where the crack opening is largest gradually transition to bridged fibers at about 0.5-mm from the notch tip. Further study of such images is required before comparison to SENB cracking patterns can be made.

RESULTS

CT and SENB crack growth data for SiC/SiC composites provide needed data for time-dependent deformation in these materials. CT specimens are larger, require more material, provide more uniform stresses during crack propagation, and have larger cracked volumes for study. SENB specimens are much less expensive to prepare and conserve materials but lack uniform stress fields and have shorter crack propagation distances. However, the crack distances may be long enough provided that the fundamental process is the interaction of the crack with single bridged fibers since each fiber bundle

includes several hundred fibers. The CT specimen may provide better characterization of crack growth rate and mechanisms if composite architecture dominates.



Fig. 4. Composite image of optical micrographs showing cracks grown in Type-S composite material tested at 1373K in argon over 4×10^5 seconds of slow crack growth.

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3.0 FERRITIC/MARTENSITIC STEELS AND ODS STEELS MECHANICAL PROPERTIES OF UNIRRADIATED AND IRRADIATED REDUCED-ACTIVATION MARTENSITIC STEELS WITH AND WITHOUT NICKEL COMPARED TO PROPERTIES OF COMMERCIAL STEELS—R. L. Klueh, M. A. Sokolov, and N. Hashimoto (Oak Ridge National Laboratory)

OBJECTIVE

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

ABSTRACT

Tensile and Charpy specimens of four normalized-and-tempered martensitic steels were irradiated to 23-33 dpa at 376–405°C in the Experimental Breeder Reactor (EBR-II). The steels were the ORNL reducedactivation steel 9Cr-2WVTa and that containing 2% Ni (9Cr-2WVTa-2Ni), modified 9Cr-1Mo (9Cr-2WVTa), and Sandvik HT9 (12Cr-1MoVW). Two tempering conditions were used for 9Cr-2WVTa and 9Cr-2WVTa-2Ni: 1 hr at 700°C and 1 h at 750°C. The 9Cr-1MoVNb and 12Cr-1MoVW were tempered 1 h at 760°C. These heat treatments produced tempered-martensite microstructures for all steels except 9Cr-2WVTa-2Ni tempered at 750°C, where, a duplex structure of tempered and untempered martensite formed. Based on changes in tensile and Charpy impact properties, the results demonstrated the superiority in strength and ductility of the 9Cr-2WVTa reduced-activation steel over the commercial steels. Comparison of the mechanical properties after irradiation of 9Cr-2WVTa-2Ni and 9Cr-2WVTa steels indicated a favorable effect of nickel that could lead to development of a heat treatment for improved irradiation resistance.

Introduction

The 9Cr reduced-activation ferritic/martensitic steels are candidates for applications as first wall and blanket structural materials for future fusion reactors. Displacement damage by neutron irradiation of this type of steel below 425–450°C hardens the steel lattice, causing an increase in strength and a decrease in toughness. The effect on impact toughness is measured in a Charpy test as an increase in the ductile-brittle transition temperature (DBTT) and a decrease in the upper-shelf energy (USE).

The possible effect of helium on hardening and embrittlement is important because large amounts of transmutation helium will form in a ferritic/martensitic steel first wall of a fusion reactor. Nickel-doped 9 and 12 Cr steels have been irradiated in the High Flux Isotope Reactor (HFIR) to study the effect of helium on fracture [1]. Helium is formed in a mixed-spectrum reactor such as HFIR by a two-step transmutation reaction between ⁵⁸Ni and the thermal neutrons; natural nickel contains 68% ⁵⁸Ni. This technique allows for the simultaneous production of displacement damage from the fast neutrons in the spectrum and helium from the thermal neutrons, thus simulating what will happen in a fusion reactor first wall.

Results from irradiation experiments on nickel-doped 9Cr-1MoVNb and 12Cr-1MoVW steels in HFIR at 300 and 400°C indicated that helium caused embrittlement in addition to that due to displacement damage alone [2–4]. On the other hand, some low-temperature irradiation experiments of nicked-doped 9Cr reduced-activation steels irradiated under conditions where no helium formed showed that the nickel-doped steels hardened more than steels without the nickel addition [5,6]. These results indicated that the nickel-doping simulation technique should be used with caution, especially below about 300°C.

In this paper, tensile and Charpy properties are reported for the reduced-activation steel ORNL 9Cr-2WVTa and this steel containing 2% Ni (9Cr-2WVTa-2Ni) after irradiation in the Experimental Breeder Reactor (EBR-II)—a fast reactor where little helium forms. The objective was to determine whether there is increased hardening in the nickel-containing steel compared to the steel without nickel. In addition, the commercial non-reduced-activation steels modified 9Cr-1Mo (9Cr-1MoVNb) and Sandvik HT9 (12Cr-

1MoVW) were irradiated and tested to determine differences between reduced-activation and conventional steels.

Experimental Procedure

Compositions and designations of the steels used in this experiment are given in Table 1. In the original Oak Ridge National Laboratory (ORNL) program to develop reduced-activation steels [7], an 18-kg heat of the electroslag-remelted 9Cr-2WVTa steel was produced by Combustion Engineering Inc, Chattanooga, TN. Material from that heat was used as the master alloy to prepare 450-g vacuum arcmelted button heats of 9Cr-2WVTa and 9Cr-2WVTa-2Ni steels. The 9Cr-2WVTa heat was a remelt of the master alloy so that the steels could be compared after similar processing.

Element ^a	9Cr-2WVTa	9Cr-2WVTa-2Ni	9Cr-1MoVNb⁵	12Cr-1MoVW ^c
С	0.098	0.098	0.092	0.20
Si	0.19	0.19	0.15	0.17
Mn	0.39	0.38	0.48	0.57
Р	0.014	0.014	0.012	0.016
S	0.003	0.003	0.004	0.003
Cr	8.71	8.55	8.32	12.1
Мо	<0.01	<0.01	0.86	1.04
W	2.17	2.15	<0.01	0.61
Ni	0.02	2.01	0.09	0.51
V	0.23	0.23	0.20	0.29
Nb	<0.01	<0.01	0.06	<0.001
Та	0.06	0.06		
N	0.016	0.016	0.054	0.027

Table 1. Chemical composition of the steels leste	Table 1.	Chemical co	omposition	of the	steels teste
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^aBalance iron

^bModified 9Cr-1Mo steel

^cSandvik HT9

The small heats were cast as 25.4 mm x 12.7mm x 152 mm ingots, after which they were rolled to 6.4mm plate and 0.76 mm sheet. The steels were normalized by austenitizing for 0.5 h at 1050°C in a helium atmosphere, after which they were quickly cooled in flowing helium. Specimens were irradiated in two tempered conditions: 1 h at 700°C and 1 h at 750°C.

The modified 9Cr-1Mo (9Cr-1MoVNb) and Sandvik HT9 (12Cr-1MoVW) steels were from large commercial-size heats that have been irradiated previously and were included in this experiment as benchmarks for the reduced-activation steels.

Tensile specimens 44.5-mm long with a reduced gage section of 20.3 x 1.52 x 0.76 mm were machined from the 0.76-mm sheet with gage lengths parallel to the rolling direction. Specimens were heat treated after machining. Tests were conducted on irradiated and unirradiated specimens at 400°C (near the irradiation temperature) in vacuum on a 44-kN Instron universal testing machine at a nominal strain rate of 4 x 10^{-4} s⁻¹.

Two tensile specimens of each heat and each heat-treated condition were irradiated in the COBRA experiment in EBR-II at temperatures of 390 to 395° C. Fluence was determined from flux monitors in the irradiation canisters. There were minor variation for different specimens, depending on their position in the canisters, but the individual sets of specimens for a given steel and heat treatment were kept together in the canisters and experienced the same irradiation conditions. Tensile specimens were irradiated to 6.7×10^{26} to 6.9×10^{26} n/m² (E>0.1 MeV), which produced between 32 and 33 dpa.

One-third-size Charpy specimens measuring $3.3 \times 3.3 \times 25.4$ mm with a 0.51-mm-deep 30° V-notch and a 0.05- to 0.08-mm-root radius were machined from normalized-and-tempered 6.4-mm plates. Specimens were machined with the longitudinal axis along the rolling direction and the notch transverse to the rolling direction (L-T orientation). The absorbed energy vs. temperature values were fit with a hyperbolic tangent function to permit the USE and DBTT to be consistently evaluated. The DBTT was determined at an energy level midway between the upper- and lower-shelf energies. Details of the test procedure for the subsize Charpy specimens have been published [10–12].

Six Charpy specimens of each heat and each heat-treated condition were irradiated in the COBRA experiment in EBR-II at temperatures of 376 to 405° C. Individual sets of Charpy specimens for a given steel and heat treatment were kept together, although the conditions were somewhat different from the tensile specimens. Charpy specimens were irradiated to 5.1×10^{26} to 6.9×10^{26} n/m² (E>0.1 MeV), which produced between 23 and 33 dpa. Helium concentrations for both the tensile and Charpy specimens were calculated as 3–6 appm, depending on the dose and composition (the 6 appm was for the steel containing 2% Ni).

Results

First, results for 9Cr-2WVTa steel with and without nickel will be presented to demonstrate the effect of tempering and the effect of nickel. After that, results for the reduced-activation 9Cr-2WVTa and 9Cr-2WVTa-2Ni will be compared with the commercial modified 9Cr-1Mo (9Cr-1MoVNb) and Sandvik HT9 (12Cr-1MoVW) steels.

9Cr2WVTa and 9Cr-2WVTa-2Ni Steels

Tensile Properties

In the unirradiated condition, the strength of the 9Cr-2WVTa was substantially higher and ductility lower when tempered at 700°C than at 750°C (Table 2 and Figs. 1 and 2). The strength of the 9Cr-2WVTa-2Ni after the 700°C temper was essentially the same as that for 9Cr-2WVTa tempered at 700°C. The yield stress for 9Cr-2WVTa-2Ni also decreased when tempered at 750°C compared to 700°C, but the relative change was much less than for 9Cr-2WVTa (≈5% vs. 26% decrease). When tempered at 750°C, the 9Cr-2WVTa-2Ni was considerably stronger than the 9Cr-2WVTa. There was no difference in the ultimate tensile strength of the 9Cr-2WVTa-2Ni for the two tempering conditions, and contrary to observations on 9Cr-2WVTa, the total elongation after the 750°C temper was less than after the 700°C temper, and there was no change in uniform elongation.

Stool	Tompor	Irradiation	Strengt	h (MPa)	Elongation (%)	
Sleel	remper	Inaulation	Yield	Yield Ultimate		Total
9Cr-2WVTa	700°C	Unirradiated	701	758	2.7	9.7
9Cr-2WVTa	700°C	390°C/32.6dpa	698	732	1.2	6.5
9Cr-2WVTa	750°C	Unirradiated	517	595	3.3	11.0
9Cr-2WVTa	750°C	390°C/32.6dpa	613	645	1.3	7.1
9Cr-2WVTa -2Ni	700°C	Unirradiated	707	788	2.7	11.3
9Cr-2WVTa -2Ni	700°C	390°C/32.6dpa	649	690	3.4	10.0
9Cr-2WVTa -2Ni	750°C	Unirradiated	674	787	2.7	8.3
9Cr-2WVTa -2Ni	750°C	390°C/32.6dpa	637	699	3.4	10.8
9Cr-1MoVNb	760°C	Unirradiated	562	636	1.4	4.6
9Cr-1MoVNb	760°C	395°C/32.1dpa	612	626	0.7	5.3
12Cr-1MoVW	760°C	Unirradiated	558	697	1.9	4.3
12Cr-1MoVW	760°C	395°C/32.1dpa	720	776	1.7	4.0

Table 2. Tensile data for unirradiated and irradiated steels tested at 400°C*

*Data are for the average of two tests.



Fig. 1. (a) Yield stress and (b) ultimate tensile strength of 9Cr-2WVTa and 9Cr-2WVTa-2Ni steels for two different tempering conditions before and after irradiation in EBR-II.



Fig. 2. (a) Uniform elongation and (b) total elongation of 9Cr-2WVTa and 9Cr-2WVTa-2Ni steels for two different tempering conditions before and after irradiation in EBR-II.

Irradiated tensile specimens were tested at 400°C (Table 2 and Figs. 1 and 2), which is near the irradiation temperature (390°C). There was little effect of irradiation on strength for the 9Cr-2WVTa tempered at 700°C and on the 9Cr-2WVTa-2Ni for both tempering conditions (Fig. 1). A small amount of irradiation hardening was observed for 9Cr-2WVTa after the 750°C temper. The effect of irradiation on ductility (Fig. 2) appeared to be greater for 9Cr-2WVTa than 9Cr-2WVTa-2Ni. For both tempering conditions, uniform elongation of the 9Cr-2WVTa-2Ni increased after irradiation, while that for 9Cr-2WVTa decreased. Total elongation of the 9Cr-2WVTa also decreased after irradiation for both tempering conditions, but the total elongation for 9Cr-2WVTa-2Ni decreased slightly after the 700°C temper and increased slightly after the 750°C temper.

Charpy Properties

Charpy data are summarized in Table 3. Both the 9Cr-2WVTa and 9Cr-2WVTa-2Ni steels with either the 700 and 750°C tempers had low DBTTs in the unirradiated condition (Fig. 3). Nickel had a beneficial effect on the transition temperature prior to irradiation, for in both heat-treated conditions, the nickel-containing steel had the lowest value.

Stool	Tompor	Irrdn Dese	Uirrd	Irrd	DBTT	Uirrd		
Sleer	remper	Temp	Dose	DBTT	DBTT	Shift	USE	
0 Cr 2) M/V/Ta	700°C	376°C	23 dpa	-77°C	-26°C	51°C	9.6 J	7.1 J
901-2000 Ta	750°C	390°C	33 dpa	-81°C	-98°C	0°C	14.0 J	9.0 J
	700°C	404°C	26 dpa	-97°C	-81°C	16°C	9.1 J	7.6 J
901-20001-200	750°C	390°C	33 dpa	-125°C	-86°C	39°C	12.8 J	7.1 J
9Cr-1MoVNb	760°C	405°C	24 dpa	-17°C	31°C	48°C	10.0 J	8.0 J
12Cr-1MoVW	760°C	405°C	24 dpa	-34°C	54°C	84°C	5.4 J	3.5 J

Table 3. Charpy data for unirradiated and irradiated steels



Fig. 3. Charpy impact transition temperature of 9Cr-2WVTa and 9Cr-2WVTa-2Ni steels in the unirradiated and irradiated conditions.

After irradiation of the two steels tempered at 700°C, the 9Cr-2WVTa steel showed the larger shift in DBTT (Fig. 3). For the steels tempered at 750°C, the steel without nickel showed a decrease in DBTT, while the DBTT of the nickel-containing steel increased 39°C. Although the 9Cr-2WVTa-2Ni showed the larger increase in DBTT, the final values for the two steels were similar (-98 and -86°C, respectively), because of the lower DBTT of the nickel-containing steel in the unirradiated condition.

Before irradiation, the USE values for the 9Cr-2WVTa were slightly greater than those for 9Cr-2WVTa-2Ni (Fig. 4); the values for both steels after the 750°C temper were higher than after the 700°C temper. Irradiation caused a decrease in the USE, with the largest decrease occurring for the steels with the 750°C temper. As a result, after irradiation there was little difference in the USE of the steels given the different tempering treatments, with the 9Cr-2WVTa having a slight advantage after the 750°C temper.



Fig. 4. Charpy upper-shelf energy of 9Cr-2WVTa and 9Cr-2WVTa-2Ni steels in the unirradiated and irradiated conditions.

Comparison of Reduced-activation and Commercial Steels

Comparison of the reduced-activation 9Cr-2WVTa and 9Cr-2WVTa-2Ni steels with the conventional 9Cr-1MoVNb and 12Cr-1MoVW steels was made for the reduced-activation steels tempered 1 h at 750°C. The commercial steels were both tempered 1 h at 760°C (typical tempering conditions for these steels).

Tensile Properties

In the unirradiated condition, there was relatively little difference in strength among the four steels (Table 2 and Fig. 5), with the 9Cr-2WVTa-2Ni somewhat stronger than the others. Despite the higher strength, the ductility was not significantly affected (Fig. 6). The 9Cr-2WVTa and 9Cr-2WVTa-2Ni had significantly higher ductility than the 9Cr-1MoVNb and 12Cr-1MoVW steels.

For all the steels but the 9Cr-2WVTa-2Ni, both the yield stress and ultimate tensile strength indicated that relatively minor irradiation hardening occurred, but in the case of 9Cr-2WVTa-2Ni, slight softening occurred (Fig. 5). This was reflected in the ductility (Fig. 6), where uniform and total elongation of the 9Cr-2WVTa-2Ni steel increased. The total elongation of the 9Cr-1MoVNb also increased slightly after irradiation. The 9Cr-2WVTa-2Ni steel had the highest uniform and total elongation of the four steels after irradiation. The greatest decrease in ductility was observed for the 9Cr-2WVTa steel, although after irradiation it had ductility as good as or better than that for 9Cr-1MoVNb and 12Cr-1MoVW. Although these latter two steels showed relatively minor ductility changes, they had lower ductilities than the reduced-activations steels after irradiation, as they also did before irradiation.

Charpy Properties

In both the unirradiated and irradiated conditions, transition temperatures of 9Cr-2WVTa and 9Cr-2WVTa-2Ni steels tempered at 750°C had significant advantages over those for the commercial steels tempered at 760°C (Table 3 and Fig. 7). After irradiation, the commercial 9Cr-1MoVNb and 12Cr-1MoVW steels had DBTT values above room temperature, whereas values for the two reduced-activation steels were well below 0°C. This occurred despite the 9Cr-1MoVNb and 12Cr-1MoVW steels being irradiated at a higher temperature and to a lower dose (Table 3). Indeed, in both the unirradiated and irradiated

conditions, the transition temperature values of the 9Cr-2WVTa and 9Cr-2WVTa-2Ni tempered at 700°C were much better than either of the commercial steels tempered at 760°C (Table 3).



Fig. 5. (a) Yield stress and (b) ultimate tensile strength of unirradiated and irradiated 9Cr-2WVTa, 9Cr-2WVTa-2Ni, modified 9Cr-1Mo (9Cr-1MoVNb), and Sandvik HT9 (12Cr-1MoVW) steels.



Fig. 6. (a) Uniform and (b) total elongation of unirradiated and irradiated 9Cr-2WVTa, 9Cr-2WVTa-2Ni, modified 9Cr-1Mo (9Cr-1MoVNb), and Sandvik HT9 (12Cr-1MoVW) steels.

Before irradiation, the USE values of the 9Cr-2WVTa and 9Cr-2WVTa-2Ni tempered at 750°C were also better than those of the 9Cr-1MoVNb and 12Cr-1MoVW steels tempered at 760°C (Fig. 8). After irradiation, USE values of 9Cr-2WVTa, 9Cr-2WVTa-2Ni, and 9Cr-1MoVNb were similar, and all three were considerably higher than that for 12Cr-1MoVW steel. Both before and after irradiation, USE values for the 9Cr-2WVTa and 9Cr-2WVTa-2Ni steels tempered at 700°C (Fig. 8) were comparable to the commercial steels before and after irradiation, even though the latter steels were tempered at a higher temperature.



Fig. 7. Charpy impact transition temperature of 9Cr-2WVTa, 9Cr-2WVTa-2Ni, modified 9Cr-1Mo (9Cr-1MoVNb), and Sandvik HT9 (12Cr-1MoVW) steels in the unirradiated and irradiated conditions.



Fig. 8. Charpy impact upper-shelf energy of 9Cr-2WVTa, 9Cr-2WVTa-2Ni, modified 9Cr-1Mo (9Cr-1MoVNb), and Sandvik HT9 (12Cr-1MoVW) steels in the unirradiated and irradiated conditions.

Discussion

As discussed above, the primary reason for irradiating 9Cr-2WVTa-2Ni is that an (n,α) reaction between ⁵⁸Ni and thermal neutrons in a mixed-spectrum reactor produce helium, thus providing a simulation technique for studying helium effects for fusion applications. Irradiation of the steels in a fast reactor, such as EBR-II, where very little helium forms, provides a control for irradiation in HFIR where much larger amounts of helium are generated.

Nickel is an austenite-stabilizing element that causes a reduction in A_1 , the equilibrium temperature above which ferrite begins to transform to austenite. If the tempering temperature is above the A_1 , then any austenite formed during tempering will transform to martensite during air cooling from the tempering temperature, and such a "normalized-and-tempered" steel will contain untempered martensite.

Previous helium-effects studies were made on steels with and without nickel tempered below the A_1 (usually at 700°C for several hours) to similar strengths [2]. In the present experiment, the 750°C temper was used to investigate the effect of untempered martensite, which should provide a strengthening effect.

For the commercial 9Cr-1MoVNb and 12Cr-1MoVW steels, previous work showed that the addition of 2% nickel lowered their A₁ temperatures to \approx 710°C [11]. In the absence of the 2% Ni, the A₁ of the steels exceeds 800°C. Because of the similarity of the commercial and reduced-activation steels, it was assumed that A₁ for the 9Cr-2WVTa-2Ni steel would also be between 700 and 750°C. This was verified by the comparison of the change in the unirradiated strengths of the 9Cr-2WVTa and 9Cr-2WVTa-2Ni for the two tempering conditions (Table 2 and Fig. 1). After a 700°C temperature, the two steels have similar strengths. Therefore, the presence of untempered martensite is indicated in the observation that the yield stress for 9Cr-2WVTa decreased 184 MPa, compared to a much smaller 33 MPa decrease for 9Cr-2WVTa-2Ni. The reduced strength for the steel without nickel given the 750°C temper is the expected behavior. Thus, the 9Cr-2WVTa-2Ni must contain considerable untempered martensite to account for the much smaller decrease and that there was no change in the ultimate tensile strength. Optical microscopy revealed a duplex structure in the 9Cr-2WVTa-2Ni that was not present in the 9Cr-2WVTa, because the untempered martensite in the 9Cr-2WVTa, because the untempered martensite in the 9Cr-2WVTa-2Ni that was not present in the 9Cr-2WVTa, because the untempered martensite in the 9Cr-2WVTa-2Ni etched darker than the tempered martensite (Fig. 9).



Fig. 9. Microstructures of normalized (a) 9Cr-2WVTa and (b) 9Cr-2WVTa-2Ni steels tempered at 750°C. The dark-etching regions in the 9Cr-2WVTa-2Ni are untempered martensite present in the steel because the tempering temperature was above the A_1 .

The tensile results for the 9Cr-2WVTa and 9Cr-2WVTa-2Ni steel are most interesting. First, before irradiation of the steels tempered at 750°C, the 9Cr-2WVTa-2Ni was 30% stronger than the 9Cr-2WVTa (Fig. 1). Second, a most unusual observation after irradiation was that the 9Cr-2WVTa-2Ni softened for both tempering conditions. The 9Cr-2WVTa tempered at 700°C also softened, but hardening occurred for this steel tempered at 750°C.

Despite the relatively small irradiation hardening, the uniform and total elongations of the 9Cr-2WVTa steel decreased for both tempering temperatures. However, the uniform elongation of the 9Cr-2WVTa-

2Ni, which was the harder steel containing untempered martensite after the 750°C temper, actually increased for both tempering conditions, as did the total elongation for this steel tempered at 750°C. A slight decrease in total elongation was observed for the 9Cr-2WVTa-2Ni steel tempered at 700°C. The ductility of the nickel-containing steel after irradiation was superior to that of the steel without nickel for all conditions.

This unexpected behavior of the 9Cr-2WVTa-2Ni was also indicated when the steels tempered at 750°C were compared with 9Cr-1MoVNb and 12Cr-1MoVW steels tempered at 760°C. In this case, the 9Cr-2WVTa-2Ni was the only steel not hardened, although none of the other three steels hardened significantly (Fig. 5). Likewise the 9Cr-2WVTa-2Ni steel had the best ductility after irradiation. Comparison of the results for the different steels also demonstrated the excellent behavior of the reduced-activation 9Cr-2WVTa steel relative to the two commercial steels.

The relatively minor hardening—and softening—was unexpected from previous experiments where these steels were irradiated at $\approx 400^{\circ}$ C [12–14]. An explanation can be found in results from several investigators who found a peak in irradiation hardening with increasing fluence for reduced-activation steels (Fig. 10) [15] and commercial-type Cr-Mo steels [16,17]. For the reduced-activation steels, the reduction in irradiation hardening with increasing dose begins to approach the unirradiated value near 30 dpa [Fig. 10(a)]. This is similar to the dose achieved in the specimens in the present experiment that showed this behavior. Figure 10(b) indicates that total elongation decreased to a plateau around 30 dpa. There is an indication of a minimum in total elongation for one of the steels in Fig. 9(b), but the minimum is beyond 30 dpa. An explanation for the peak in strength is that irradiation-enhanced recovery of the microstructure offsets irradiation hardening [17].



Fig. 10. The (a) yield strength and (b) total elongation as a function of irradiation dose for several reduced-activation steels [14].

The positive effect of nickel and untempered martensite in irradiated 9Cr-2WVTa-2Ni steel tempered at 750°C can also be explained in terms of an effect of irradiation-enhanced recovery and, in particular, irradiation-enhanced recovery of the untempered martensite. In this case, the effect of recovery is dominant from the beginning of the irradiation, and it is hypothesized that the higher rate of recovery of the untempered martensite irradiation hardening. This assumes that the effect is not due to the nickel, which is a reasonable assumption, since there is relatively little difference in the tensile properties between the 9Cr-2WVTa and 9Cr-2WVTa-2Ni tempered at 700°C, either before or after irradiation.

The microstructure of the 9Cr-2WVTa-2Ni is expected to be a duplex structure with hard zones (untempered martensite) and soft zones (tempered martensite), as indicated in Fig. 9. The excellent ductility and strength of the steel implies that ductility is determined by the tempered martensite, and the strength is determined by the untempered martensite. If this explanation is correct, then the irradiation resistance of reduced-activation 9Cr-2WVTa steel could be improved by tempering above the A_1 or adding nickel to the steels. The former is preferred because nickel additions are known to decrease creep strength [18]. Experiments would be required to determine the relative amount of untempered and tempered martensite for optimum properties. This microstructure could be tailored to produce a higher-strength steel with less irradiation hardening. Since irradiation hardening causes embrittlement, as measured in a Charpy impact test, less embrittlement should occur. The Charpy results discussed below support this conclusion.

Irradiation-enhanced recovery can also explain the observations on the lack of hardening for the steels tempered at 700°C (Table 2). These steels were tempered to a significantly lesser extent than was the 9Cr-2WVTa steel tempered at 750°C. Tempering at 700°C instead of 750°C results in smaller and more numerous precipitates plus a higher dislocation density. Equilibrium for the steels involves larger precipitates and a reduced dislocation density, and in the absence of irradiation, it is approached by thermal aging. Enhanced diffusion rates due to the excess vacancies and interstitials produced by irradiation should speed up the recovery/aging process and also enhance vacancy/interstitial annihilation. Irradiation-enhanced thermal aging has been observed for irradiations at 550°C [19].

In the normalized-and-tempered condition, the Charpy results demonstrated the excellent impact properties of the reduced-activation 9Cr-2WVTa steel compared to the commercial steels modified 9Cr-1Mo (9Cr-1MoVNb) and Sandvik HT9 (12Cr-1MoVW) (Figs. 7 and 8). Even for the 700°C temper (a low tempering temperature for these martensitic steels) the stronger normalized-and-tempered 9Cr-2WVTa had excellent impact properties relative to the commercial steels.

Excellent Charpy impact behavior was also observed for the 9Cr-2WVTa-2Ni steel, with the irradiation resistance almost as good (after the 750°C temper) or better (after the 700°C temper) than the steel without nickel. This occurred with the 750°C temper despite the presence of martensite and a 30% greater strength than the steel without nickel.

Recent irradiations of 9Cr-2WVTa-type steels with and without nickel at 200-270°C in fast reactors found excess hardening and a larger shift in DBTT in the nickel-containing steel compared to the steel without nickel [5,6]. This is contrary to the present experiment where there was no indication that the nickel-containing steel hardened excessively relative to the steel without nickel or had a larger shift in DBTT. The difference in hardening behavior for the present tests and the previous tests that showed no hardening effect caused by nickel when irradiated in a fast reactor [20,21] and the previous tests that showed hardening [5,6] appear to be due the different irradiation temperatures. The low-temperature, nickel-enhanced irradiation hardening was attributed to finer defect clusters in the nickel-containing steels [5]. Such clusters apparently become unstable at the higher temperatures of the present experiments [22,23].

Previous work to determine helium effects was on the 9Cr-1MoVNb and 12Cr-1MoVW steels with and without nickel additions irradiated in EBR-II and FFTF, fast reactors where little helium forms, and in HFIR, a mixed-spectrum reactor where much higher helium concentrations form [2-4]. Observations on the 9Cr-1MoVNb and 12Cr-1MoVW steels with and without nickel indicated that there was no increased hardening or enhanced shift in DBTT attributable to nickel for the steels irradiated in the fast reactor [20], as observed for the 9Cr-2WVTa-2Ni steel in this experiment. However, when irradiated in HFIR to \approx 40 dpa and over 200 appm He, a larger shift with little difference in hardening was observed for the nickel-containing steel. This additional shift was attributed to helium causing a decrease in the fracture stress that causes a transition to intergranular fracture on the lower shelf [2].

Summary and Conclusions

Tensile and Charpy specimens of normalized-and-tempered reduced-activation steel 9Cr-2WVTa, this steel with 2% Ni (9Cr-2WVTa-2Ni), and two commercial steels, 9Cr-1MoVNb (modified 9Cr-1Mo) and 12Cr-1MoVW (Sandvik HT9), were irradiated in EBR-II to 20-30 dpa at 376-405°C. The reduced-activation steels were irradiated in two tempered conditions: 1 h at 700°C and 1 h at 750°C; the commercial steels were tempered 1 h at 760°C.

The results demonstrated the superior irradiation resistance to embrittlement of the reduced-activation steels compared to the commercial steels. Results for the 9Cr-2WVTa-2Ni steel indicated that nickel did not adversely affect the hardening or shift in DBTT of this steel relative to the steel without nickel. This occurred even though the microstructure of the 9Cr-2WVTa-2Ni containing untempered martensite after the 750°C temper. In fact, a steel with untempered martensite may have greater irradiation resistance than a steel that is entirely tempered martensite, even though the steel with untempered martensite is considerably stronger. Further work is required to verify the advisability of using a steel such as the 9Cr-2WVTa in a heat-treated condition that produced a duplex microstructure of tempered and untempered martensite.

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THE THERMAL STABILITY OF NANOSTRUCTURED FERRITIC ALLOYS—P. Miao, G. R. Odette, T. Yamamoto, and D. Klingensmith (University of California, Santa Barbara)

OBJECTIVE

The objective of this work was to characterize the stability of the microstructure and mechanical properties for a nanostructured ferrite alloy, MA957, under high temperature thermal aging conditions.

SUMMARY

The excellent tensile and creep strength and the potential for managing radiation damage make nanostructured ferritic alloys (NFAs) promising candidates for high temperature applications in spallation proton, advanced fission, and fusion neutron environments. The thermal stability of NFAs is critical for such applications, hence, this has been investigated in a series of aging experiments on MA957 at 900°C, 950°C, and 1000°C for times up to 8000 h. Optical and transmission electron microscopy (TEM) studies for 3000 h aged MA957 showed the fine scale grain and dislocation structures are stable up to 1000°C. TEM and small angle neutron scattering (SANS) showed that the nm-scale solute cluster-oxide features (NFs), that are a primary source of the high strength of NFAs, were stable at 900°C and coarsened only slightly at 950°C and 1000°C after 3000 h aging. Porosity that developed during high temperature aging was minimal at 900°C and modest at 950°C, but was much larger after 1000°C. Microhardness for the 3000 h aged MA957 was basically unchanged after the 900°C aging and decreased only slightly ($\leq 3\%$) after aging at 950°C and 1000°C. However, the hardness was significantly reduced after 8000 h aging at 1000°C.

PROGRESS AND STATUS

Introduction

Nanostructured ferritic alloys (NFAs) have outstanding low-temperature tensile and hightemperature creep strength [1 - 9] and the potential for managing radiation damage [1, 10, 11], including high helium levels in fusion, advanced fission, and spallation proton environments. The excellent properties of NFAs primarily derive from a high density of nm-sized Y-Ti-O precipitate cluster and/or complex oxides, such as $Y_2Ti_2O_7$ and Y_2TiO_5 , which form during hot consolidation following mechanical alloying [1, 7, 12-18]. The nm-scale features (NFs) are reported to be stable, at least for a limited range of irradiation conditions [1, 10, 19-21]. A key issue for NFAs is stability of their excellent properties and microstructures at high temperatures.

The high temperature and short time thermal stability of NFAs were previously investigated in a series of aging experiments of MA957 at 1150 to 1400°C for various times ranging from 1/3 to 480 h. These experiments showed significant coarsening of the NFs, rapid growth of porosity, and large decrease of microhardness with increasing aging temperature and time [7, 12]. However, the aging temperatures in these experiments were much higher than those that are expected for application of NFAs, in the range from \approx 650 to 850°C. Indeed, fits of kinetic coarsening models yielded parameters for the high temperature aging data that predict very high NF stability at lower temperatures. Analysis of the aging data covering the initial period of coarsening, at NF sizes less than 5-6 nm, yielded activation energies in excess of 850kJ/mole and a t^{1/5} time-dependence [7, 12]. Atom probe tomography studies have also suggested that the NFs are remarkably stable at high temperature and during creep [17, 22]. Thus, to confirm these observations, we initiated a series of aging experiments of MA957 at temperatures from 800 to 1000°C for planned times up to 20,000 h or more. Interim microstructure, NF analysis, and hardness results on the effects of aging at 900°C, 950°C, and 1000°C up to 3000 h and the hardness results for 8000 h aging at 900°C and 1000°C are reported here.

Experimental Procedure

Coupon specimens of as-received MA957 alloy extruded at 1150°C with a nominal composition of Fe-14wt% Cr, 0.9% Ti, 0.3% Mo, and 0.25% Y_2O_3 were thermally aged for 3000 h at 900°C, 950°C, and 1000°C and for 8000 h at 900°C and 1000°C in quartz capsules which were vacuum evaporated and backfilled with dry helium at 50kPa.

The coarser scale and NF microstructures of the as-extruded and the 3000 h aged MA957 were characterized using optical microscopy, TEM (JEOL2010HR), and SANS (NG7 at the National Institute of Standards and Technology). Standard 3 mm TEM discs, taken from a region of \approx 1mm away from sample surface, were ground to a thickness of \approx 0.15 mm and then thinned to electron transparency in a TENUPOL twin-jet electro-polisher with H₂SO₄ + 80%CH₃OH at room temperature. The thinned samples were carefully washed in methanol, transformed to a vacuum desiccator, and then loaded to TEM for observation within one hour to minimize contamination. TEM images for the measurement of the NFs were taken in a near the [011] orientation. The thickness of the TEM samples was measured by the convergent beam diffraction technique. Details of the experiment, data reduction, and analysis for SANS are given elsewhere [7].

Mechanical properties of the MA957 samples were evaluated by Vickers microhardness at a 500g load.

Results

As shown in the TEM micrographs in Figs. 1 and 2 in a region \approx 1mm away below the sample surface, the as-extruded MA957 has fine ferrite grains and a high dislocation density (Figs. 1a and 2a) that remain stable after 3000 h aging at 900°C, 950°C, and 1000°C (Figs. 1b and 2b, 1c and 2c, 1d and 2d). Note that ferrite grains in a very thin layer (\leq 30µm for 950°C and \leq 200µm for 1000°C) close to the sample surfaces coarsened at 950°C and 1000°C. Composition analysis of these regions indicates that the local coarsening was due to the sublimation of the elements like Cr. Thus protection coatings, like alumina scale, will be needed to use NFAs at temperatures higher than 900°C in environments such as helium coolants.



Fig. 1. TEM micrographs of (a) the as-extruded MA957 and MA957 aged for 3000 h at (b) 900°C, (c) 950°C, and (d) 1000°C.



Fig. 2. Higher magnification of Fig. 1, showing dislocations in (a) the as-extruded MA957 and MA957 aged for 3000 h at (b) 900°C, (c) 950°C, and (d) 1000°C.

The as-extruded and the aged MA957 contain a large number of NFs, as seen in Fig. 3. Their diameter (d), number density (N), and volume fraction (f) were measured using computer assisted image analysis of TEM micrographs and convergent beam estimates of the foil thickness. These data are shown in Figs. 4 and 5. Large particles, with diameters greater than \approx 10 nm, were not included in the measurements. The average diameters are 2.1±0.4, 2.1±0.4, 2.6±0.5, and 3.1±0.9 nm for the as-extruded and the 900°C/3000h, 950°C/3000h, and 1000°C/3000h aged MA957, respectively. The corresponding total number density of NF after 900°C aging is similar to that for the as-extruded MA957, within the uncertainties associated with single area measurements, resolution limits, and other possible sources of error. However, the number densities of NF decrease significantly after 950°C and 1000°C, aging. Nevertheless, the total volume fraction did not change significantly. Note these evaluations are in qualitative agreement with measurements by SANS. The absence of coarsening at 900°C, which does occur at 950°C and 1000°C, is more clearly shown in the number density distribution histograms presented in Fig. 5. The NF distributions at 900°C are nearly the same as those in the as-extruded, but they shift to larger diameters at 950°C and even more so at 1000°C.

The NF coarsening at 1000°C was also qualitatively confirmed by the SANS experiment, as shown in Fig. 6. The open and filled symbols are the NF scattering cross sections measured at 45° to the magnetic field (this includes the nuclear plus 50% of the magnetic scattering) as a function of the square of the scattering vector, q, for the as-extruded and 1000°C-3000 h aged conditions, respectively. The decrease in the magnitude of d Σ /d Ω versus q² for 1000°C-aged MA957 at higher q and increase at very low q in the aged condition indicates a slight coarsening of the NFs.



Fig. 3. NFs in (a) the as-extruded MA957 and MA957 aged for 3000 h at (b) 900°C, (c) 950°C, and (d) 1000°C.



Fig. 4. Average diameter, total number density, and volume fraction of NFs in the as-extruded and aged MA957.


Fig. 5. Number density distribution of NFs in the as-extruded and aged MA957.



Fig. 6. SANS cross section curves at a 45° angle to the direction of the magnetic field.

Porosities of the as-extruded and the 3000 h aged MA957 were measured on optical micrographs of as-polished cross-sections normal to the extrusion are shown in Table 1 and illustrated in Fig. 7. The pore diameters and area fractions increased $\approx 25\%$ and 200%, respectively, after aging at 900°C and 950°C, respectively. Much of this increase is due to the growth of pores that are visible in the as-received condition; however, as indicated in Table 1, the pore density may also increase slightly due to the growth of previously invisible submicron-sized pores [23] formed during mechanical alloying. The average diameter and area fraction of the pores grow much more significantly after aging at 1000°C, with increases of $\approx 350\%$ and 1150%, respectively. The apparent decrease in the number density of pores may be due to coalescence.

Heat treatment	Average diameter of pores (µm)	Area fraction of pores (%)	Number density of pores (×10 ⁹ , 1/m ²)
As-extruded	2.2±1.2	0.5	1.0
900°C/3000h	2.8±2.4	1.5	1.4
950°C/3000h	2.7±2.5	1.2	1.1
1000°C/3000h	10.1±8.7	6.2	0.5

Table 1. Average diameter, area fraction, and number density of pores



Fig. 7. Optical micrographs in cross-sections normal to the extrusion direction of (a) the asextruded MA957 and MA957 aged for 3000 h at (b) 900° C, (c) 950° C, and (d) 1000° C. Note that the black features in (a) – (d) are pores.

Vicker's diamond pyramid hardness (DPH, kg/mm²) measurements on polished cross-sections parallel to the extrusion direction are shown in Table 2. The measurements were made at \approx 1mm (for 3000 h aging) and \approx 1.5mm (for 8000 h aging) depth, which is sufficient to avoid the artifacts associated with the near surface environmentally induced instabilities noted above. Slight softening is observed after 3000 h aging but is insignificant (< 1%) except perhaps at 950°C, where the DPH decreases by \approx 3%. However, given the one standard deviation uncertainties in the hardness of $\approx \pm$ 6 to 8 DPH, it is concluded that softening after 3000 h aging is minimal to non-existent.

The microhardness of MA957 aged for 8000 h at 900°C is nearly the same as those for the 3000 h aged MA957, but it is significantly reduced after 8000 h aging at 1000°C.

Heat	As-	900	С°С	950°C	100	0°C
treatment extrud	extruded	3000 h	8000 h	3000 h	3000 h	8000 h
DPH	333±8	332±7	325±8	323±7	330±6	306±6

Table 2. DPH of as-extruded and aged MA957

Discussion

The SANS investigation [7] of MA957 after high temperature ($1150^{\circ}C - 1250^{\circ}C$) and short-time (1/3 - 480 h) aging showed significant NF coarsening. The data in the initial coarsening regime for aging at 1150°C to 1250°C for 1/3 to 480 h were least square fitted using expression with the form

$$d(T,t) = d_0 [tk'_{co} \exp(-Q_{ec} / RT) + 1]^p$$
(1)

Here d₀ and d(T, t) are the NF sizes before and after aging, respectively, t is the aging time, T is

the aging temperature (°K), and R is the gas constant. The fits yielded a rate coefficient, $k_{co} = 2.94 \times 10^{27}$ /s, an effective activation energy for coarsening, $Q_{ec} \approx 884$ kJ/mole, and a time scaling exponent, p = 0.2. The fitted p is consistent with a dislocation pipe diffusion mechanism, but the rather remarkably high value of Q_{ec} is not well understood. Assuming a $d_0 = 2.6$ nm for the asextruded MA957 based on SANS measurement [7], predictions of Equation 1 for high temperature aging for 3000 h are shown by the open circles in Fig. 8, along with the longest time data from the previous high temperature aging study. Extrapolations of Equation 1 to lower temperatures predict insignificant coarsening below ≈ 1050 °C. Thus, the high temperature aging model is somewhat inconsistent with the current lower temperature results at 950°C and 1000°C. While the coarsening is modest even at 1000°C and does not lead to significant softening, data at longer times will be needed to refine the aging model for predicting thermal stability in the application regime for NFAs below ≈ 850 °C.

The small hardness changes at 1000°C and 3000 h in spite of the NF coarsening is consistent with previous estimates of the relation between the strengthening contribution of the NFs and their corresponding d and f [7]. This work showed that the individual NF contribution to the yield stress is proportional to HP = log(d/4b)b/d, where HP is a hardening parameter and b is the Burgers vector (0.25 nm) for Fe. Figure 9 shows that the HP plotted versus d has a broad maximum, peaking around d \approx 2.5 nm; the predicted HP actually increases slightly between d = 2 and 2.5 nm and is almost constant between d = 2.5 and 3 nm.



Fig. 8. Size variation of NFs with temperature for the as-extruded and the aged MA957. The filled circles: NF sizes measured by TEM, the open diamonds: NF sizes measured by SANS, and the open circles: NF sizes predicted using equation 1 for 1150°C/3000h, 1200°C/3000h, and 1250°C/3000h aging.



Fig. 9. Variation of hardening parameter (HP) with the NF size (d).

SUMMARY AND CONCLUSIONS

The interim MA957 aging data show that the fine ferrite grains and high dislocation densities are thermally stable at 900°C, 950°C, and 1000°C for 3000 h. The NFs are thermally stable at 900°C, but coarsen slightly at 950°C and 1000°C for 3000 h aging. However, the NF coarsening did not lead to significant softening, consistent with expectation. The growth porosity is much smaller at 900°C and 950°C compared with the 1000°C aging.

Future Work

The aging experiments are continuing at all temperatures. Emphasis during the next reporting period will be on detailed microstructural characterization of the specimens aged for 8000 h and additional hardness measurements for the longest aging times at all temperatures.

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4.0 COPPER ALLOYS

No contributions.

5.0 REFRACTORY METALS AND ALLOYS

No contributions.

6.0 AUSTENITIC STAINLESS STEELS

INFLUENCE OF SILICON ON SWELLING AND MICROSTRUCTURE IN RUSSIAN AUSTENITIC STAINLESS STEELS IRRADIATED TO HIGH NEUTRON DOSES—S. I. Porollo, S. V. Shulepin, Yu. V. Konobeev (State Scientific Center of Russian Federation, Institute of Physics and Power Engineering), and F. A. Garner (Pacific Northwest National Laboratory)

OBJECTIVE

The object of this effort is to ascertain if the parametric sensitivities of void swelling observed in welldefined, single-variable experiments conducted on simple model alloys can be confidently and generally applied to commercially produced alloys operating under complex, multivariable and timedependent conditions. In this report the influence of silicon level on swelling of austenitic steels is examined.

SUMMARY

Void swelling and microstructural development of EI-847 austenitic stainless steel were investigated by destructive examination of fuel pin cladding irradiated in three fast reactors located in either Russia or Kazakhstan. The tendency of void swelling to be progressively reduced by increasing silicon concentration appears to be a very general phenomenon, whether observed in simple single-variable experiments on well-defined materials or observed in multivariable, time-dependent irradiations conducted on commercially-produced steels over a wide range of irradiation temperatures, neutron spectra and dpa rates. The role of silicon on microstructural development is expressed both in the solid solution and via its influence on formation of radiation-induced phases that in turn alter the matrix composition.

PROGRESS AND STATUS

Introduction

In a review by Garner, many experiments have shown silicon is a very effective elemental addition to delay the onset of void swelling during neutron or charged particle irradiation of austenitic stainless steels [1]. The majority of the available data to support this conclusion were developed from single variable studies conducted on well-characterized experimental specimens, however, and not from actual reactor components produced by commercial vendors and which have been irradiated in time-dependent, multivariable reactor environments. To test the universal applicability of conclusions concerning the role of silicon under a wide range of both production practices and reactor-relevant environmental conditions, it was decided to examine commercially-produced fuel pin claddings irradiated in fast reactors located in Russia and Kazakhstan.

In this report results are presented of investigations on the effect of silicon concentration on void swelling and microstructure of commercial heats of austenitic stainless steel EI-847 (0.06C-16Cr-15Ni-3Mo-Nb) irradiated as fuel pin cladding of both regular and experimental fuel assemblies in three fast reactors to neutron doses up to 49 dpa.

Materials and Methods

The study of the silicon effect on void swelling in the steel EI-847 was carried out on pin claddings of regular and experimental fuel assemblies of the BOR-60, BN-350 and BN-600 fast reactors. Irradiation conditions experienced in the three fast reactors are shown in Table.1. Note that there are significant differences in neutron flux-spectra between the three fast reactors, reflecting different fuel types and different neutron flux levels.

Fuel pin claddings of 6.9 mm×0.4 mm size were made of the steel EI-847 in the austenized condition (1050°C for 5 min). The chemical composition of all cladding specimens examined corresponded, in general, to the specification requirements for this steel: C(0.04-0.06); Mn(0.4-0.8); Si≤0.4; S≤0.010; P≤0.015; Cr(15.0-16.0); Ni(15.0-16.0); Mo(2.7- 3.2); Nb≤0.9; N≤0.025; B≤0.001; Co≤0.02; Cu≤0.05; Bi≤0.01; Pb≤0.001; Ti≤0.05, all in wt. %. Note that for all "impurity" elements (such as Si, P, N, S) only an upper limit of concentration is specified, thereby allowing some significant variations in composition in heats produced by different vendors.

#	Assembly	Reactor	Maximum burn-up, % heavy atoms	Maximum neutron fluence, 10 ²² n/cm ² , E>0.1 MeV	Maximum dose, dpa
1	P-34	BN-600	6.21	10.7	35
2	OP-4	BN-350	11.8	10.8	49
3	OP-3	BN-350	9.84	10.5	48
4	CC-15T	BN-350	6.0	10.0	46
5	ZAR-2	BOR-60	10.46	7.29	42
6	ZAR-8	BOR-60	11.7	7.34	42
7	BN-6	BOR-60	10.9	6.4	37

Table 1. Irradiation conditions for assemblies investigated

After irradiation, segments of 15 mm in length and 4 mm in width were cut from fuel pin cladding at various heights along the pin, from which disks of 3 mm diameter were then punched. From these disks TEM-specimens were prepared using the two-jet "TENUPOL" polishing technique. The microstructure of the irradiated steel was investigated using a JEM-100CX electron microscope equipped with a lateral goniometer. A Kamebax x-ray micro-analyzer was used to measure the composition of the irradiated steels, unless certificates were available that certified the measured composition.

Experimental Results

Claddings of BN-600 Reactor Fuel Pins

Thin-wall tubes of 6.9 mm \times 0.4 mm size fabricated by two western firms from the austenitic stainless steel EI-847 in the solution treated condition were used for fuel pin claddings of the first BN-600 core loading. The first post-irradiation examination of these fuel pins began with subassembly P-34 which was irradiated in the low-enrichment zone of the BN-600 core. This subassembly had reached a burn-up of 6.2 % heavy atoms. The first visualization of the fuel pin bundle in the hot cell after removal of the hexagonal wrapper revealed that the increase of fuel pin length was not uniform, with the pins appearing to exhibit two different ranges of length (Fig. 1). Measurements of length and diameter confirmed that there were two groups of fuel pins with essentially different changes in dimensions. The location of fuel pins with different length changes appeared to be random across the pin bundle, with no obvious relationship to the orientation of the subassembly in the neutron field or to the temperature regime of fuel pin operation.

Therefore it was assumed that different length changes of each set of fuel pins was caused by variations of the chemical composition of EI-847 steel made by different firms. Indeed, an analysis of certificate data for cladding tubes showed that the chemical composition of the steel made by different firms was within the specifications and were essentially identical, but their silicon and nitrogen contents varied by a factor of about two, with the largest changes of length and diameter occurring in the steel with the lower silicon content. Nitrogen content has been shown to influence the swelling of austenitic stainless steels [2-4] but to a much lesser extent than silicon so it was assumed that the silicon content was probably the dominant variable influencing swelling in these experiments.

Two fuel pins of subassembly P-34 with larger (#18) and smaller (#122) length changes were selected for further investigation. Using a Kamebax x-ray micro-analyzer the silicon content in these fuel pins was found to be 0.10 \pm 0.015 wt. % for pin #18 and 0.18 \pm 0.011 wt. % for pin #122. Certificate specifications for these steels were 0.09 and 0.20% silicon, indicating rather good agreement between the current measurements and certificate data. Nitrogen was experimentally measured at 0.011 and 0.033 wt. %, respectively.



Fig. 1. View of the top end of the fuel pin bundle of the P-34 subassembly [4].

The microstructure of both EI-847 lots was similar before irradiation (Figs. 2 and 3) and consisted of a dislocation network with (6-10) × 10^{13} m⁻² density and Nb(CN) precipitates with sizes of 50 to 500 nm and concentrations of (0.7-2.2)× 10^{19} m⁻³. The volume fraction of Nb(C, N) precipitates was equal to ~ 0.5 %.



Fig. 2. Microstructure of cladding of the fuel pin #18 of subassembly P-34 before irradiation.



Fig. 3. Microstructure of cladding of fuel pin #122 of subassembly P-34 before irradiation.

Microscopy of claddings of pins #18 and 122 has shown, that after irradiation, voids, dislocation loops, linear dislocations and various types of precipitates are observed with characteristics depending on the irradiation conditions. In Figs. 4 and 5 are shown the void and precipitate microstructures observed at the core center plane. The axial profile of swelling in fuel pins #18 and 122 is shown in Fig. 6, with swelling peaking near the core center.

From Fig. 4, it can be seen that the maximum swelling value for fuel pin #18 cladding is more than three times larger than that of fuel pin #122. This difference in swelling arises primarily from the difference in void size (see Figs. 4, 5, and 7) since the void concentrations are similar in both steel lots.



Fig. 4. Voids and G-phase precipitates observed at the core center plane cross section of fuel pin #18 cladding.



Fig. 5. Voids and precipitates (G-phase and NbC) observed at the core center plane of fuel pin #122 cladding.



Fig. 6. Axial profile of the void volume fraction in the cladding of fuel pins #18 and #122.

The dislocation structure of the irradiated steel EI-847 consists of dislocation loops and dislocation network. At irradiation temperatures higher than 500°C the dislocation density was similar in both steel lots at $\sim 2 \times 10^{10}$ cm⁻². The mean diameter of Frank loops in the cladding of fuel pin #18 was approximately twice larger than in fuel pin #122. In pin #18 the mean loop diameter increased from 42 to 110 nm with increasing irradiation temperature, but in pin #122, it increased from 26 nm to 61 nm.

Several types of the precipitates were observed in the irradiated steel, namely, fine dispersed precipitates of niobium carbonitrides in the bulk of grains, G-phase precipitates, many of which were adjacent to or attached to voids, Laves phase precipitates were observed in top sections of the fuel pins, and type $M_{23}C_6$ precipitates on grain boundaries. Nb(C,N) precipitates were observed in all fuel pin cross sections investigated. Their size increased slightly with increasing temperature and reached the value of ~10 nm in top sections of the fuel pins. The concentration of these precipitates in fuel pins #18 and #122 changed differently along the axial direction as shown in Fig. 8. In fuel pin #122, the maximum concentration of Nb(C, N) precipitates was observed at the core center plane at 2.7×10^{22} m⁻³. On the contrary, however, in fuel pin #18, the concentration of these precipitates was minimal at the central plane location and did not exceed ~10²⁰ m⁻³.

The most significant precipitation of G-phase was observed in the fuel pin cross sections near the core midplane where the swelling of the cladding was highest. In this case the volume fraction of G-phase in pin #18 was 0.7 % (35 nm diameter at 1.3×10^{20} m⁻³) and was 0.2 % (25 nm diameter at 1.3×10^{20} m⁻³) in pin #122.



Fig. 7. Axial profiles of mean void diameter and void concentration in claddings of fuel pins #18 and #122.

The microstructure of the fuel pins #18 and #122 cladding was also investigated at the bottom of the pins at a distance of 700 mm from the core midplane where the temperature and dose were 380°C and 2.8 dpa, respectively. The microstructural characteristics are shown in Table 2 and Figs. 9-11.

From these data it can be seen that the higher silicon level not only delays the onset of void nucleation but also is involved in the evolution of the loop and dislocation microstructure. In the low silicon pin #18 there are small voids and a higher concentration of Frank loops at 2.8 dpa with no line dislocations. In the steel with higher silicon content there were no voids and the Frank loop concentration was significantly lower than in the low silicon steel but line dislocations were present. From these micrographs alone we can not be certain whether the observed line dislocations were remnants of the original population or resulted from unfaulting of some of the Frank loops.



Fig. 8. Axial profiles of the concentration of Nb(C,N) precipitates in cladding from pins #18 and #122 of subassembly P-34.

Note also in the higher magnification micrograph of Fig. 11, however, that the dislocation loops are clustered closely to both the network dislocations and the precipitates. This implies that the line dislocations are remnants of the original population and that such dislocations participate in loop nucleation. Since both loops and precipitates are known to segregate nickel and many impurities in their vicinity, the presence of such segregation might be influencing loop nucleation.

Fuel pin T °C day		dpa	Voids			Lo	-2 m ⁻²	
#	T _{irr.} , C	upa	d _v , nm	N _v , m⁻³	ΔV/V, %	d _l , nm	N₁, m⁻³	- ρ _d , π
18	380	2.8	8.3	1.9×10 ²⁰	0.01	32	13×10 ²⁰	-
122	380	2.8	-	-	-	30	6×10 ²⁰	6.1×10 ¹³

Table 2. Microstructural characteristics of cladding of pins #18 and #122 at the bottom of the pins

Fuel Pin Claddings of the BN-350 Reactor

Both regular and experimental subassemblies were irradiated in the BN-350 reactor with fuel pin claddings made from annealed EI-847 steel with various silicon contents. Two subassemblies designated OP-3 and CC-15T are discussed in this report that were irradiated to approximately the same dose but had fuel pin cladding with certificate-specified silicon levels to be 0.04 and 0.47 wt. %, respectively. In Fig. 6 the axial profiles of fuel pin diameter after irradiation in BN-350 to maximum doses of 47.5 and 46 dpa, respectively, are shown.



Fig. 9. Microstructure of the cladding of pin #18 at the bottom of the pin (380°C/2.8 dpa). Note the crenulated nature of the Frank loops at this lower silicon level.



Fig. 10. Microstructure of the cladding of pin #122 at the bottom of the pin (380°C/2.8 dpa). Note that the loops are not as irregular at the higher silicon level.

As seen in Fig. 12, the maximum deformation of irradiated fuel pins corresponds to heights in the range 100 to 150 mm above the core midplane (T_{irr} . = ~ 500°C). The increase in diameter in subassembly OP-3 is almost four times larger than in subassembly CC-15T. Since swelling is the main contribution to the cladding diameter increase and irradiation creep is only a minor contributor for most fuel pins, the maximum swelling of fuel pin cladding in and CC-15T and OP-3 might approach 4.3% and 16.9%, respectively. Based on microscopy the maximum swelling appears to be 3.6 and 12.0%, respectively, in relatively good agreement considering the limitations of microscopy on heterogeneously swelling alloys. In Figs. 13 and 14 the mean void diameter and void concentration along the pin length are shown.



Fig. 11. Microstructure of pin #122 at the bottom (380°C/2.8 dpa), showing clustering of Frank loops near precipitates and line dislocations.



Fig. 12. Axial profiles of fuel pin diameter in the subassemblies OP-3 and CC-15T containing 0.04 and 0.47 wt. % silicon, respectively.

From Figs. 13 and 14 it follows that up to the irradiation temperature of 550°C the void size is larger in the steel with lower silicon content. At higher irradiation temperatures the situation is reversed. Void concentrations in the steel with higher silicon content is less tan those of the low silicon steel the temperature range investigated.



Fig. 13. Axial profile of mean void diameter observed in pins from OP-3 and CC-15T subassemblies irradiated in the BN-350 reactor.



Fig. 14. Axial profile of void concentration observed in fuel pins from OP-3 and CC-15T subassemblies irradiated in the BN-350 reactor.

Fuel Pin Claddings of the BOR-60 Reactor

A series of experimental subassemblies (ZAR, BN) with fuel pin cladding made in Russia and various Western firms were irradiated in the BOR-60 reactor. In particular, in the subassemblies ZAR-8 and BN-6 the fuel pin cladding constructed from annealed EI-847 steel with certificate-specified silicon contents of 0.1 and 0.4 wt. %, respectively, were irradiated under almost identical conditions. The variation of swelling measured by electron microscopy along fuel pin length for these subassemblies is shown in Fig. 15.



Fig. 15. Axial swelling profile measured by microscopy in fuel pin cladding of the subassemblies ZAR-8 and BN-6 irradiated in the BOR-60 reactor.

From Fig. 15, it is seen that the swelling of low silicon EI-847 steel is significantly higher, and the maximum of swelling of both pins is located just below the core center plane at approximately the same temperature.

In Figs. 16 and 17 are shown the variations of mean void diameter and void concentration along the axial length of fuel pins from subassemblies ZAR-8 and BN-6 irradiated in BOR-60. In general it appears that the relationship between void size and concentration is a little more complex than observed in the other two data sets presented previously.



Fig. 16. Axial swelling profiles of the mean void diameter of fuel pins from subassemblies ZAR-8 and BN-6 irradiated in the BOR-60 reactor.



Fig. 17. Axial swelling profiles of the void number density of fuel pins from subassemblies ZAR-8 and BN-6 irradiated in the BOR-60 reactor.

Discussion

The results presented above provide evidence of a significant influence of silicon on void swelling in fuel pin claddings fabricated from stainless steel EI-847 regardless of vendor production technology or reactor irradiation conditions. Since the three sets of fuel pins investigated were irradiated to different doses and at different dose rates it is difficult to make a direct comparison between the three data sets. Therefore in Fig. 18 the average swelling rate is plotted to show the dependence of swelling on silicon concentration near the swelling peak over the dose range of 35-49 dpa at temperatures of 485-550°C. As shown in Fig. 18 the average swelling rate decreases continuously over the range investigated, regardless of the neutron spectrum or dpa rate.



Fig. 18. Dependence of average swelling rate in solution treated EI-847 on silicon content. These data are plotted vs. certificate-specified silicon levels and include not only the six pins presented in this report but also from four other pins with slightly different silicon levels, with all pins taken from the assemblies listed in Table 1.

The general features of silicon's influence on swelling of austenitic stainless steels are known from experiments on neutron and charged particle irradiation [1, 3-21]. In the majority of studies it appeared that swelling decreased monotonically with increasing silicon, but other studies showed more complicated swelling behavior. At very low silicon levels the swelling actually increases somewhat before decreasing at higher concentrations. The data in Fig. 18 at <0.05% Si may actually reflect such behavior but unfortunately there is no datum at 0.0% Si for comparison.

It has also been shown that at very high silicon levels the austenite matrix becomes unstable as precipitation of nickel-silicide phases remove sufficient nickel from the matrix to produce lower swelling ferrite, leading to first an increase and then a reduction of swelling with increasing concentration [4, 15, and 20]. Such behavior was not observed in the concentration range explored by these irradiation experiments.

The influence of silicon on swelling can occur by many, often interconnected mechanisms. First, by interacting with point defects formed under irradiation, silicon atoms in the solid solution change the mobility of both interstitials and vacancies thereby change the fluxes of point defects to sinks. The first increase of swelling at low silicon levels has been ascribed to silicon-interstitial binding, leading to enhanced formation of Frank interstitial loops [22, 23] similar to the behavior observed for small additions of phosphorus [24]. The subsequent decrease of swelling at higher concentrations has been ascribed to silicon-enhanced diffusivity of vacancies, leading to lower vacancy supersaturation and void nucleation, as was also seen with higher phosphorus additions.

Although it has not been treated theoretically, the known radiation-induced segregation of silicon at defect sinks (grain boundaries, voids, dislocations etc.), probably changes the absorption ability of these sinks. And finally, in steels with different Si content the process of solid solution decay and the formation of second phase precipitates occur differently. These phases usually remove not only silicon but also nickel from the matrix, with both elements known to influence the onset of void swelling. The identity, composition and volume of these phases vary with irradiation temperature, dpa rate and concentration of other solutes.

Two types of silicon influence on the swelling of EI-847 steel are presented in this paper. The first type is illustrated by the low temperature, low dose rate case in BN-600. At low irradiation temperatures no new phase precipitates formed. So, the influence of silicon on void formation must arise primarily from the interaction of Si atoms with point defects, leading to changes in mobility and annihilation of preexisting dislocations, and changes in the density and morphology of Frank loops. Under low temperature irradiation the preexisting dislocations have almost disappeared at 2.8 dpa in the steel with the low silicon content, concurrent with formation of voids and high concentrations of Frank loops. In the higher silicon steel both annihilation of initial dislocations and loop nucleation appear to have been slowed, resulting in an increase in the incubation period of void formation.

The second type is illustrated by the higher-flux, higher-temperature irradiations conducted in BN-600. At 500°C the influence of silicon leads to decreasing void sizes and insignificant change of void concentration, i.e. silicon appears to suppress the growth of voids rather than void nucleation, although significant differences in phase stability appear to be involved. In the low silicon steel only G-phase precipitates were present, with a volume fraction of 0.7 %. In the steel with higher Si content the volume fraction of G-phase was only 0.2 %, but a high concentration of small Nb (C, N) precipitates was observed

In this work the chemical composition of G-phase precipitates was not determined. Williams and coworkers showed that the composition of G-phase in neutron irradiated steel FV-548 (a close analogue of steel EI-847) was determined to be $Nb_6Ni_{16}Si_7$ [25]. If we postulate that silicon reduces the swelling only when it is in the solid solution, the precipitation of silicon-rich G-phase is certainly an undesirable process, leading to a lowering of both silicon and nickel from the matrix. In addition, G-

phase also depletes the solid solution of niobium, making it more difficult to form NbC precipitates which are known to improve the resistance to swelling [25, 26].

Conclusions

The investigation of neutron-induced void swelling and microstructure of the annealed EI-847 steel with different silicon contents after neutron irradiation to doses in the range of 35-49 dpa at the temperatures from 280 to 650°C it is possible to make the following conclusions.

- 1. The tendency of void swelling to be progressively reduced by increasing silicon concentration appears to be a very general phenomenon, whether observed in simple single-variable experiments on well-defined materials or in multi-variable, time-dependent irradiations conducted on commercially-produced steels over a wide range of irradiation temperatures, neutron spectra and dpa rates.
- 2. The swelling of the steel at irradiation temperatures 485-550°C is markedly reduced with increasing silicon content. The most appreciable reduction is observed at Si contents in the range from 0.05 to 0.20 wt. % with further increases in Si content influencing swelling less strongly.
- 3. Under low dose and dose rate conditions at 380°C the influence of silicon on the microstructure evolution in the steel EI-847 reveals itself by slowing down the processes of annihilation of preexisting dislocations and Frank loop formation.
- 4. At temperatures in the 485-550°C range and at high doses and dose the swelling is affected by silicon not only by its action in the solid solution but by its influence on the formation of precipitates enriched in both silicon and nickel.

Acknowledgements

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7.0 MHD INSULATORS, INSULATING CERAMICS, AND OPTICAL MATERIALS

TRANSFORMATION OF AI₂O₃ TO LiAIO₂ IN Pb-17Li AT 800°C—B. A. Pint and K. L. More (Oak Ridge National Laboratory)

OBJECTIVE

One proposed U.S. test blanket module (TBM) for ITER uses ferritic-martensitic alloys with both eutectic Pb-Li and He coolants at ~475°C. In order for this blanket concept to operate at higher temperatures (~750°C) for a DEMO-type reactor, several Pb-Li compatibility issues need to be addressed. One is materials for the transport of Pb-Li between the first wall and heat exchanger.

SUMMARY

A FeCrAl substrate was pre-oxidized at 1000°C to thermally grow an external AI_2O_3 scale and then isothermally exposed to Pb-17Li for 1000h at 800°C to determine if this layer would protect the underlying alloy from dissolution. After exposure, a small mass gain was measured, indicating that the layer did inhibit dissolution. However, characterization of the external layer determined that it had transformed to LiAlO₂ with an increased thickness and a much larger grain size than the original layer. This observation has implications for the use of AI_2O_3 as a tritium diffusion barrier.

PROGRESS AND STATUS

Introduction

A recent focus of the U.S. fusion energy program has been on developing a proposal for a test blanket module (TBM) for ITER. The dual coolant Pb-Li (DCLL) TBM concept has both He and eutectic Pb-Li coolants and uses ferritic steel as the structural material and a SiC/SiC composite flow channel insert (FCI).[1] The interest in this concept has focused compatibility-related research on Pb-Li. Many materials have poor compatibility with liquid Li,[2] but the activity of Li is much lower in Pb-17Li,[3] and this allows a wider range of materials to be considered. However, Pb-Li still readily dissolves many conventional alloys. While the TBM maximum operating temperature will be <500°C, this blanket concept would be more attractive for a reactor with a higher maximum operating temperature, perhaps >700°C if oxide dispersion strengthened (ODS) ferritic steels[4] were used. However, at these higher temperatures, compatibility is even more of a concern. Therefore, static capsule testing is being conducted on materials at 700° and 800°C. One of the materials reported on in a previous report,[5,6] ODS FeCrAl, was selected for further characterization to determine changes in the surface reaction layer after exposure to PbLi at 800°C.

Experimental Procedure

Specimens of ODS FeCrAl (Plansee alloy PM2000) with dimensions of ~15 x 18 x 1-1.5mm and a composition given in Table 1 were polished to a 0.3μ m finish. Pre-oxidation of both specimens was conducted with a rapid insert to a pre-heated furnace at 1000°C in dry, flowing O₂ for 2h. One specimen was then held with Mo wire in a Mo capsule containing 125g high purity (99.9999%) Pb shot (chemical composition in Table 2) and 0.86g Li to make Pb-17at.%Li. The Mo capsule was loaded in an argon-filled glove box and it was then welded shut to prevent interstitial contamination during the test. The Mo capsule was then sealed inside a type 304 stainless steel capsule and was heated inside a resistively-heated box furnace in air to 800°C for ~1h to allow the Pb and Li to melt. The capsule was then inverted to submerge the specimen in Pb-Li. After 1,000h at 800°C, the system again was inverted to allow the liquid metal to drain away from the specimen. To remove residual Pb-Li on the specimen, it was soaked in a mixture of acetic acid, hydrogen peroxide and ethanol for up to 72h. Specimen mass was measured before and after exposure on a Mettler-Toledo balance with an accuracy of $\pm 0.01 \text{mg/cm}^2$. The composition of the Pb-Li remaining in the capsule after cooling was measured and reported in Table 2. Both specimens were

Table 1. Alloy chemical composition (atomic% or ppma) determined by inductively coupled plasma analysis and combustion analysis.

Material	Fe	Ni	Cr	AI	0	С	Ν	S	Other
ODS FeCrAl	67.8	0.02	20.0	10.6	7430	340	210	50	0.44Ti,0.23Y 0.04Si, 0.04Mn

characterized using field emission gun, scanning electron microscopy (SEM) equipped with energy dispersive x-ray analysis (EDXA), x-ray diffraction (XRD) and transmission electron microscopy (TEM). Part of the specimen was mounted in epoxy for a metallographic cross-section. Cross-sectional TEM specimens were prepared using focused ion beam thinning. A W layer was applied to the specimen surface to protect the outer surface of the reaction product.

Results and Discussion

The specimen mass gain after pre-oxidation for 2h at 1000°C in O₂ was 0.08 mg/cm². These conditions were selected to ensure the formation of α -Al₂O₃. Oxidizing at lower temperatures risks the formation of less protective, faster-growing metastable alumina polymorphs such as θ -Al₂O₃.[7-10] Assuming fully dense α -Al₂O₃, this mass gain corresponds to a ~0.4 μ m thick oxide layer. After exposure to PbLi for 1000h at 800°C, the specimens gained an additional 0.24 mg/cm². Post-test analysis of the PbLi showed no detectable Fe or Cr dissolution, Table 2. The increase in O and Mo after testing may be due to handling and sampling problems. Mo was not detected in the PbLi from the other 800°C capsule tests.[5,6]

The initial characterization[5,6] of the ODS FeCrAl specimen surface after exposure to PbLi showed a uniform adherent surface layer with coarse-grains, Figure 1b, unlike the fine-grained alumina observed after pre-oxidation, Figure 1a. Nodules on the surface of pre-oxidized ODS FeCrAl are typically rich in Y and Ti, but were absent after PbLi exposure. In cross-section, the surface layer after PbLi exposure was dense and adherent but obviously thicker, Figure 2, consistent with the mass gain after exposure to PbLi. Nodules, like those observed in plan view Figure 1a, could be embedded in the surface oxide and cause local variations in the thickness, Figure 2a. Coarse Al-rich oxide particles can be seen in the metal in both cross-sections.

Because the pre-oxidized α -Al₂O₃ layer was so thin, a TEM cross-section was necessary to examine the microstructure of the reaction product, Figure 3. Even after this relatively short exposure, a columnar grain structure had developed with the grains elongated normal to the metal-oxide interface. This is the typical grain structure observed for Y-doped alumina on FeCrAl.[10,11] The outer oxide layer was rich in Fe and Cr, typical of the transient stage of oxidation for a FeCrAl alloy and indicative of an inward growing oxide.[12] However, closer to the metal-oxide interface the oxide is Al₂O₃ with only minor impurities in the bulk oxide. A faceted metal-oxide interface also was evident. As found in many studies,[10,13] Y and Ti ions were segregated to the oxide grain boundaries. Fine voids could be observed in the oxide, but generally the layer was dense and adherent.

Table 2. Chemical composition using inductively coupled plasma and combustion analysis of the starting Pb, commercial Pb-Li ingot and the Pb-Li after capsule exposures at 800°C for 1000h (in ppma except for Li in atomic%).

Test	Li	Fe	Cr	Ni	Mn	Si	AI	Мо	С	0	Ν	S
Starting Pb	n.d.	<4	<4	<4	<4	<40	<8	<2	<170	1270	<40	<50
FeCrAl	17.3%	<30	<30	<30	<30	<120	<60	90	460	5280	<40	<50



Figure 1. SEM secondary electron plan-view image of the oxide on ODS FeCrAl (a) after oxidation for 2h at 1000°C and (b) after oxidation and exposure to PbLi at 800°C.

Consistent with the metallographic cross-section, the oxide layer after PbLi exposure was much thicker with much larger grains, Figure 4. Where grain boundaries intersected the metal-scale interface, the oxide was locally thicker, arrows in Figure 4a. The metal protrusion in Figure 4b is typical of inward growth along grain boundaries and has been observed in Pt-containing alumina-formers.[14] The nucleation of smaller grains at the metal-scale interface is not typical of alumina formation. However, rapid grain growth and densification were observed when a vapor-deposited Y_2O_3 coating was exposed to Li.[15]

Selected area diffraction showed a four-fold symmetry rather than the expected hexagonal close-packed α structure. The lattice spacing was consistent with the tetragonal structure of LiAlO₂. This observation was confirmed using XRD, where all of the major peaks on the Pb-Li exposed specimen were matched with JCPDS card #38-1464 for tetragonal LiAlO₂. Typical SEM and TEM chemical analysis using EDXA detected Al and O but not Li, thus the prior incorrect assumption of Al₂O₃. The pre-oxidized specimen matched major peaks with JCPDS card #10-0173 for α -Al₂O₃.

While only a single observation, the transformation of AI_2O_3 to $LiAIO_2$ at 800°C in Pb-Li confirms a hypothesis[16] for the problems that have been observed with using alumina as a tritium permeation barrier in Pb-Li.[16,17] The permeation reduction factor dropped from >100X in gas to only 15X when the alumina barrier layer was exposed to PbLi.[17] However, the LiAIO₂ layer seems to perform reasonably well as a corrosion barrier. The observed mass gain can be attributed to reaction of AI_2O_3 with Li to form LiAIO₂ and further reaction with O in the PbLi (Table 1) to form additional LiAIO₂.



Figure 2. SEM secondary electron images of polished cross-sections of ODS FeCrAI (a) after preoxidation for 2h at 1000°C and (b) after pre-oxidation and exposure for 1000h at 800°C in Pb-Li.



Figure 3. TEM bright field images of the α -Al₂O₃ scale formed on ODS FeCrAl after 2h at 1000°C in dry O₂. The W coating protected the oxide surface during specimen preparation.

The thermodynamic analysis did indicate that $LiAIO_2$ was more stable than AI_2O_3 in the presence of Pb-Li.[16,18] However, the kinetics of this transformation require further study as 800°C is a relatively high temperature for most fusion blanket operating temperatures. At lower temperatures, the transformation could be much slower or negligible. However, the rapid diffusion of Li through most materials suggests that this reaction is not limited to 800°C.

One point to emphasize in these results is that the alumina formed on ODS FeCrAl is quite different from the alumina formed on an aluminide coating or by a fabrication process like MOCVD.[17] The presence



Figure 4. TEM bright field image of the LiAIO₂ layer on the surface of pre-oxidized ODS FeCrAI after exposure to PbLi at 800°C for 1000h.

of Y has long been known to have a dramatic beneficial effect on alumina adhesion to FeCrAl[10-13], it also reduces the oxide growth rate and changes the growth mechanism. While this particular alloy was selected as a model substrate for evaluation and is no longer commercially available, other commercial alloys with reasonable creep strength are available.[19] The general class of FeCrAl alloys may be sufficiently compatible with PbLi to be used without a coating outside of the first wall of a fusion reactor.

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8.0 BREEDING MATERIALS

No contributions.

9.0 RADIATION EFFECTS, MECHANISTIC STUDIES, AND EXPERIMENTAL METHODS

PREDICTION OF STRUCTURAL AND ELECTRONIC PROPERTIES OF Y-Ti-O COMPLEX OXIDES USING AB-INITIO CALCULATIONS—Y. Jiang, J. R. Smith, and G. R. Odette (University of California, Santa Barbara)

OBJECTIVE

The broad objective of this study is to develop a rigorous understanding of the fundamental character of the nm-scale Y-Ti-O enriched features (NFs) that impart high strength and radiation damage resistance to nanostructured ferritic alloys (NFAs) using ab inito density functional theory (DFT) calculations. The short-term objective, was to use DFT to model the crystal structural and electronic properties of the two major equilibrium Y-Ti complex oxide phases, as a baseline for examining non-equilibrium features.

SUMMARY

Our objective is to develop a fundamental understanding of the identity and character of nm-scale features (NFs) in nanostructured ferritic alloys (NFAs), especially at the smallest sizes. The NFs' features are believed to be responsible for the very high creep strength and radiation damage resistance of NFAs. Atom probe tomography studies have indicated that the NFs have Ti + Y to O ratios greater than 1 and Ti to Y ratios much greater than 1. These elemental ratios are inconsistent with the known complex oxide phases in the Ti-Y-O system, which include complex cubic pyrochlore $Y_2Ti_2O_7$ and orthorhombic (at lower temperatures) Y_2TiO_5 . Both of these phases have been observed in transmission electron microscopy studies of NFAs, but generally in a size range that is larger than the smallest, and very likely, non-equilibrium NFs. There are also a number of other open questions including the basic thermokinetics of NF precipitation and coarsening; and the basic characteristics of NFs, such as elastic properties and interface structures, that mediate their interactions with dislocations. Since it is difficult, if not impossible, to fully address many of these questions with direct experimental measurements, we have developed a multiscale modeling approach that will complement a range of characterization techniques that are needed to obtain reliable answers.

As a starting point we have carried out first-principles DFT calculations for the equilibrium bulk phase $Y_2Ti_2O_7$ and Y_2TiO_5 . The minimum 0°K energy, relaxed structure of these oxides was determined and used to calculate selected ground state properties, such as lattice constants, bulk modulus and internal structure parameters. Our results compare favorably with available experimental measurements and other first principles calculations. For example, the DFT calculations predict $Y_2Ti_2O_7$ has a higher bulk modulus than Fe, which is, in turn, higher than that for Y_2TiO_5 . These moduli differences may influence the interactions of dislocations with oxide pinning features in a way that influences high temperature creep strength, for example, as mediated by detachment mechanisms. We also performed analysis of electron localization functions and densities of state to describe the nature of chemical bonding. It is found that although both oxides are highly ionic, the (Ti,Y)-O bonds contain some covalent character and that the Ti-O bonds have higher covalency than Y-O bonds.

PROGRESS AND STATUS

Introduction

Nanostructured ferritic alloys (NFAs) are being developed for use as high temperature structural materials, and they are especially promising for advanced fission and fusion energy applications [1,2]. NFAs contain a high number density of nm-scale clusters, or precipitates features (NFs), which provide creep resistance at elevated temperatures, as well as sites for annihilating radiation displacement damage and trapping of transmutation product helium. Small angle neutron scattering (SANS) and atom probe tomography (APT) studies have shown that the NFs are rich in Y, Ti, and O, but the measured (Ti + Y)/O and Ti/Y ratios are not consistent with known Y-TI-O equilibrium oxides, like $Y_2Ti_2O_7$ and Y_2TiO_5 [3,4]. However, transmission electron microscopy studies have observed both $Y_2Ti_2O_7$ and Y_2TiO_5 particles in NFAs, but generally at a larger size than the smallest NFs [5,6]. While the basic structures of the equilibrium oxides are well known, many of their other key characteristics are not understood. Thus

as a baseline for a larger longer-term effort, we have used ab-initio calculations to obtain better understanding of these bulk oxides through determination of atomic and electronic structures.

RESULTS

Structural Properties

 $Y_2Ti_2O_7$ has a pyrochlore structure which has a high symmetry (space group, $Fd\overline{3}m$, O_h^7). Atoms are located at the following Wyckoff positions: Y at 16d (1/2, 1/2, 1/2), Ti at 16c (0, 0, 0), O at 48f (δ , 1/8, 1/8), and O' at 8b (3/8, 3/8, 3/8). The two non-equivalent oxygen sites, O and O', differ in chemical environment: each O resides in a Y + Ti-tetrahedron (defined by two Y and two Ti atoms), while each O' is in a Y-tetrahedron (defined solely by Y atoms). The displacement of each O-site due to the neighboring unoccupied Ti-tetrahedrons (defined solely by Ti atoms), δ , is the only internal structure parameter.

Figure 1a shows the pyrochlore lattice of $Y_2Ti_2O_7$ before structural relaxation. To optimize the structure, we used the DFT simulation package VASP [7]. DFT calculations were performed by using pseudo-potentials generated with the projector-augmented wave (PAW) method [8]. The semi-core 3p electrons of Ti and 4s and 4p of Y were all treated as valence electrons. The local density approximation (LDA) and the generalized gradient approximation (GGA-PW91 [9] and PBE [10]) were used to describe the exchange-correlation effects. For electron eigenvalues and Brillouin-Zone integrations, a uniform $4 \times 4 \times 4$ Monkhorst-Pack k-mesh was used. During the structural relaxation, all force components converged within 0.01 eV/Å. Figure 1b shows the 1/8 corner of the conventional cell of $Y_2Ti_2O_7$ after structural relaxation.

Table 1 summarizes the results of our calculation compared to both those with those from a previous full-potential calculation [11] as well as experimental data [12]. The overall agreement is good. The discrepancies with the measured values on lattice constant are 0.89% (PW91), 1.09% (PBE) or -0.89% (LDA), respectively. The experimental bulk modulus has not been found. Our results deviate from the full-potential results by 0.69% (PW91), 0.89% (PBE) or -1.09% (LDA) in lattice constant and by -5.26% (PW91), -6.30% (PBE) or 8.17% (LDA) in bulk modulus, respectively. This trend is consistent with the general observation that GGA often overestimates the lattice constant and underestimates the bulk modulus, while LDA does the opposite. The theoretical $Y_2Ti_2O_7$ best estimate bulk modulus is \approx 190±10 GPa. Our pseudo potential approach is fairly accurate, compared to the full-potential method, but is much more computationally efficient. The Ti-O bond length is calculated as 1.97 Å and the Y-O as 2.50 Å.

To the best of our knowledge, no theoretical calculations have been reported for α -Y₂TiO₅. The α -Y₂TiO₅ orthorhombic structure is stable under 1330°C, which is the temperature range of interest, transforming to the hexagonal β -Y₂TiO₅ between 1330°C and 1520°C and a fluorite-type phase at higher temperatures [13]. The orthorhombic α -Y₂TiO₅ has a complicated structure (with a space group of Pnma or D_{2h}^{16}). All atoms are in Wyckoff positions of 4c: (x, ¼, z), (-x+1/2, ¾, z+1/2), (-x, ¾, -z) and (x+1/2, ¼, -z+1/2), lying in the mirror planes at y=1/2 or ¾. The experimentally determined [14] internal structure parameters, x and z, for each atom were used to specify the initial positions for structural optimization. Figure 2 is the optimized crystal structure of α -Y₂TiO₅. Table 2 summarizes the calculated bulk properties using various methods that are compared to experimental structural data. No experimental data of bulk modulus has been found. The theoretical best estimate of the bulk modulus of α -Y₂TiO₅ is ≈ 130 ± 5 GPa. The optimized atomic coordination parameters are compared with experiment in Table 3. The five-coordinated Ti-O distances vary in the range of 1.79-1.97 Å, with an average of 1.89 Å (the same as the experimental value [14]). The seven-coordinated Y-O distances vary in the range of 2.28-2.38 (Y(1)-O) and 2.32-2.40 Å (Y(2)-O), with an average of 2.32 and 2.36 Å, respectively (compared with the experimental values of 2.32 and 2.35 Å [14])



Fig. 1. (a) The pyrochlore lattice of Y2Ti2O7 before structural relaxation. Y, Ti and O atoms are represented in green, blue and red respectively. (b) The 1/8 corner of the conventional cell after relaxation. The Ti-tetrahedron is empty (free of oxygen) and located at the lower left corner. All O-sites displace by an amount of δ towards the neighboring Ti-tetrahedrons, while the O'-site (3/8, 3/8, 3/8) is unaffected.

Table 1. Calculated lattice constant, bulk modulus, internal structure parameter of Y2Ti2O7, compared with previous theoretical and available experimental data

Method	Lattice Constant a (Å)	Bulk Modulus B (GPa)	Oxygen Displacement (δ)
PAW-LDA	10.0	208.76	0.330
PAW-PW91	10.18	182.85	0.329
PAW-PBE	10.20	180.84	0.329
FP-GGA [11]	10.11	193	0.329
Expt [12]	10.09	-	0.328



Fig. 2. The optimized crystal structure of α -Y₂TiO₅. The heavier bars represent bonds of atoms at y=3/4, the lighter at y=1/4 and between.

Mathad	Lattic	ce Consta	Bulk Modulus	
Method	а	В	С	B (GPa)
PAW-LDA	10.24	3.65	11.13	132.30
PAW-PW91	10.48	3.71	11.34	128.70
PAW-PBE	10.46	3.73	11.36	128.91
Expt[14]	10.35	3.7	11.25	-

Table 2. Calculated lattice parameters of $Y_2Ti_2O_5$ compared with experiment. The experimental bulk modulus has not been found.

Table 3. The calculated coordination parameters (using PAW-PW91) compared with experiment [14]

	Ato	mic Coordinati	on Parameters (y=3/4)			
atom	E>	kpt (Calc			
	Х*	Z*	х	Z		
Y(1)	0.1156	0.2231	0.1150	0.2242		
Y(2)	0.1366	0.5578	0.1361	0.5568		
Ti	0.1745	0.8806	0.1738	0.8813		
O(1)	0.4947	0.1024	0.4930	0.1046		
O(2)	0.2229	0.0449	0.2232	0.0432		
O(3)	0.2594	0.7340	0.2567	0.7306		
O(4)	0.5085	0.6601	0.5070	0.6566		
O(5)	0.2690	0.3833	0.2637	0.3841		

The results of these first principles calculations of the bulk moduli of the complex oxides indicate that $Y_2Ti_2O_7$ (B \approx 190 GPa) is stiffer than Fe (B \approx 168 GPa [15]) and that $Y_2Ti_1O_5$ (G \approx 130 GPa) is less stiff. Thus, to first order, it would be expected that dislocations would be repelled by incoherent $Y_2Ti_2O_7$ and attracted by incoherent Y_2TiO_5 . Such differences could play a critical role in the relative effectiveness of these two phases in providing high temperature creep strength. Specifically, Y_2TiO_5 would be expected to provide more effective high temperature dislocation pinning since it would activate the detachment barrier mechanism. Of course the actual physics of high temperature creep strength is much more complex, but this example illustrated how materials by design approach to developing NFAs could be very powerful.

Electronic Properties

While the electronic properties of the oxides are not themselves of direct interest, they provide physical insight on the corresponding structural and physical properties. Electronic structure calculations are also of interest in interpreting experimental measurements based on techniques such as extended x-ray absorption spectroscopy (EXAFS). As shown in Fig. 3, the dimensionless electron localization function (ELF) that ranges from 0 to 1 [16] can be used to visualize the nature of the bonds in both oxides. High ELF values are typically associated with inert cores, covalent bonds or lone pairs. The ELF value is high at each ion and is small, but not zero, in between, suggesting some covalent character of the dominantly ionic bonds. The Ti-O bonds appear to be somewhat more covalent than the Y-O bonds.

To be more quantitative, we computed the electron density of states (DOS) for both oxides using the tetrahedron method [17]. The site- and Im-projected DOS are shown in Fig. 4. The valence bands are largely composed of O-2p and (Y,Ti)-d states, and the unoccupied conduction bands by a mixing of Ti-3d and Y-4d states. The calculated band gaps are 2.84 and 3.14 eV for $Y_2Ti_2O_7$ and Y_2TiO_5 , respectively.

The stronger hybridization of (Ti-3d, O-2p) than that of (Y-4d, O-2p) is evident in both oxides. This is associated with the shorter Ti-O bond length than the Y-O in both oxides. The Ti-3d states interact with the O-2p over a wider energy range in $Y_2Ti_2O_7$ than in Y_2TiO_5 , but the difference is small. Due to their different structural surrounding, differences in the (Ti,Y)-O interactions do not directly explain the difference of elastic moduli in the two oxides. Indeed, each Ti (or Y) is coordinated with six (or eight) O ions in $Y_2Ti_2O_7$, while in Y_2TiO_5 each Ti (or Y) is coordinated with five (or seven) O. The different coordination numbers are also responsible for the difference in bond lengths: the bond lengths of (Ti,Y)-O in $Y_2Ti_2O_7$ are even larger than in Y_2TiO_5 by 4~6%, even though the former has a higher predicted bulk modulus.



Fig. 3. ELF plots showing the degree of covalency of the (Ti,Y)-O bonds in both (a) $Y_2Ti_2O_7$ and (b) Y_2TiO_5 . The $Y_2Ti_2O_7$ plot is at about 10 degree tilt from the (111) plane, in order to present both Y-O and Ti-O bonds in the same plane, while the plot of Y_2TiO_5 right is at y=3/4.

Future Work

The results reported here represent the beginning phase of a longer term, broader effort to understand and model the basic characteristics and thermokinetics of a range of NFs that form in NFAs. Future work will extend the first principles models to treat finite temperature effects on both physical (e.g., elastic) and thermodynamic (e.g., elemental and (Y,Ti)-0 complex activities) properties of various possible phases (including non-equilibrium atom positions and structures), interfaces (including diffuse and segregated/chemically partitioned structures) and diffusion coefficients.


Fig. 4. Calculated site-projected partial DOS of (a) $Y_2Ti_2O_7$ and (b) Y_2TiO_5 . Blue, green, and red solid lines represent Ti, Y, and O sites respectively. The vertical dotted line denotes the valence band maximum.

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THE FORMATION AND STABILITY OF HE-VACANCY CLUSTERS WITHIN DISPLACEMENT CASCADES IN α -Fe—F. Gao, H. L. Heinisch, and R. J. Kurtz (Pacific Northwest National Laboratory)^{*}

This extended abstract highlights results in a series of published papers [1-5] on recent work partially funded by the Office of Fusion Energy Science.

EXTENDED ABSTRACT

Molecular dynamics (MD) methods have been utilized to study the formation of vacancy clusters created by displacement cascades in α -Fe containing concentrations of substitutional He atoms varying from 1-5%. These He concentrations are not necessarily intended to represent specific conditions within a fusion reactor (average end-of-life He concentrations in the first wall are expected to be on the order of 0.15%), but they provide an opportunity to investigate the effects of substantial amounts of He on cascade processes and microstructure development under damage producing conditions.

Results of cascade simulations show that

- There are distinct differences in the number and size of vacancy clusters within displacement cascades in α -Fe with and without substitutional He atoms.
- Many large vacancy clusters are formed within cascade cores in α-Fe containing helium atoms, in contrast to a few small vacancy clusters observed in pure α-Fe.
- The number of Frenkel pairs at 600K is slightly lower than that at 100K, but the number of Hevacancy clusters increases with increasing temperature for the same He concentration and energy recoils.

The stability of He-vacancy clusters during single cascade and multiple cascade overlap has also been investigated for helium-to-vacancy ratios ranging from 0.2 to 3. Results indicate that

- The effect of displacement cascades on a helium-vacancy cluster strongly depends on the helium-to-vacancy ratio and PKA energy.
- He-vacancy clusters (He-V) can be dissolved when the He/V ratio is less than 1, but for He/V ratios equal to and larger than 1, the He-V clusters are very stable for the energies considered.

Most of the details pertaining to the methodology used in the simulations of the cascade induced Hevacancy (He-V) cluster formation and their stability within single or multiple cascades are described in detail in references [1-3]. For the present studies, the Finnis–Sinclair [6], Wilson–Johnson [7], and Beck [8] potentials were used to describe the interactions of Fe–Fe, Fe–He and He–He, respectively. All simulations were carried out using MD methods with periodic boundary conditions and constant volume. To study formation of He-V clusters, several He concentrations have been considered, ranging from 1 at% to 5 at%, where Fe atoms in the test cells are randomly replaced by He atoms. For each concentration, primary knock-on atom (PKA) energies, *Ep*, ranged from 500 eV to 20 keV at temperatures of 100 and 600 K. A total of 200 cascades were simulated for each condition. In order to study He-V cluster stability within displacement cascades, initial clusters with 10 and 20 vacancies were chosen, having He/V ratios varying from 0.2 to 3. Individual cascades from single primary knock-on atoms (PKA) with recoil energies of 2, 5, and 10 keV were initiated.

To investigate the influence of He atoms on defect production, displacement cascades were also generated in α -Fe without helium, and these simulations are in general agreement with the previous studies, where large vacancy clusters are not observed, and most of the vacancies are single vacancies. Figure 1 shows the defects remaining in 10 keV cascades with 5 at% He concentration at a temperature of 100 K. It is somewhat surprising to see that a large number of vacancies are formed within the cascade

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

core, together with He interstitials removed from their substitutional positions. These helium atoms are retrapped by vacancies, forming He-vacancy (He_nV_m, n<m) clusters. The total defect density within the cascade core in this case is much higher than that for cascades in pure a-Fe, and the clustering of He is significant. Another interesting result in the He-doped Fe is that only a few self-interstitial atoms (SIAs) are generated, which is much less than that in pure α -Fe, as shown in Fig. 1. Also, the size and number of interstitial clusters are found to be much smaller than those in pure α -Fe. Moreover, the fraction of surviving SIAs that are in clusters of size two or larger decreases with increasing He concentration [1,4].



Fig. 1. Typical point defect distributions within 10 keV displacement cascade simulations at 100 K after 20 ps in (a) pure α -Fe and (b) α -Fe with 5 at% substitutional He, where the defect type is identified by the different size of spheres, as indicated in the plots.

The probability of He/vacancy clustering and the size of the largest clusters tend to increase with increasing He concentration and PKA energy. Also, a higher proportion of vacancies than SIAs form clusters, in contrast to those found in pure α -Fe. Data for the final numbers and size distributions of helium-vacancy (He_nV_m) clusters for all the cascades in Fe with 1 at% He and 5 at% He, respectively, are plotted in the form of histograms as a function of PKA energy in Fig. 2. The figure demonstrates quantitatively that the number and size of clusters both increase with increasing He concentration. Furthermore, a striking result of the present series of damage cascade simulations is that the majority of He_nV_m clusters contain more vacancies than helium interstitials, with helium-to-vacancy (He/V) ratios in the range from 0.5 to 0.8.

The temperature dependence of He–V clusters within displacement cascades, as discussed in Ref. [5], demonstrates that the total number of Frenkel pairs (counting both He and Fe point defects) increases with increasing PKA energy and He concentration, but decreases slightly with increasing irradiation temperature for the same He concentration and PKA energy. The number density of He–V clusters slightly increases with increasing temperature, while the mean size of He–V clusters remains almost constant for the same He concentration and PKA energy. Such clusters might act as the smallest nucleation sites for the formation of large He bubbles observed experimentally.



Fig. 2. Size distribution of $\text{He}_n V_m$ (*n*<*m*) clusters with concentrations of 1 at% and 5 at% substitutional He at 100 K. Note that the horizontal axis for number of vacancies is nonlinear.

The stability of pre-existing He-V clusters within cascades was studied for clusters of different He/V ratio, and the results were analyzed using graphical depictions of the cascade damage. Figure 3(a) shows the peak displacements of the cascade, from which it can be seen that the thermal spike phase completely involves the He/V cluster. The final damage state is shown in Fig. 3(b), and it is surprising to note that the vacancies produced by the cascade are swept into the He-V cluster, which results in an increase in the number of vacancies in the cluster. The total number of vacancies in this cluster is 41, as compared to 20 vacancies in the original cluster, which decreases the He/V ratio to 1.44. However, the simulations with the He/V ratio less than 1 demonstrate that the initial cluster has been partially dissolved after cascade impacting and two small clusters are re-nucleated in the center of the cascade. Besides two small He-V clusters, there were some single vacancies and small vacancy clusters formed in the cascade core. In contrast, the He-V clusters with initial He/V ratios of about 1.0 are very stable even when impacted by a high energy cascade. It is clear from these simulations that the effect of a cascade of a given PKA energy on a He-V cluster depends on the He/V ratio. A high He/V ratio leads to the increase in the number of vacancies in the clusters, whereas the lower ratio may provide a possibility for the cluster to be dissolved.



Fig. 3. Atomic structures of a cluster with a He/V ratio of 3: (a) the peak displacements of the cascade with PKA energy of 5 keV and (b) the final damage state.

Conclusions

Formation of He-V clusters within cascades and the stability of these clusters under cascade-producing irradiation, as well as temperature effects, have been studied using molecular dynamics methods. The number and size of vacancy clusters within displacement cascades are distinctly different in the cases with and without substitutional helium atoms examined in these simulations. Large numbers of helium/vacancy clusters are generated directly in displacement cascades, and the sizes of these clusters are much larger than those observed for clusters in pure α-Fe. The effect of temperature on the total number of Frenkel pairs produced is small, but the number density of He–V clusters increases with increasing temperature. The displacement cascades have significant effects on the stability of He-V clusters. The growth or dissociation of He-V clusters strongly depends on the He-V ratio and recoil energy. For an initial He/V ratio larger than 1, the cascades dramatically change the vacancy concentration in the clusters, resulting in an increase in the He-V cluster size and a decrease in the He/V ratio. The He-V clusters with initial He/V ratios less than 1 can be completely or partially dissolved by a cascade, and one or a few small He/V clusters can be renucleated. In contrast, the He-V clusters with initial He/V ratios of about 1.0 are very stable even when impacted by a high energy cascade.

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

OBJECTIVE

This research has two main objectives:

- The development of computational tools to evaluate alloy properties, using the information contained in thermodynamic functions. We aim at improving the ability of classical potentials to account for complex alloy behavior, and
- The application of these tools to predict properties of alloys under irradiation, in particular the FeCr system.

SUMMARY

Atomistic simulations of alloys at the empirical level face the challenge of correctly modeling basic thermodynamic properties. In the periods reported previously we develop a methodology to generalize many-body classic potentials to incorporate complex formation energy curves. Application to Fe-Cr allows us to predict the implications of the ab initio results of formation energy on the phase diagram of this alloy and to get a detailed insight into the processes leading to precipitation of α ' phase under irradiation. In particular in this period we report on the consequences of the negative heat of formation at low Cr composition on the short range order SRO existing in the α phase. We elaborate a simple description of SRO on a two-phase alloy and compare the predictions with experiments. We provide a key to rationalize a diversity of experiments on SRO versus annealing time or irradiation dose.

PROGRESS AND STATUS

Two main activities were developed in the period covered by this report.

- 1. Short-range order (SRO) in Fe-rich Fe-Cr alloys was investigated by means of atomistic offlattice Monte Carlo simulations in the semi-grand canonical ensemble using classical interatomic potentials. The parameters defined by Cowley are used to quantify the SRO. In agreement with experiments we observe a strong ordering tendency in the Cr distribution at low Cr concentrations $c \sim < 5\%$ as manifested in negative values of the SRO parameters. For intermediate Cr concentrations, 5% < c < 15%, the average SRO parameter for the α -phase goes through a minimum and eventually approaches zero indicating the formation of a random solid solution. However, in this concentration range the system is actually in a twophase region. In thermodynamic equilibrium the SRO parameter measured over the entire system therefore comprises the contributions from both the α and α ' phases. Taking into account these contributions we were able to quantitatively reproduce the experimental results and interpret their physical implications.
- 2. Impurity segregation at grain boundaries in polycrystalline materials. We applied a novel approach to computationally model the problem of impurity segregation at grain boundaries in polycrystalline materials. It is based on the parallel Monte Carlo algorithm that places the impurities according to the local chemical potential for the species, following the thermodynamic driving force for segregation. We described this code in previous reports. We report now on a test case of a CuFe alloy and study the role played by Fe impurities in nanocrystalline Cu (nanocrystalline because it is a way to explore many different grain boundaries in a single simulation) from three different perspectives. (1) We found a strong decrease in grain boundary mobility resulting in an enhancement of the stability of nanophase grain boundaries upon annealing. (2) Virtual tensile tests of samples with and without

impurities reveals a hardness that is unaffected by the presence of the Fe impurities. We interpret the striking difference between these two results in terms of impurity dragging versus sliding, and derive general conclusions regarding hardness at the nanoscale in dirty materials. (3) Grain boundary cohesion, in turn, is studied via spall resistance to tensile stress produced by simulated laser irradiation, which shows enhanced grain boundary cohesion in the case of the sample bearing impurities. All these examples help us preparing the field for the study of Cr segregation, a problem whose main characteristics where already reported in the previous period.

In what follows we briefly describe the first of these achievements.

Short-range order (SRO) in Fe-rich Fe-Cr alloys

Iron-chromium steels are used in reactor environments because of their swelling and corrosion resistance as well as their high-temperature creep resistance and hardness. The precise origin of many of these beneficial features is still uncertain. Creep resistance is customarily associated with the presence of small α' precipitates, while embrittlement has been related to the presence of larger α' precipitates. The α and α' phases are the Fe-rich and Cr-rich solid solutions into which the body-centered cubic (bcc) phase of the alloy decomposes at temperatures below about 1000 K.

The standard phase diagram for this alloy has been assessed using the CALPHAD methodology. In this approach the mixture has been assumed to behave like a standard segregating mixture at temperatures below the existence range of the σ -phase. There are, however, well known anomalies in the location of the solvus in annealed and irradiated samples which suggest a more complex behavior. A breakthrough in the understanding of the microstructure of these alloys was made through neutron diffraction measurements which showed (1) negative Cowley short-range order (SRO) parameters at small Cr concentrations indicating strong short-range ordering of Cr atoms, and (2) an inversion of the sign of these parameters with increasing Cr concentration suggesting the formation of α ' precipitates.

The implications of these discoveries for the interpretation of enhanced creep resistance and embrittlement are apparent since SRO is known to affect the mobility of dislocations9 and precipitation plays a role in intergranular cracking. Nonetheless the understanding of the atomistic details of the complex behavior of this alloy is still incomplete. This situation has motivated a number of recent first principles studies which addressed the energetics of this system. These calculations revealed a change of sign in the heat of formation of the solution from the negative to the positive side as the Cr concentration increases above 10%. Detailed analysis of the origin of this anomaly showed that, while the heat of solution of a Cr impurity in Fe is large and negative, magnetic frustration leads to a strong Cr-Cr repulsion, causing the heat of formation to assume large positive values as the Cr content increases.

These advances in the improved understanding of the energetics of Fe-Cr alloys have provided the basis for the development of accurate interatomic potential models, which enable large scale simulations of the microstructural evolution. Two approaches were developed known as the twoband model and the composition dependent model, which both address the complex shape of the heat of formation curve at 0K as determined from the aforementioned first-principles calculations. Using our composition dependent model, we recently studied the implications of the change in sign of the heat of formation on the thermodynamic behavior at finite temperatures and proposed a modified phase diagram for Fe-Cr in the region of low Cr content and temperatures below the range of existence of the σ -phase. In fact compared to the CALPHAD assessment, which is based on the assumption of a standard segregating binary mixture, a better agreement with the experimental location of the solvus was obtained.

From our viewpoint, three aspects render the study of SRO in Fe-Cr alloys particular interesting: (1) Experimental measurements of SRO parameters of heterogeneous systems (such as

mixtures of α and α') provide only compound quantities equivalent to averages over the entire sample. (2) In Fe-Cr this situation is further complicated by the ordering tendency of the system at low Cr concentrations. (3) The recent advances in the development of Fe-Cr interatomic potentials and the availability of suitable simulation techniques (semi-grand canonical Monte Carlo) provide the possibility to explore the atomistic details of these processes. Thereby, we are able to resolve the contributions to the experimentally measured quantities and understand the microscopic behavior of the material. In this paper, we discuss the evolution of SRO in a mixture of two phases and the influence of the kinetics of alloy decomposition on the time evolution of the SRO parameters.

Figure 1 shows the equilibrium Cr concentration which is established for a given chemical potential and temperature. The curves can be well fit assuming a regular solution on temperature, as shown by the lines in Fig. 1.

$$\Delta \mu = \Delta \mu^0 + \Omega (1 - c_{\rm Cr})^2 + k_B T \ln c_{\rm Cr} \tag{1}$$

The concentration range shown in Fig. 1 slightly exceeds the thermodynamic equilibrium solubility as given by the phase diagram of this model (see our previous report). The system can thus be driven to some extent into the two-phase region without precipitation taking place during the course of the simulation, which is a natural consequence of a small chemical driving force, short simulation time, and/or small sample size combined with the fact that the transition has a nucleation barrier.



Fig. 1. Relation between chemical potential and Cr concentration in α -Fe. The data points were obtained by simulation. The lines are fits to equation 1.

The SRO parameters were obtained by averaging over all configurations along the Markov chain (for a given chemical potential and temperature) for which the α phase encompassed the entire sample (single phase system). The results for the bcc SRO parameter are shown in Fig. 2. Several observations can be made: For smaller concentrations the SRO becomes more negative with increasing Cr concentration. With decreasing temperature the curves approach the theoretical lower limit for the SRO parameter (dashed line in Fig. 2). For larger concentrations the SRO parameter reaches a minimum between 8 and 12% Cr, the location of which is only weakly dependent on temperature (very much unlike the solubility limit).



Fig. 2. Dependence of the short-range order parameter on the total Cr concentration. Circles show simulation data. Solid lines serve as guide to the eyes. The dashed line represents the maximum possible order. E1: experimental data from Ref. 20; E2: experimental data from Ref. 21; E3: experimental data from Mirebeau, M. Hennion, and G. Parette, Phys. Rev. Lett. 53 (1984) 687.

Figure 3 shows the number distribution of SRO parameters obtained by averaging over every Cr atom in the sample after 1100 MC steps per atom which is a representative configuration for the Fe-rich homogeneous solid solution (pure α -phase). There is one pronounced peak on the negative side equivalent to the SRO of the α phase. Note that the range of SRO parameter also includes some positive values. This is related to the saturation of the α -phase which in equilibrium at this temperature would contain only about 8.2% Cr. For further illustration the configuration is shown in Fig. 4(a) clearly indicating the absence of precipitation.



Fig. 3. Number distribution of SRO parameter before (A) and after (B) the formation of supercritically sized α ' precipitates. The corresponding configurations are shown in Fig. 5.



(b) configuration B: after 1500 MC steps/atom

Fig. 4. Atomic configurations before (a) and after (b) the formation of super-critical α' precipitate. Only Cr atoms are shown with a color coding based on their SRO parameter: blue/green: negative or small positive SRO parameter (Fe-rich solid solution, α phase), yellow/red: positive SRO parameter (α' precipitates, α - α' interface).

Continuing with the simulation we observe the appearance of the precipitated α' phase, and the SRO parameter histogram shows two distinct peaks (See Fig. 3B), one at about -0.02, characteristic of the α phase, and one at about 1, characteristic of the α' phase. Figure 4B shows the microstructure corresponding to this situation. Clearly, the average SRO parameter is the result of a combination of these two peaks in the bimodal histogram.

The results presented above demonstrate that particular care must be exercised when interpreting the SRO parameter in the case of a two-phase mixture. While the average SRO parameter for Cr atoms in the α phase is typically small and negative, the SRO parameter for Cr precipitates is close to one. Since experimentally the SRO is obtained over the entire sample, the measured value is an average over all types of local short-range order. This average is the weighted sum of the contributions from the α and α phases, as well as the α/α interface.

The consequence of these observations is that the sample-averaged SRO shows a composition dependence as shown in Fig. 5, together with some experimental results. We do not give here

the details on how these curves are obtained, but just say that they are the consequence of this simple observation that in a heterogeneous sample, the measured SRO parameter is the weighted average of the SRO in each phase. This analysis provided as with a key to interpret a series of experimental results.



Fig. 5. Theoretical prediction for the average SRO parameter. Experimental references as given in the caption of Fig. 2.

This work has been submitted for publication to PRB and it can be summarized as follows: We have investigated the short-range order (SRO) in Fe-rich Fe-Cr alloys using atomistic simulations based on an empirical potential description of the alloy. For low temperatures and small concentrations the SRO in the α phase is found to be close to the theoretical maximum possible SRO. As temperature increases SRO is reduced due to entropic effects. For somewhat larger Cr concentrations the SRO curves go through a minimum and subsequently approach zero. This behavior reflects the competition between energy induced ordering and entropy-driven randomization. In the two-phase region the experimentally assessed SRO parameter is a mixture of both the SRO in the α phase and the α precipitates. The simulations show that the two contributions can be clearly separated. When using a weighted average of these contributions the average SRO parameter is predicted as a function of concentration in good agreement with experiment. This model has also been used to investigate the effect of temperature on the SRO parameter which shows the temperature dependence of the solubility of Cr in Fe to be the dominating factor. The results reported here are anticipated to support future research in at least two aspects: (1) As indicated in the introduction the SRO affects the mobility of dislocations. The present paper therefore constitutes a basis for a detailed atomistic study of the mobility of dislocations in Fe-Cr allovs. (2) The second aspect is the role of SRO on the behavior of Cr at interfaces and free surfaces. In fact, as we described in a previous report, Cr has an unexpected behavior close to interfaces, namely it seems to be rejected from grain boundaries and surfaces. This effect, in addition to SRO, may affect grain boundary cohesion, a subject of our future research.

The present paper clarifies the contributions to the average SRO parameter in a two-phase system and introduces a simple predictive model. It thereby provides a better understanding of previous experimental results and provides the basis for a more elaborate interpretation of future experiments.

Impurity segregation at grain boundaries in polycrystalline materials

In the last few years of work in this project we have developed the grounds to model real alloys using computer simulations. The path followed involves the development of models and tools. At the present stage of our work, we are able to explore a diversity of relevant problems in metallurgy, in particular those related to impurities/solute segregation at defects like grain boundaries.

As a first application of our tools to this problem, we studied nanophase 'dirty' materials, i.e., a large collection of grain boundaries with a small amount of solute or impurities. We just submitted a paper in which we present this novel computational approach to model the problem of segregation at grain boundaries, whose content can be summarized as follows: using our new parallel Monte Carlo code in the transmutation ensemble with displacements and a thermodynamically assessed classical potential for the alloy of interest, we have been able to prepare nanocrystalline samples showing heterogeneous precipitation of an insoluble impurity at grain boundaries. This result is in agreement with experimental evidence of the segregation of Fe impurities to Cu grain boundaries reported by Bernardini and coworkers.

Our methodology allows us to construct realistic microstructures of a highly non ideal binary alloy thus enabling quantitative studies of impurity effects on several relevant properties. Pure and dirty samples have been subjected to different tests: aging, tensile deformation and fracture resistance. Our simulations show that a small concentration of insoluble impurities that precipitate at GBs are capable of causing drastic reductions in GB mobilities, increase cohesion, and have negligible effects on its mechanical properties. We interpret the results in terms of different atomic motion in the grain boundary region.

Grain boundary sliding or motion of the grains relative to each other in a direction parallel to the grain boundary does not require mass transport to maintain the preferred equilibrium partition of the impurities between grain boundary and bulk. Sliding can occur through atomic shuffles not involving diffusion of the impurity. On the other hand, grain boundary migration and grain growth imply motion of the grain boundaries perpendicular to the grain boundary plane and require mass transport of the impurity together with GB motion in order to maintain the equilibrium segregation ratio. This distinction can be extremely important in the effects of impurities in the mechanical and annealing behavior of nanocrystalline materials. Our results show that grain boundary sliding and mobility can be affected in dramatically different ways by the addition of impurities.

These two processes are controlled by different characteristics of the impurity. The effects on grain boundary mobility are controlled by the tendency of the impurity to segregate to the grain boundary. On the other hand, one may speculate that grain boundary sliding is controlled by the effect of the impurity on the free volume of the grain boundary. In our case, there is a negligible effect of the impurities on the free volume in the boundary region because of the similar sizes of the Fe and Cu atoms.

Grain boundary embrittlement can be controlled by both size and chemical effects and can be influenced by the chemical part, even in the absence of size effects. Our newly developed tools allowed us to explore the important process of heterogeneous impurity segregation at GB and its effect on GB stability and plasticity, opening in this way the possibility of modeling more realistic - dirty- samples. Our technique will allow the engineering of interfaces for desired grain boundary mobility and mechanical response, something that is crucial for a number of applications such as building better first wall materials for Magnetic Confinement Fusion or targets for the National Ignition Facility which requires reduced GB motion, and also improved materials for the new generation of nuclear reactors, where GB of nanophase materials could act as sinks for radiation-induced defects.

Conclusions

In the period reported here, several applications of the model developed previously have been completed and show novel properties of this alloy. These results are being published and presented in numerous conferences, many of them as invited talks.

EFFECT OF MASS OF THE PRIMARY KNOCK-ON ATOM ON DISPLACEMENT CASCADE DEBRIS IN α**-IRON**—A. F. Calder, D. J. Bacon, A. V. Barashev (The University of Liverpool), and Yu. N. Osetsky (Oak Ridge National Laboratory)

SUMMARY

Results are presented from molecular dynamics (MD) simulations of displacement cascades created in α -iron (Fe) by primary knock-on atoms (PKAs) with energy from 5 to 20 keV and mass chosen to represent C, Fe and Bi. Molecular Bi₂ has also been simulated using two Bi PKAs, and PKA-Fe interaction potential has also been varied. Four effects are reported. First, the PKA mass has a major effect on cascade damage while the interaction potential has little if any. Second, the total number of point defects produced in a cascade decreases with increasing PKA mass. This fact is not accounted for in models used conventionally for estimating damage. Third, interstitial loops of $\frac{1}{2}$ (111> type and both vacancy and interstitial loops of <100> type are formed, the latter being observed in MD simulation for the first time. The probability of <100> loop appearance increases with increasing PKA mass as well as energy. Finally, there is a correlation between production of large vacancy and interstitial clusters in the same cascade.

PROGRESS AND STATUS

Introduction

Degradation of mechanical properties of iron (Fe) and ferritic alloys in nuclear reactors is associated with microstructural changes occurring under neutron irradiation. One of the principal effects is the formation of point defect clusters, which are obstacles to moving dislocations causing radiation the induced strengthening and loss of ductility. Understanding of this process is still poor. For example, the occurrence of interstitial-type loops with the Burgers vector $\mathbf{b} = \langle 100 \rangle$ remains unexplained [1,2]. Eyre and Bullough [3] proposed that such a loop can form as a result of $\frac{1}{2} < 1\overline{10}$ shear of a faulted 1/2<110> loop. Molecular dynamics (MD) simulations with existing interatomic potentials have not confirmed this, however. They show that, first, only 1/2<111> clusters of self-interstitial atoms (SIAs), which are the most stable configuration, are produced in displacement cascades [4]. Second, although rhombus-shaped ½<110> 16-SIA clusters and larger do transform into <100> configuration at temperature T = 0K [5], all clusters, independently of the starting state, transform into $\frac{1}{2}$ <111> configuration on simulating T > 0K [5-7]. Another mechanism of a <100> loop formation resulting from coalescence of two ½<111> loops was proposed by Masters [2]. However, it too is not supported by MD simulations because, although segments of <100> type do form due to interaction between two mobile $\frac{1}{2}$ <111> clusters, they are unstable and a single $\frac{1}{2}$ <111> loop eventually forms [8,9]. In fact, there has been only one reported observation of the formation of a <100>-type vacancy loop by Soneda et al. [10] and none of interstitial type. Soneda et al. ran a hundred 50 keV PKA cascades to detect one such event, which indicates that it is rare and perhaps more probable in high energy cascades.

Many experimental studies have been reported that use either self-ion or heavy-ion irradiation of thin foils to simulate bulk damage from neutrons and investigate the effects of cascade parameters on damage. Although there are problems in interpretation of the results due to proximity of surfaces and resolution limit of the transmission electron microscope (TEM), there are clear trends for α -iron. For example, Jenkins et al. [11] have shown that self-ion irradiation does not result in visible damage up to the dose level where cascade overlap is significant. Further, an increase of the incident ion mass increases the defect yield, i.e., the number of visible loops formed per incident ion after irradiation to the same dose level, and also leads to an increase of the mean loop size. (We use the term 'loop' here to refer to a cluster of point defects that creates diffraction contrast consistent with a dislocation loop.) Loops with Burgers vector **b** of $\frac{1}{2}$ <111> and <100> type have been observed, both are reported to be of vacancy type. Thus, there is clearly an effect of varying ion type in defect production in cascades, while simple models conventionally used to estimate the damage, e.g., NRT standard [12], are insensitive to the ion nature.

To the best of our knowledge, the effect of PKA mass on displacement cascades has not been studied systematically by MD and is the subject of the present report.

Simulation Method

A simulation box with periodic boundary conditions at a temperature of 600K was used. It was maintained at a constant volume with the lattice parameter a_0 corresponding to zero-pressure conditions at a given temperature before introduction of a PKA. The inter-atomic interaction was described using an embedded-atom-method-type (EAM) empirical potential developed recently with a specific emphasis on a correct description of the relative stability of <111>, <110> and <100> configurations of self-interstitial atoms and the vacancy migration energy [13]. In particular, the formation energy of the <110> dumbbell is ~0.5 eV lower than that of a <111> crowdion with this potential, cf. 0.7 eV obtained ab initio [14], and the <110> configuration is more stable with respect to the <111> for clusters of up to four SIAs. PKA energy of 5, 10 and 20 keV was considered. The size of the model system depended on the PKA energy, being 250 000 for 5 keV, 500 000 for 10 keV and 2 000 000 for 20 keV. No temperature control was applied and the temperature increase due to introduction of the PKA in the corresponding simulations was approximately 60, 70 and 30K, respectively. The integration of equations of motion was performed using a leapfrog algorithm with a variable time-step, determined by a fixed value for the displacement of the fastest atom in the system, typically ~0.003 a_0 .

The calculations were performed to simulate cascades in bulk iron with one of three different PKAs: C, Fe, Bi and one molecular Bi_2 . In the latter case, two nearest atoms of the lattice were used as the PKA atoms with the same direction and the same energy, equal to half the total energy. The potential for the PKA-Fe interaction was the same as for Fe-Fe over most of the range of atom-atom spacing, but at short range (≤ 0.1 nm), well below the nearest-neighbour spacing, the Universal screened-Coulomb potential [15] for the required atomic pair was used for the pair part of the potential. The two potentials were joined smoothly by an exponential spline over the range 0.100-0.205 nm. Two sets of simulations were performed to elucidate whether PKA mass or interaction potential was primarily responsible for the effects observed. This was done by changing either the mass or potential whilst retaining the other property as that for an Fe atom. The combinations studied and the notation used later for identifying them are summarised in Table 1. The statistics of up to 30 cascade events for each set of conditions (temperature, PKA energy, mass and potential) was accumulated. Independence of calculations was provided by using different <123> and <135> type PKA direction, as well as by introducing the PKA at different times for different atoms.

PKA	C (12.0)	Fe	Bi	Fe	Bi	Bi ₂
	(12.0)	(55.6)	(209.0)	(55.6)	(209.0)	(410.0)
PKA-Fe potential	Fe-Fe	Fe-Fe	Fe-Fe	Bi-Fe	Bi-Fe	Bi-Fe
Notation	C^{Fe}	Fe ^{Fe}	Bi ^{Fe}	Fe ^{Bi}	Bi ^{Bi}	Bi ₂ ^{Bi}
5 keV	30	30	30	30	30	-
10 keV	30	30	30	30	30	-
20 keV	30	30	30	-	30	21

Table 1. Summary of the number of cascades modelled for each cascade energy for the combinations of PKA mass and PKA-Fe interatomic potential considered. The notation is used in subsequent figures.

MD Results

The dependence of the mean value of the total number, $N_{\rm F}$, of either vacancies or SIAs produced in a cascade on the PKA mass for different PKA energy is presented in Fig. 1. Empty symbols are from modelling when only mass of the PKA was changed, while full symbols represent results produced with the Bi-Fe interaction potential for the PKA-Fe pair. The bars are the standard error. It can be seen that within statistical uncertainty, $N_{\rm F}$ for a given mass does not depend on the PKA-Fe interatomic potential. In contrast, $N_{\rm F}$ decreases with increasing mass across the mass range 12 to 209 amu for 5 and 10 keV cascades, but only decreases between 12 and 56 amu at 20 keV. For all PKA types, the number of defects increases approximately linearly with PKA energy, a trend similar to that observed previously, e.g., in [16]. An increase of PKA mass also leads to an increase in variability of $N_{\rm F}$ over different cascades and this effect is particularly strong for heavy PKAs. This is demonstrated by the histogram for the 20 keV simulations in Fig. 2. For example, as seen from Fig. 2, $N_{\rm F}$ ranges from 4 to 82 in the 21 cascades created by Bi₂ PKAs, compared with 26 to 63 in 30 cascades by Fe PKAs.



Fig. 1. Dependence of the mean value of the total number, $N_{\rm F}$, of either vacancies or SIAs produced in a cascade on the PKA mass for different PKA energy. Empty symbols are for simulations when only mass is changed, while full symbols are for calculations with the Bi-Fe interaction potential for the PKA-Fe pair.

The finding that the PKA mass has a significant effect on defect production is at variance with simple binary collision approximation (BCA) used conventionally to estimate the damage, e.g., the NRT standard [12]. In the absence of inelastic effects, which is the situation in the MD modelling, the NRT number is independent of mass. Furthermore, when electronic energy loss is allowed for, BCA actually predicts a decrease in N_F with decreasing atomic number, which is contrary to the mass effect due to elastic collisions found in the present study.



Fig. 2. Distribution of cascades creating N_F defects in the simulations for each type of 20 keV PKA.

Figure 3(a) shows the mass dependence of the fractional population distribution of vacancies as a function of cluster size for all cascades of 20 keV. A cluster is defined such that every vacancy has at least one other vacancy in a nearest-neighbour site. The histogram bin width is 5, except for small size where the first two bins are for defects of size 1 and 2-5, respectively. It is seen that the size distribution broadens with increasing mass, resulting in an increase of the mean cluster size and the creation of larger clusters by the Bi and Bi₂ PKAs. This is qualitatively consistent with TEM observations by Jenkins *at al.* of vacancy loops produced by cascade collapse in iron [11]. The fraction of vacancies created in clusters is also affected by PKA mass, for the fraction of singles decreases from approximately 0.6-0.7 for C and Fe PKAs to around 0.4 for the heavier PKAs.

Similar trends with increasing PKA mass are found in the distribution of clustered interstitials, as can be seen from the data for 20 keV plotted in Fig. 3(b). Here, the influence on the total clustered fraction is particularly strong, for the fraction of single SIAs falls from 0.6 for C to 0.1 for Bi₂.

Interstitial loops of ½<111> type and both vacancy and interstitial loops of <100> type were formed in these simulations. Clusters of the first type are commonly found in MD studies of displacement cascades in α -Fe, even for energy of only a few keV (see, e.g., [4]), but <100> loops are not. As noted in section 1, the only observation reported previously was by Soneda et al. [10], who found one <100> vacancy loop in the damage of one hundred simulations of 50 keV cascades created by Fe PKAs.

Examples of the <100> dislocation loops in the present work are presented in Figs. 4(a) and (b). They show atoms (solid circles) in two (001) planes through the centre of loops with b = [100]: isolated single vacancies are shown as empty squares in Fig. 4(a). The lines are added to aid visualisation of the distortion around the loops. The clusters in Figs. 4(a) and (b) contain 57 vacancies and 30 SIAs, respectively. Each loop formed directly in the cascade process by the creation of vacancies or SIAs on two adjacent (100) atomic planes.







(b)

Fig. 3. Variation of population fraction with cluster size for the 20 keV simulations for each type of PKA: (a) vacancies and (b) SIAs.

No clusters with <100> loop morphology were found in cascade damage created by C and Fe self-ion PKAs. The <100> interstitial defect in Fig. 4(b) is the only one of this type found in all the simulations. It is the first of its kind created in simulation and was formed when molecular Bi_2 irradiation was mimicked by two Bi PKAs. <100> vacancy loops are more common, for six examples were found in 20 keV cascades: two out of 60 simulations with a Bi PKA and four out of 21 with Bi_2 . It is clear, therefore, that the probability of <100> cluster formation increases with increasing PKA mass as well as energy. Note that clusters reported above are ~2 nm diameter, implying that the defects observed in TEM experiments can be produced directly in cascades.

Recent MD simulations of cascades in zirconium [17] and copper [18] have revealed a correlation in the production of interstitial and vacancy clusters, in that cascades with a high proportion of vacancies in clusters are more likely to have a high proportion of clustered interstitials. The results obtained here for iron support this. Furthermore, a correlation exists not only for the cluster fractions but also the size of the clusters. This correlation is clear in Fig. 5, where the maximum size of a vacancy cluster is plotted against the largest SIA cluster produced in the same cascade for the 20 keV simulations. For cascades created by C and Fe PKAs, and those created by heavier PKAs but with only small clusters, most data points fall below the line drawn at 45°, reflecting the difference in the vacancy and interstitial cluster size distribution seen in Figs. 3(a) and (b). For heavy PKAs, there is still a spread of points below the 45°line, but with a tendency to lie near it with increasing cluster size.

Discussion

As has already been mentioned in the Introduction, TEM analysis of loop images in iron foils irradiated to low dose provides evidence that the damage from self-ions differs from that due to heavy ions. The former does not result in visible damage up to the dose level where cascade overlap is significant [11], while the latter produces <100> vacancy-type loops. The situation is different in bulk samples irradiated by neutrons to a similar NRT dose level. In this case, the PKAs are Fe atoms and the damage might be expected to be comparable to that for self-ion irradiation. Although visible defect clusters do form under neutrons, they are of interstitial-type with **b** equal to either $\frac{1}{2}$ <111> or <100> (see [19] and references cited therein).



Fig. 4. (a) Cross section through a vacancy cluster of <100> type containing 57 vacancies. (b) Cross section through an interstitial cluster of <100> type containing 30 SIAs.

On the basis of the present work it is possible to speculate on the link to experiments as follows. With regard to the vacancy component of damage, the MD simulations are in agreement with experiment that the Burgers vector of vacancy loops produced in cascades is <100> rather than $\frac{1}{2}<111>$, despite the fact that the formation energy of the latter is lower [14]. Furthermore, the probability of vacancy loop formation increases with increasing PKA mass and is very small for Fe PKAs. Hence, there is satisfactory correspondence between the modelling and the observed vacancy component of damage in both the bulk and TEM foils. For the interstitial component, the MD simulations predict, and neutron irradiation experiments reveal, the formation of a high density of ½<111> SIA clusters in the bulk of iron and much smaller probability of <100>-type cluster formation. The absence of SIA clusters in ionirradiated foils is believed to be due to the free surfaces acting as efficient sinks for 1/2<111> SIA clusters, which are highly mobile [6]. This annihilation increases the vacancy population left in the foil in both single and clustered form, which also acts as recombination centres for the SIA clusters. These processes suppress survival and growth of SIA loops in foils with respect to the bulk of iron, where the density of annihilation centres for SIA clusters is lower. Nevertheless, there does not seem to be an obvious reason why a fraction of <100> loops, however small, in heavy-ion irradiated iron foils should not have interstitial nature and it is hoped that experiments known to be underway in several laboratories may confirm or disprove this conjecture.



Fig. 5. Maximum size of a vacancy cluster versus that of an SIA cluster produced in the same cascade for 20 keV PKA simulations.

The question arises as to why the probability of <100> loop formation increases with increasing PKA mass, both in experiment and MD simulation. In order to explain the former, it has been argued on the basis of binary-collision estimates that, although $N_{\rm F}$ is independent of PKA mass, the cascade volume decreases with increasing mass [11,20]. Thus, higher energy and vacancy density is achieved, and this results in a higher probability of cascade collapse and loop formation. This was supported by the first MD simulations of collapse by Matthai and Bacon [21], who used a pair wise interatomic potential to simulate a small void placed in the zone of a thermal spike and found that an extended dislocation defect, namely a loop in iron and a stacking fault tetrahedron in copper, was formed during the spike lifetime. Interestingly, the loop in iron was of <100> type, even though a 1/2<111> loop with the same number of vacancies has lower formation energy. Kapinos et al. [22, 23] also showed by MD modelling that conditions of high energy and vacancy density favour collapse to vacancy dislocation loops in metals. Observations made in the present work are qualitatively consistent with this. As an illustration of this, in Fig. 6 we plot the variation with PKA mass of the mean value of the maximum number, N_{max} , of atoms displaced from a lattice site by more than $0.3a_0$ in a 20 keV cascade and the mean of the time, t_{max} , at which this maximum is reached. As can be seen, the higher the PKA mass the higher the number of atoms displaced from their original position. This is an indication, however indirect, of localisation of the cascade energy both in space and time. It seems probable that a corresponding decrease in the final defect yield might be just a consequence of closer proximity of the vacancy and interstitial in cascades produced with heavier PKA, and hence a more efficient recombination process.



Fig. 6. Variation with PKA mass of the mean value of the maximum number, N_{max} , of atoms displaced by $\ge 0.3a_0$ in a 20 keV cascade and the mean of the time, t_{max} , at which this maximum is reached.

Conclusions

- 1) The PKA mass has a major effect on cascades while the interaction potential has little if any.
- The total number of point defects produced in a cascade decreases with increasing PKA mass, and the effect is stronger for lower PKA energy. This fact is not accounted for in the binarycollision models.
- In addition to usual the ¹/₂<111>-type SIA loops, one <100> SIA loop has been observed for the first time in MD, when simulating molecular Bi irradiation.
- 4) <100> vacancy loops have been observed with heavier PKAs.
- 5) With heavier PKA the cluster size is bigger and the probability of <100> cluster formation increased. This correlates with the observations by Jenkins *at al.* [11].
- 6) Strong correlation between the maximum size of a vacancy and an SIA cluster produced in the same cascade has been established.

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EFFECT OF SIZE ON THE DESTRUCTION MECHANISMS OF STACKING FAULT TETRAHEDRA INDUCED BY GLIDING DISLOCATIONS IN QUENCHED GOLD—Y. Matsukawa (Argonne National Laboratory), Y. N. Osetsky, R. E. Stoller, and S. J. Zinkle (Oak Ridge National Laboratory)

OBJECTIVE

The destruction processes of stacking fault tetrahedra (SFTs) induced by gliding dislocations were examined by transmission electron microscopy (TEM) in situ straining experiments for SFTs with edge lengths ranging from 10 to 50 nm. At least four distinct SFT destruction processes were identified: (1) consistent with Kimura model for both screw and 60-degree dislocations, (2) stress-induced SFT collapse into a triangular Frank loop, (3) partial annihilation leaving an apex portion, and (4) complete annihilation. Process (4) was observed at room temperature only for small SFTs (~10 nm); however, this process was also frequently observed for larger SFTs (~30 nm) at higher temperature (~853 K). When this process was induced, the dislocation always cross-slipped, indicating only screw dislocations can induce this process.

Introduction

Stacking fault tetrahedra (SFT) are common, sessile, vacancy-type defect clusters in vacancy supersaturated face-centered cubic (fcc) metals having low stacking fault energy like copper, gold, and austenitic stainless steels. The vacancy supersaturation can be introduced by quenching from close to the melting point [1-4] and also by cascade damage due to high energy particle irradiation [5-10]. SFT-dislocation interactions are currently of particular interest as a key mechanism for materials hardening and accompanying ductility reduction of neutron-irradiated fcc metals in nuclear reactor environments [9-16]. An SFT consists of intrinsic stacking faults on four crystallographically equivalent {111} planes locked by six stair-rod dislocations [1,17]. Those sessile stair-rod dislocations act as a strong obstacle against the motion of gliding dislocations responsible for plastic deformation. Also, the complex structure of multiple, interlocked stair-rod dislocations cause the SFT to be highly stable under shear stress. However, defect-free cleared channels (dislocation channels) are commonly observed in the deformation microstructure of both quenched and irradiated metals [12-16,18-22]. This has led to great interest in resolving how SFTs are annihilated during plastic deformation.

The proposed mechanisms for SFT annihilation by gliding dislocations fall into two general categories: 1) annihilation due to the large stress-field associated with nearby dislocations, i.e. SFT destruction by indirect interaction with dislocations, and 2) annihilation due to direct interaction with dislocations. Regarding the first category, Sun et al. and Hiratani et al. used elasticity theory to investigate the stability of an SFT under the stress-field of a nearby dislocation [23-24]. Their calculations showed that the stress-field from a single dislocation could never cause the destruction of SFTs. Regarding the second category, Kimura and Maddin examined conceivable reactions between a gliding perfect dislocation (screw or 60-degree) and the stair-rod dislocation can annihilate an SFT if the perfect dislocation dissociates into a pair of Shockley partial dislocations on the surface of the SFT to eliminate the stacking fault. The other three stacking faults in the SFT are then eliminated by a chain reaction starting from the elimination of the first stacking fault.



Fig. 1. Kimura's model for SFT destruction induced by direct interaction with (a) a screw dislocation and (b) a 60-degree mixed dislocation [25].

Recent remarkable progress in computer technology has enabled molecular dynamics (MD) computer simulations to investigate the dynamic processes of SFT-dislocation interactions. In 2002, Wirth et al. examined the interaction of a small SFT (~2 nm) with edge dislocations in copper [26]. They observed that the SFT remained intact even after multiple (up to six) interactions with a dislocation. SFT destruction took place only when the SFT was initially set up as an imperfect, so-called truncated SFT, which corresponds to an SFT without an apex. Later, Osetsky et al. examined the interaction of both edge and screw dislocations with larger SFTs up to 10 nm using MD simulations [27-31]. They demonstrated that 1) both edge and screw dislocations could destroy a perfect SFT: the destruction was achieved by the absorption of the major part of the SFT into the dislocations, leaving just the apex of the original SFT. 2) Edge dislocations could destroy SFTs larger than ~3 nm (3 nm SFT contains ~70 vacancies for copper and ~54 vacancies for gold), but there is no such SFT size limitation for screw dislocations. 3) The specimen geometry (whether thin foil or bulk) could affect the final configuration of the screw dislocation after the SFT destruction. However, to date, no MD simulations have reproduced the Kimura's SFT destruction processes where the whole SFT is incorporated into the dislocation (Fig 1(a)) or converted into a triangular Frank loop (Fig 1(b)). The disparity between the Kimura model and simulation results remains unclear. Also, in the simulation-based SFT destruction processes, dislocations absorb only part of the SFT. Annihilation of the whole SFT by an impinging dislocation has not been reported in the MD simulations. This is inconsistent with the fact that numerous experiments reported nothing remains in the cleared channels following deformation in quenched or irradiated materials.

The most direct experimental method to investigate SFT destruction processes involves in situ straining experiments using a transmission electron microscope (TEM). Concurrently with the MD computational research mentioned above, Matsukawa et al. examined the interaction of large SFTs (27~76 nm) with gliding dislocations in quenched gold at deformation temperatures

between 100 K and room temperature [32-35]. They identified various SFT destruction processes including those consistent and inconsistent with Kimura's model. Those inconsistent with Kimura's model involved the process leaving behind an apex of the original SFT, which is quite similar to the simulation-based predictions described above. Shäublin et al. examined small SFTs (~2 nm) introduced into copper by proton irradiation [36]. They observed the formation of elongated debris (a super jog or super kink) on a gliding dislocation upon interaction with an SFT. However, since 2 nm is close to the current TEM resolution limit for diffraction imaging techniques, the detail of the observed process is unclear. Robach et al. examined large SFTs (~90 nm) in quenched gold and small SFTs (~4 nm) in quenched copper [37]. They observed the conversion of those SFTs into different configurations; however, the obtained micrographs were unclear in terms of the detailed morphology of those configurations.

Those preceding TEM results are not comprehensive mainly due to the difficulty of the experiments. The straining stages are in many cases single-tilt, which often prevents the capture of clear images for informative model constructions. More systematic and comprehensive TEM results are desired for a complete understanding of SFT-dislocation interaction processes. Such experimental results are necessary for proper comparison with and validation of atomic-scale MD simulations, which are essential inputs of mesoscopic-scale computer simulations such as dislocation dynamics [38-39]. In this report, we present the results of systematic in situ TEM experiments on the SFT size dependence of SFT destruction processes in gold. The examined SFT edge lengths (referred to as "sizes" in the following) were 10~50 nm, which encompass the size range where direct comparison with MD results can be made. Also, the SFT size range examined in the present study brackets the critical size in an SFT's stability. A previous elasticity theory calculation indicates that SFTs larger than 26.5 nm are energetically meta-stable whereas smaller SFTs are stable compared to faulted vacancy loops throughout the comparison of energy hierarchy between an SFT, a triangular Frank loop, and a truncated SFT [40]. In a comparison between an SFT and a circular Frank loop, the critical size below which the SFT is the stable configuration was reported to be ~10 nm [5].

Experimental Procedure

SFTs were introduced into 99.9975% pure polycrystalline gold specimens, whose thickness was 100 m, by guenching from 1273 K in an open vertical furnace to 233 K in a CaCl₂ solution. The specimens were kept at 1273 K for 1-30 min in the furnace, and then at 233 K for 10 min in the quenched-in solution. Longer annealing time at 1273K resulted in larger SFTs. The tensile specimens had a rectangular shape (10 mm x 2.5 mm x 100 m), and the central portion was electro-polished using a twin jet method. The electrolytic polishing solution was a KCN 67 g/l water solution, and the polishing temperature was 276 K. The TEM accelerating voltage was 200 kV, which introduces negligible irradiation damage into gold. The specimen stage was a GATAN Model 671 single-tilt cooling straining stage, whose crosshead speed is variable ranging from 0.01 to 1.00 m/s. In the present observation, the velocity of dislocations was 10-100 nm/s, which is roughly ten orders of magnitude slower than the dislocation velocity in MD simulations [35] (see also Appendix). The motion pictures of SFT-dislocation interaction processes were captured with a GATAN Model 622 camera, at a frame rate of 30 frames/s, recorded on DV tapes, and then computer processed into sequential images. The in situ straining experiments were carried out at room temperature. The SFT-dislocation interaction processes at higher temperatures (~873 K) were observed using GATAN Model 628 single-tilt heating stage. Dislocations glided without applying external stress during heating. The dislocation motion was driven by local specimen bending due to thermal-softening.

SFT Destruction Processes Observed in In Situ TEM Experiments

As addressed in our preliminary report [32], the SFTs introduced by quenching exhibit perfect

pyramidal shape without any truncation [41-44]. Hence, the following descriptions of the destruction processes induced by gliding dislocations are valid for perfect SFTs, as opposed to truncated or imperfectly formed SFTs [26,37].

SFT Destruction Processes Consistent with the Kimura Model

We observed SFT destruction processes consistent with Kimura's model for both screw and 60degree dislocation interactions. Figure 2 shows the SFT destruction processes leaving multiple super jog segments on the impinging dislocation. In this figure the beam direction was close to <001>, where the SFT appears square in shape. This process was confirmed at all SFT sizes (10~50 nm) without any significant difference in the configuration of multiple super jogs. Figure 3 is a sketch of the configuration of multiple super jog segments in the Kimura model for screw dislocation interactions seen from the <001> direction. These configurations are consistent with the experimental results: Fig. 2(a) corresponds to Fig. 3(c), and Figs. 2(b) and 2(c) correspond to Fig. 3(a). Those multiple super jogs consist of 60-degree and edge components. Although each segment is glissile, the multiple segments together are practically sessile due to their complicated configurations: in our experiments these super jog dislocations did not glide. In Fig. 2(a), a segment of the gliding dislocation, indicated by the arrow, cross-slipped prior to the interaction with the SFT. This is consistent with Kimura's assumption that this process is induced by a screw dislocation. Since the Kimura model is based on a simple summation of the Burgers vectors of the dislocations, the exact position of dislocation interaction with the SFT should not be a critical factor for inducing these destruction processes (the place of interaction does not affect the sum of the Burgers vectors). However, we never observed the configurations of multiple super jog segments shown in Figs. 3(b) and 3(d). The Kimura mechanism for screw dislocation interaction was induced only when dislocations impinged on SFTs near their base triangle.

Figure 4 shows the SFT destruction process that leaves behind a triangular Frank loop. The beam direction was close to <001>, where the shape of a triangular Frank loop can be readily distinguished from an SFT. The SFT size was 19 nm. After the leading dislocation in a dislocation queue collapsed the SFT into a triangular Frank loop (corresponding to the 95.93 sec frame), the subsequent dislocations interacted with the triangular Frank loop (the 140.53 sec frame). The slip planes of those dislocations are parallel to each other. This indicates that the residual Frank loop was on a plane nonparallel to the glide-plane of the dislocation that destroyed the SFT, which is consistent with Kimura's model for a 60-degree dislocation interaction.

More interactions were seen leaving super jogs than Frank loops since most of the observed interactions involved screw dislocations: Fig. 4 is the only example clearly identified as the Kimura process for a 60-degree dislocation interaction among ~30 observed SFT-dislocation interactions: the process shown in Figs. 1 and 3 in our previous report [35] is categorized in the variant addressed in the following section rather than the Kimura process for 60-degree dislocation. This tendency is consistent with in situ straining experiments carried out by other investigators on gold [1], copper [18,22], and nickel [19-20]. For in situ straining experiments using wedge-shaped thin foil specimens, dislocations were, in many cases, generated at the specimen edge and followed by crack initiation. Those cracks were, in many cases, out-of-plane mode-III shear cracks, as shown in Fig. 5(a). The two areas across the crack were accompanied with thickness fringes, indicating that the crack propagated with significant thickness reduction, which is induced only by out-of-plane shear. Screw dislocations compensate the out-of-plane shear displacements of mode-III cracks as shown in Fig. 5(b), whereas edge dislocations compensate mode-II in-plane shear. Screw dislocation activity is more dominant, presumably because the out-of-plane shear was favorable due to the unique specimen geometry having less of a constraint force in the thickness direction.



Fig. 2. SFT destruction process at room temperature leaving multiple super jog segments on the impinging dislocation: consistent with the Kimura model for SFT destruction by a screw dislocation. The SFT size was (a) 46, (b) 21, and (c) 12 nm, respectively.

Stress-induced SFT Collapse into a Triangular Frank Loop

Figures 6 and 7 are also SFT destruction processes leaving behind a triangular Frank loop; however, they are different from the Kimura model. The beam direction was close to <001> for Fig. 6 and <112> for Fig. 7, and the SFT size was 37 nm for Fig. 6 and 52 nm for Fig. 7. In contrast to Fig. 4, after the leading dislocation in a dislocation queue collapsed the SFT into a triangular Frank loop, the subsequent dislocations never interacted with the triangular Frank loop indicating that the Frank loop was lying on a plane parallel to the glide-planes of those dislocations. In the Kimura model for a 60-degree dislocation, the Frank loop must form on the planes nonparallel to the glide plane of the incident dislocation, as shown in Fig. 1. Large SFTs (>~37 nm) always collapsed in this manner when they interacted with the leading dislocation in a dislocation queue.

Large SFTs are energetically meta-stable [5,40], where it is more favorable to transform into a lower energy configuration, i.e. a Frank loop. Accordingly, this transformation would be a stress-induced SFT collapse via an inverse Silcox and Hirsch mechanism [1] due to high stress from a dislocation pile-up. Note that the impinging dislocation is slightly bent when it induces this collapsing process (the 0.97 sec frame in Fig. 6). This indicates that the stress-induced SFT collapse process occurs when the dislocation is in physical contact with the SFT.



Fig. 3. Configuration of multiple super jog segments assumed in the Kimura model for a screw dislocation, seen from the [001] zone axis: (a) when the Burgers vector $b = \overline{BA}$ and dislocation impingement is near the base triangle ABC, (b) when $b = \overline{BA}$ and dislocation impingement is near the apex D, (c) when $b = \overline{AB}$ and impingement is near the base ABC, and (d) when $b = \overline{AB}$ and impingement is near the apex D.

The smallest SFT that we confirmed that collapsed via this process was 37 nm. SFTs larger than this size always collapsed via this process upon interacting with the leading dislocation in a dislocation queue. Considering that this process was not confirmed for an SFT of 34 nm [33,35], it is highly possible that a critical size is located between 34 and 37 nm. The critical size above which SFTs are meta-stable was estimated to be roughly 26.5 nm in an elasticity theory calculation previously reported by Jøssang and Hirth [40,45]. The discrepancy with the present results may be because Jøssang and Hirth used 55 mJ/m² for the stacking fault energy of gold in their calculations whereas more recent values as low as 32 mJ/m² have been reported [45].

Partial Annihilation of an SFT Base Leaving a Small SFT

Occasionally, a gliding dislocation destroyed a large SFT leaving behind a small SFT. The small SFT corresponds to the original SFT's apex: the dislocation absorbs only the base portion. This SFT destruction process is rather complicated due to three variants regarding the configuration of the impinging dislocation after the destruction of the SFT, as previously reported elsewhere: 1) formation of sessile segments on the dislocation (super jogs on screw dislocations) [32,34-35], 2) glissile segments (super jogs on edge dislocations) [33], and 3) no super jog segments [33,35].



Fig. 4. SFT destruction process leaving behind a triangular Frank loop, consistent with the Kimura model for a 60-degree dislocation. The conversion from an SFT to a triangular Frank loop is captured in the 95.93 sec frame. The Frank loop was finally removed by the following dislocations. The initial SFT size was 19 nm.

Figure 8 shows an example of the case where sessile super-jog segments are created on the impinging dislocation. The size of the original SFT and the remnant small SFT is 26 nm and 5 nm, respectively. The sessile segments formed on the second dislocation in the dislocation queue. Since those segments pinned the dislocation, it inevitably encountered the following dislocations as deformation proceeded. Surprisingly, the sessile segments were transferred from one dislocation to another through dislocation-dislocation interaction. The position and morphology of the sessile segments were unchanged but the segments could transfer to adjacent dislocations within the queue. The dislocations released from the sessile segments were then glissile. To the best of our knowledge, this is the first experimental result that shows the sessile super-jog segments can be transferred among dislocations.



Fig. 5. (a) Typical example of a crack initiated at the specimen edge. Thickness fringes are clearly identified along the clack in the two fractured pieces, indicating that this is a mode-III outof-plane shear crack. (b) Schematic diagram of the mode-III crack: screw dislocations compensate the out-of-plane shear displacements.



Fig. 6. SFT destruction process leaving a triangular Frank loop, inconsistent with the Kimura model for a 60-degree dislocation. After the first dislocation collapsed the SFT to a triangular Frank loop, the following dislocations never interacted with the Frank loop. This indicates the Frank loop was lying on a plane parallel to the glide plane of those dislocations, which is inconsistent with the Kimura model. The initial SFT size was 37 nm and the observation direction was near [001].



Fig. 7. Same SFT destruction process as Fig. 6 but observed from [121]. The initial SFT size was 52 nm.

Figure 9 shows an example of the case leaving no sessile/glissile segments on the impinging dislocations. The leading dislocation (indexed as A) in a dislocation queue destroyed an SFT (31 nm). No jog segments were confirmed on the dislocation after the SFT destruction (at 7.57 sec). The dislocation finally glided away, leaving surface traces unparallel to the surface traces of previous motion. This indicates that the whole dislocation A cross-slipped, indicating that this is a screw dislocation. A small SFT (~5 nm) remained where dislocation A interacted with the original SFT. The following Shockley partial dislocations indexed as B constricted immediately after the disappearance of dislocation A: the constriction is conjectured to be induced by a stress



Fig. 8. SFT destruction process leaving behind an apex portion of the SFT and sessile segments on the impinging dislocation. The SFT original size and the remnant apex portion were 26 and 5 nm, respectively. After the SFT destruction by the first and second dislocations, sessile segments formed on the second dislocation. When the second dislocation interacted with the trailing dislocations, the sessile segments were transferred to those dislocations. The leading dislocations that released the sessile segments could then glide as usual.



Fig. 9. SFT destruction process leaving behind an apex of the SFT and no sessile segments on the dislocation. The SFT size and the remnant apex were 31 and 5 nm, respectively. After the SFT destruction, the dislocation glided away on a slip plane different from the original plane via cross-slip.

concentration at the front of the dislocation queue. Exactly the same feature was confirmed in another example that we previously reported [33,35]: upon the annihilation of the SFT base portion, the dislocation glided away on a different slip plane from the original plane via cross-slip.

Figure 10 shows a different case where dislocation segments are not observed following destruction of the SFT base. After the annihilation of an SFT (11 nm) leaving behind the 5 nm apex portion, the dislocation continued to glide on the same slip plane as before the interaction with the SFT. Therefore, cross slip to another glide plane does not always occur when destruction of the SFT base occurs without super jog formation.

Complete SFT Annihilation without any Remnants

Figure 11 shows an example of complete SFT annihilation leaving no remnants and no sessile segments on the impinging dislocation. This process is important especially for understanding the formation mechanism of cleared channels, because the other SFT destruction processes leave some remnants or sessile segments on the impinging dislocation whereas nothing remains in cleared channels. In Fig. 11, one of two ends of the dislocation line intersected by specimen surfaces moved away from the trace of previous locus upon annihilation of the 11 nm SFT. This indicates that the whole dislocation cross-slipped rather than having local cross-slip as seen in the Kimura model for a screw dislocation (Figs. 2 and 3). This process was frequently observed for small SFTs (~10nm) at room temperature and never observed for larger SFTs.

At high temperature (~873K) SFT destruction without any visible remnants was the dominant SFT annihilation process even for large SFTs, as shown in Fig. 12 (SFT size: 30 nm). This is understandable considering the fact that cross-slip can occur more easily at higher temperatures.

The SFT destruction processes observed in the present TEM in situ experiments fall into four categories, as summarized in each section: (3.1) Kimura processes, (3.2) stress-induced SFT collapse, (3.3) apex remnant, and (3.4) no remnants. To date we have observed roughly 30 SFT destructions induced by dislocations for a wide range of SFT sizes (10~>50 nm): most of the results were obtained at room temperature and a few of them at 100 K [35] and 873 K. Process (3.1) was confirmed at all SFT sizes (at least the one for a screw dislocation) at room temperature and 100 K. Process (3.2) occurred for SFTs larger than 34 nm at room temperature and 100 K. Process (3.3) was confirmed at all SFT sizes at room temperature. Process (3.4) occurred only for small SFTs (~10 nm) at room temperature but frequently occurred for larger SFTs (~30 nm) at 873 K.

Judging from the remnant type, process (3.3) would appear to be essentially the same process as found in MD models. Formation of super jog segments was not confirmed in Fig. 9 and Fig. 10. In this situation, MD simulations have indicated that the dislocation should exhibit a double cross-slip. However, such a double cross-slip was not detected in Fig. 9 or Fig. 10. In Fig. 10, although the dislocation appeared to continue to glide on the same plane, this may be regarded as a double cross-slip onto a plane near the original slip plane. In Fig. 9, the dislocation exhibited only a single cross-slip, which is inconsistent with MD results. Process (3.4) may also be regarded as a variant of the MD models if remnant size was small (a few angstroms) invisible to TEM observation. However, this process was also achieved by a single cross-slip. These results indicate that a double cross-slip of the whole dislocation is not necessary: a partial/complete SFT annihilation was achievable by a single cross-slip.


Fig. 10. Same SFT destruction process as Fig. 9. The original SFT size and the remnant apex portion were 11 and 5 nm, respectively. The schematic diagram shown in the lower right is the trace of the gliding dislocation in each frame. After the SFT destruction, the dislocation continued to glide on the same slip plane as before.

In the present in situ deformation study, the velocity of dislocation motion was roughly $10^{-8} \sim 10^{-7}$ m/s [35], which is significantly slower than the dislocation velocity in MD simulations ($10^{1} \sim 10^{3}$ m/s [26,28]). The significant difference in the dislocation velocity is a conceivable factor causing the discrepancy in results. Another conceivable factor is the effect of non-uniform deformation in the TEM specimens. As addressed in detail in the Appendix section, the stress state in the non-uniformly deforming specimens may be multiaxial. Pure uniaxial stress conditions applied in MD simulations would be more favorable for double cross-slip.

To date the Kimura process has never been confirmed in MD simulations, whereas our TEM observation revealed that the Kimura process (for a screw dislocation) can occur for small SFTs within the size range reproducible in MD simulations. The reason for this discrepancy is unclear. The SFT size range where processes (3.1) and (3.3) were observed in the present study overlaps each other: both of them were observed at all SFT sizes (10~50 nm). Therefore, the SFT size is not the crucial factor distinguishing these two processes. As confirmed in the present TEM study, the Kimura process for a screw dislocation was induced when the screw dislocation impinged on the SFT near the base triangle. This is a possible key point to distinguish process (3.1) from (3.3). However, in MD simulations the Kimura process was not reproduced even when the dislocation impinged the SFT at the base triangle [30]. The complexity of the stress state mentioned above is therefore the remaining major factor causing the absence of the Kimura process in MD simulations.



Fig. 11. SFT destruction process leaving behind no remnants and no sessile segments on the dislocation. The SFT size was 11 nm. The schematic diagram shown in the lower right is the trace of the gliding dislocation in each frame. The dislocation cross-slipped upon SFT annihilation.

Conclusions

We confirmed the following four SFT destruction processes by incident dislocations.

(1) *Kimura process* - We observed SFT destruction processes consistent with the Kimura model for both screw and 60-degree dislocations [25]: i.e. the processes that leave multiple super jog segments on the gliding dislocation (for screw) and a triangular Frank loop (for 60-degree). For screw dislocations this was confirmed in a wide SFT size range (10~50 nm). These TEM observations support the validity of the Kimura model. To date the Kimura process has not been reproduced in limited MD simulations, whereas the Kimura process for a screw dislocation was experimentally confirmed for SFTs as small as ~10 nm.

(2) *Stress-induced SFT collapse* - This was the dominant destruction process for large SFTs (>34 nm) when interacting with the leading dislocation in a dislocation queue (dislocation pile-up). Since such large SFTs are meta-stable [5,40], they favor a collapse into a triangular Frank loop via an inverse Silcox and Hirsch or a related mechanism [1] with the aid of high stress at the pile-up front. This collapse process is similar to Kimura's model for a 60-degree dislocation in terms of the remnant type but different in the position (habit plane) where the Frank loop forms.



Fig. 12. Same SFT destruction process as Fig. 11 but observed at 873K. The SFT size was 30 nm. The schematic diagram shown in the lower right is the trace of the gliding dislocation in each frame.

(3) Partial SFT annihilation leaving an apex portion – It appears as though this is essentially the same process as recent MD models. This process was confirmed at all SFT sizes (10~50 nm). Occasionally, sessile segments were formed on the impinging dislocation (super jogs on a screw dislocation). However, the dislocation released those sessile segments through the interaction with other gliding dislocations. The dislocation that released the sessile segments was then mobile.

(4) Complete SFT annihilation without any remnants – This process was observed only for small SFTs (~10 nm) at room temperature; however, at high temperature (~873K) this process was induced for larger SFTs (~30 nm) as well. When this process was induced, the gliding dislocation always cross-slipped, indicating that this process can be induced only by screw dislocations.

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A COMPRESSION ANVIL BEAM TEST METHOD TO MEASURE THE ARREST FRACTURE TOUGHNESS OF SEMI-BRITTLE MATERIALS WITH SMALL SPECIMENS—M. Y. He, G. R. Odette, and M. Hribernik (University of California)

OBJECTIVE

The objective of this work was to develop a compression anvil loaded double-chevron beam test method fracture toughness test method to measure the arrest fracture toughness of cleavage oriented single crystal iron and other semi-brittle materials, based on a comprehensive finite element analysis that was used to select an effective specimen geometry and to quantify the stress intensity factor.

SUMMARY

Our goal was to design a specimen and test procedure that allowed the measurement of cleavage arrest (K_{Ia}) fracture toughness in very small oriented iron single crystals (< 10 mm). This was accomplished by incorporating iron single crystal slices into composite specimens. The test method described here is based on compression loaded, double-anvil beam fracture specimen, illustrated in Fig. 1. Conceptually, slow, uniform compression (σ) loading of a beam with a shallow fatigue starter crack (thick black line) in an double anvil fixture (shown in black) results in Poisson stresses normal to the crack faces, and elastic energy is released as the crack (thin black line) propagates. Composite specimens were fabricated by a sequence of diffusion bonding single crystal slices (light grey) to low alloy steel arms (darker grey), followed by a sequence of electro-discharge machining (EDM), fatiguing and final EDM to the precracked bar configuration shown in Fig. 1. The mode I stress intensity factor (SIF), K_I, is a strong function of the crack depth (a/W). The SIF first increases to a maximum at a small a/W, and subsequently decreases very rapidly approaching 0 as a/W goes to 0.9 or less. The test is carried out by gradually increasing σ to the point where the crack initiates at σ_c and propagates until it arrests at a lower SIF K_I = K_{Ia}, terminating a substantial pop-in jump.



Fig. 1. A schematic perspective view of the compression loaded, double-anvil beam test fixture and specimen.

Implementation of this concept required an extensive finite element (FE) analysis, both to select an effective the specimen geometry, and quantify the SIF, in terms of its relation to the test parameters. In addition to the effects of varying specimen geometry, the FE analysis was used to examine the other factors such as friction effects, bi-material beams, composite beams, debonding and elasticity of the fixture. 4

This so-called compression anvil beam (CAB) test method was evaluated with tests on notched (ρ) TiAl bars. The average initiation toughness $K_{l\rho} = 7.1 \pm 0.7$ MPa \sqrt{m} is consistent with previous measurements of the fracture toughness of TiAl, using fatigue cracked 3-point bend bars, of about $K_{lc} = 8 \pm 1$ MPa \sqrt{m} [10], as well as recent tests using a chevron notched, wedge loaded double cantilever beam (CWB) test method, described in a companion report in this semiannual [11], also yielding an average $K_{lc} = 7.1 \pm 1$ MPa \sqrt{m} . The corresponding K_{la} were 2.8 and 3.7 MPa \sqrt{m} for the CAB and CWB tests, respectively. Note the CAB test method can also be applied to other brittle and semi-brittle materials

PROGRESS AND STATUS

Introduction

A convenient method to initiate a sharp precrack in brittle materials was introduced by Sadahiro [1] and Warren [2] for tungsten carbide and by Nose [3] for ceramics. This method involves initiating and arresting a pop-in crack from a shallow starter flaw, such as a hardness indent, by loading a beam specimen in compression as shown in Fig. 1. The method has been extended to a range of brittle materials [4-7], and incorporated in the ASTM Standard C1421-99 method for introducing pre-cracks in ceramic bend bars prior to fracture toughness testing [8]. Preliminary experiments have shown the effects of such test parameters as indentation load, anvil spacing and surface friction [1-3, 5, 7]. In addition, the stress intensity factor (SIF) as a function of crack length was determined by a finite element (FE) method [3]; however, some potentially invalid assumptions were made in this case regarding friction effects and the fixture-specimen geometry. A later FE analysis considered contact surface friction effects and the differences in the elastic properties of the specimen and fixture materials [5]. The present work builds upon these initial assessments and represents a comprehensive FE determination of the SIF, for the CAB test method. The effects of the anvil spacing, friction between upper and lower contact surfaces, as well as elastic deformation and geometry of the anvil, were examined. The stress intensities of a composite beam (see Fig. 1) made of materials with different elastic constants were also evaluated, as well as for specimens that experienced limited debonding.

The Finite Element Model

An attractive feature of the bridge-indentation specimen is its ability to initiate and arrest a macroscopic cleavage crack over a very short distance. The test requires a shallow flaw at the center of the specimen bottom. The elastic energy release is provided by Poisson strains under compression loading. A shallow (a/W < 0.1) crack first experiences an increasing SIF, $K_l(a/W)$, or energy release rate, J, that peaks at a/W \approx 0.1 - 0.2. The K_l decreases rapidly at higher a/W as the corresponding elastically strained volume of the material decreases. The crack arrests at $K_l(a/W) = K_a$. The $K_l(a/W)$ is given by the standard SIF expression

$$K_1 = Y_a(a,b,D,W,L)\sigma \sqrt{W}$$

Here, $Y_a(a/W)$ is a non-dimensional SIF, $K_1(a/W)/[\sigma\sqrt{W}]$, for a specified specimen and anvil geometry including the crack length (a/W), the anvil span (2b/W) and height (D/W), the beam length (2L/W) where W is the width dimension. The SIF also depends on non-geometric effects, such as friction, represented by a coefficient μ , and the elastic constants of the various test fixture and specimen materials. Thus development of the CAB test method required careful FE evaluation of $Y_a(a/W)$.

(1)

The Mode I SIF was analyzed by the FE method for the geometry shown in Fig. 2. The calculations were conducted using the general-purpose finite element code, ABAQUS. Only a half specimen was modeled (ABCD), due to symmetry considerations. One boundary condition involved applying a uniform vertical displacement, u_y , at the top surface (DC) of the specimen, which was allowed to slide on the anvil with the friction coefficient, μ . The boundary at the top of the specimen was modeled for limiting friction free and no slip conditions. The specimen was modeled using a 40x50 rectangular mesh comprised of 2000 uniformly sized eight node isoparametric elements and 6506 nodes as shown in Fig. 2. The results for rigid anvil elements were compared to FE calculations for an elastic anvil, modeled using a uniformly sized 20x20 rectangular mesh. The whole mesh is comprised of 2400 eight node isoparametric elements 15

o ntaining 7462 nodes. The applied stress was found by averaging the compression/reaction force per unit area on the specimen top contact surface. A careful convergence study showed these meshes were sufficiently accurate to calculate the SIF. The energy release rate, J, was calculated by the domain integral method, for three to ten contours. The SIF is related to J as

$$K_{I} = \sqrt{[JE/(1 - v^{2})]}$$

Here E is the elastic modulus and v is Poisson's ratio.





(2)

Fig. 2. A cross-section schematic view of specimen and load fixture, illustrating the key dimensions and the FE mesh.

The FE calculations for a particular specimen geometry and set of assumptions (like μ), represented by the normalized SIF curve, $Y_a(a/W) = K_l/\sigma \sqrt{W}$, are used to evaluate K_{la} . For example, assuming an arrest $a_a/W = 0.74$, $Y_a(0.74) = 0.06$, b/W = 0.5, B/W = 0.5, L/W = 1.15, D/W = 0.5, W = 7.7 mm and pop-in load, P = 30,870 N, gives $\sigma_c = 452$ MPa and $K_{la} = 2.4$ MPa \sqrt{m} .

Results

Monolithic Specimen

The normalized SIF $[Y_a(a/W) = K_l/(\sigma W^{1/2})]$ for L/W = 1 and D/W = 0.5, as a function of crack length, a/W, for rigid anvils spaced by b/W = 0.25, 0.5 and 1.0, assuming friction free contacts the specimen with both the lower anvils and upper pusher plate, $\mu = 0$, are shown in Fig. 3. The SIF reaches a maximum at a/W ≈ 0.1 to 0.2, depending on b/W, and then decreases to zero as a/W approaches 0.9. These results show that an anvil spacing of b/W = 0.5 provides the largest SIF range in the crack initiation-arrest region, between a/W of about 0.15 to 0.8. Except as otherwise noted, the FE computations described below will be for L/W = 1, D/W = 0.5, b/W = 0.5, rigid anvils and $\mu = 0$.



Fig. 3. The normalized SIF, $Y_a(a/W) = K/(\sigma\sqrt{W})$, as a function of the crack length a/W for L/W = 1, b/W = 0.25, 0.5, and 1.0, and μ =0.

The effect of friction between the specimen and anvil is shown in Fig. 4. Increasing μ from 0 and 0.3 significantly reduces the SIF and shifts both the peak and post peak SIF curves to lower a/W. For example, the maximum SIF for μ = 0.3 is approximately one half of that for the μ = 0 case, and K_I approaches 0 at a/W = 0.4, versus 0.9 for the friction fee conditions. These results assume the top surface is friction free. Figure 5 shows the liming cases of friction free versus no slip conditions, when the specimen is not allowed to displace along its top surface, while μ = 0 for the specimen-anvil contact surface. The difference between these two limiting cases becomes increasingly significant for larger crack lengths at a/W > 0.3. Clearly it is important to minimize friction with the use of effective lubricants.



Fig. 4. The effects of the friction coefficient, μ , between the specimen and anvil.

The normal (σ_{22}) stress distributions, divided by the average applied stress (σ) along the top surface of the specimen are shown in Fig. 6 for various crack lengths, μ and b/W. The σ_{22} compressive stresses are not uniform, and increase from a minimum at the center (x/L = 0) to a maximum at the edge (x/L = 1). The uniformity of σ_{22} increases with decreasing a/W and b/W and increasing μ .



Fig. 5. The effects of the friction along the top contact surface for b/W = 0.5.



Fig. 6. The normal stress distributions along the top surface of the specimen for (a) L/W = 1, b/W=0.5 and μ =0, and various a/W. (b). The corresponding normal stress distributions are shown for a/W = 0.1 at b/W = 0.25, 0.5, and 1.0 and μ =0.1.

Figure 7 shows the effect of anvil stiffness on the SIF for two anvil heights, D/W= 0.5 and 3. The modulus for the anvil is taken as 200 GPa, the same as assumed for the modulus of steel, and μ = 0. These results show that the effects of anvil elastic deformation are significant, even though the geometry of the anvil itself (D/W) does not have a large effect. The assumption of a rigid support decreases the maximum SIF by about 30% compared to that for the elastic support.

Bi-material Specimen

A bi-material specimen shown in Fig. 8 consists of bonded beams of brittle and ductile materials. The motivation for this specimen lies in the possibility of initiating a crack in the brittle material, such as a ceramic, and arresting the crack in a more ductile material, such as a single crystal iron. This case was analyzed with a modulus mismatch of $E_1/E_2 = 2$, for crack initiation in the more rigid, brittle material ($E_1 = 340$ GPa). The normalized SIF is shown in Fig. 9 as a function of a/W for $\mu = 0$, and brittle to ductile layer thickness ratios of 1/1 (Fig. 9a) and 1/9 (Fig. 9b). The curve for a monolithic specimen (E = 170 GPa) is show for comparison. The stress intensity of the crack in the brittle material is about 40 % higher than that for the monolithic specimen, roughly scaling with the square root of the local modulus for the layer that the crack lies in (E_L), indicating that the total energy release rate is independent of the local E_L but scales

roughly with the rule of mixtures composite modulus $[E_c = (W_1E_1 + W_2E_2)/(W_1 + W_2)]$. Note, this evaluation did not consider the behavior of the crack at or in the interface itself, or effects such as residual stresses due to CTE mismatches or interface debonding.



Fig. 7. The effects of anvil stiffness on stress intensity for D/W = 0.5 and 3.



Fig. 8. Schematic of the bi-material specimen.



Fig. 9. The normalized SIF [K/($\sigma\sqrt{W}$)] for the bi-material specimen with b/W = 0.5, μ = 0, and two interfacial positions (a) W₁/W = 0.5 and (b) W₁/W = 0.1.

Composite Beam Specimen

The composite beam specimen, shown in Fig. 10 is representative of a single crystal iron (E = 130 GPa, for the <100> directions along the beam axis) layer bonded between two polycrystalline steel sections (E = 200 GPa). The motivation for this specimen configuration lies in the high cost and relatively small size of single crystal iron. The crack is intended to initiate and arrest entirely within the thin single crystal center section. The composite beam normalized SIF [K/(σ W^{1/2})] is shown in Fig. 11 as a function of a/W. Figure 11a shows the SIF for b/W = 0.5, a center section thickness h/W = 0.1, and μ = 0 in. The results for monolithic specimen with the same geometry are also included in Fig. 11a for comparison. Incorporating the single crystal section lowers the SIF approximately 24% compared to the Monolithic specimen. However, this is almost entirely due to the local E_L used to convert J to K_I, where E_L = 130 GPa for the iron single crystal and 200 GPa for the polycrystalline steel. Thus the overall J is not sensitive to the local modulus. In contrast, Fig. 11a shows that both the J and the SIF decrease with increasing L/W. A stout L/W = 1 provides the most effective CAB specimen geometry. Figure 11b shows a minor SIF decrease with increases in h/W from 0.1 to 0.2. Again, this is due to the effect of a higher rule of mixtures composite modulus, E_c, associated with the larger h/W that results in a decrease in J.



Fig. 10. Schematic of the composite beam specimen.



Fig. 11. The normalized stress intensity factor, K/($\sigma\sqrt{W}$), for the sandwich specimen, (a) for a specimen with b/W = 0.5, h/W = 0.1, and L/W = 1-2.25, (b) effects of the center section thickness, h/w = 0.1-0.2.

The composite steel-iron single crystal specimens have been observed to undergo limited interface debonding in some cases. This initially occurs during fatigue precracking and may be followed by additional interface crack growth to a depth, a_2 , during compression anvil loading. The effects of the debonding on K₁ for the main crack are shown in Fig. 12. Figure 12a shows that the interface cracks on both sides of length a_2 /W result in shifts in the initial portion of the Y_a(a/W) SIF curves to higher a/W but has little effect beyond the peak. The peak SIF position increases roughly as $a_2/W + 0.1$. Thus these results show that if a_2 is significantly less than the arrested crack length a_a , the effects of interfacial cracks are negligible. Figure 12b shows the effect of a_2/W on the non-dimensional energy release rate (JE/ σ^2 W) for both the main crack at a/W = 0.7, and the interface crack itself. The energy release rate of the main crack is independent of a_2/W at a typical arrest depth, while the corresponding energy release rate for the interface crack is much lower and decreases with a_2/W . These result suggests that, if formed, interface debonding cracks will arrest at much shallower depths that the main crack, and thus will have little influence on the measured value of K_{la}.



Fig. 12. (a) Effects of the interfacial crack length (a_2) on the stress intensity factor of the main crack. (b) Stress intensity of the main crack at a/W = 0.7 and the interface cracks versus a_2/W .

The FE results in this section can be summarized as follows.

- An effective geometry for shallow precracked CAB specimens is L/W = 1, b/W = 0.5.
- The SIF are not sensitive to h/W, D/W and limited interface debonding.

- The SIF are sensitive to friction effects, especially between the CAB specimen and anvil. Higher μ decreases the K_I. Uncertainties about friction effects contribute the largest uncertainty to SIF and to the corresponding evaluations of K_{Ia}.
- The SIF are sensitive the elasticity of the anvils, so this effect, which also reduces the K_i, must be properly accounted for.
- The SIF depend on the elastic modulus, and the effects of moduli in bimaterial and composite beam specimens affect K_I. Fortunately, the SIF roughly scales with $\sqrt{(E_I/E_c)}$, where E_I is the local elastic modulus and E_c is the rule of mixtures composite modulus.

Evaluation and Implementation of the CAB Test Method

The FE determination of the SIF was evaluated by static tests on 14 monolithic γ -TiAl specimens at room temperature [9]. The K_{lc} and K_{la} tests were performed on electro-discharge machined (EDM) TiAl bars with dimensions of 4 x 8 x 18 mm, on an compression anvil fixture with L/W = 1, b/W = 0.5 and D/W = 0.5. A shallow half round notch ≈ 0.1 mm (a_i/W ≈ 0.05) in depth was EDM at the center of the bottom of the specimen to act as the crack initiating flaw, eliminating the potential effects of indentation load. However, the notch is not a sharp crack, so the initiation toughness is actually K_{lo} . Thus there could be an effect of the notch root radius of $\rho \approx 50 \ \mu m$ on the measured toughness. Nevertheless, K_{l_0} may be approximately equal K_{lc} for the semi-brittle TiAl intermetallic alloy. The upper pusher plate was a polished Si₃N₄ plate and the anvils were hardened tool steel. Lubrication of the contact surfaces between both the top pusher plate and the specimen and the bottom anvils and the specimen was provided by graphite powder. The specimens were loaded at a rate of 0.42 µm/s on a servo-hydraulic MTS load frame until a pop-in was detected by both an acoustic emission sensor and a crack gauge glued on the specimen. Due to the low compliance of the rigid, compressively stressed system, a load drop does not occur at crack initiation at the critical applied compressive fracture stress, σ_c . The final arrest a_a/W was measured after the specimen was broken under four-point bending. The a_a/W , $a_i/W = 0.05$ and σ_c were used to determine the K_{lo} and K_{la} based on the SIF [Y_a(a/W) = K_l/($\sigma \sqrt{W}$)], derived from the FE analysis, the compression anvil dimensions cited above, assuming elastic anvils, frictionless contact surfaces with $\mu = 0$, and a TiAl modulus E =170 GPa.

The measured K_{Ir} and K_{Ia} results shown in Fig. 13 give an average K_{Ip} = 7.1 ± 0.7 MPa \sqrt{m} and K_{Ia} = 2.8 ± 1.4 MPa \sqrt{m} . The initiation K_{Ip} value is reasonable agreement with the initiation toughness for static tests on fatigue precracked TiAl three point bend specimens of K_{Ic} ≈ 8 ± 1 MPa \sqrt{m} [10]. This average is also consistent with the average K_{Ic} = MPa \sqrt{m} for the CAB specimens containing the sharp pop-in precracks tested under 4-point bending at dynamic loading rates of about 1000 MPa \sqrt{m} /s [9]. Finally, the K_{Ip} is also identical to the average measured K_{Ic} = 7.1 ± 1 MPa \sqrt{m} for TiAl chevron notched wedge loaded, double cantilever beam (CWB) specimens. The corresponding K_{Ia} for the CWB tests on TiAl was 3.7 ± 0.4 MPa \sqrt{m} .



Fig. 13. Initiation and arrest toughness values at room temperature for TiAl evaluated through the finite element analysis of the single-edge notched-beam specimen.

Summary Discussion and Concluding Remarks

A compression loaded, double-anvil beam (CAB) test method has been developed to measure the crack arrest fracture toughness (K_{la}) of cleavage oriented single crystal Fe and other semi-brittle materials using very small composite specimens that can be fabricated using minimal amounts of critical materials. This report focuses on finite element (FE) calculations that were used to select a specimen geometry that is appropriate, and to quantify the stress intensity factor (SIF) for the CAB specimen. An effective geometry to facilitate initiation and arrest events was found to be a total beam length on the anvils, 2L/W = 2, and an anvil span, 2b/W = 1. The SIF for the CAB specimen geometry first increases, and then decreases rapidly, with increasing a/W between 0 to 1. Thus crack initiation and arrest are manifested as a significant pop-in event. The FE solutions for normalized provide the SIF, [Y_a(a/W) = KI/ σ √W], to evaluate K_{la} based on the specimen-fixture geometry, the critical stress at crack initiation (σ_c) and the crack depth at initiation (a_i /W) and arrest (a_a /W).

Implementation of the CAB test method was carried out using a double anvil fixture loaded on a MTS servohydraulic test frame. The test was instrumented with a crack gauge and acoustic emission sensor to detect crack initiation and σ_c . Evaluation of the CAB method was carried out by tests on TiAl specimens,

Caution must be used in using the CAB test to measure initiation toughness (K_{lc}) for specimens with sharp cracks. While, as noted previously, the CAB technique appears to work well for the initiation of a crack from a shallow starter notch in the TiAl tests at room temperature, other issues are encountered in CAB tests of composite specimens containing iron single crystals. In this case, a shallow fatigue crack is grown to provide a favorable initiation site. However, the fatigue cracks tend to be slanted in their preferred growth direction, and the cyclic loading generates dislocation structures in very soft single crystal iron that might affect the magnitude of K_{lc} . For example, static CAB tests at -196°C give an average $K_{lc} = 12.5 \pm 2.7$ MPa \sqrt{m} . This compares well with a corresponding values of 11.4 ± 3.8 measured by CWB tests, but is much higher than the 5.8 ± 0.6 MPa \sqrt{m} measured in static sharp pop-in crack 4-point bend tests. Indeed, the difficulty of initiating propagation from fatigue cracks represents a major limitation of the CAB test method, at least to measure K_{la} in single crystal Fe. The high effective values of K_{lc} for the composite single crystal Fe specimens resulted in an effective upper temperature limit for the CAB tests of about -100°C. At higher temperature the σ_c increased to the point where it resulted in deformation of the low alloy steel arms of the composite beams.

The largest uncertainty in the K_{la} measurements is the effects of friction. While the experimental procedure involved the use of graphite powder as a lubricant between the specimen and anvil and pusher surfaces, the neglect of possible friction effects may result in an overestimate of K_{la} in the CAB tests. There is not an independent calibration material for measuring K_{la} with the CAB test. However, it is notable that the K_{la} in single crystal Fe measured with the CWB and CAB tests were very consistent with one another [11]. For example at -196°C the K_{la} was 3.34 ± 1.15 and 3.54 ± 0.6 MPa√m for the CAB and CWB tests, respectively.

In summary, CAB tests on polycrystalline TiAl and single crystal Fe were successfully carried out using very small specimens with length, with and thickness dimensions of about 16x8x4 mm. Thus the CAB test method, including the use of composite specimens, offers a powerful new tool to measure the fracture toughness of brittle and semi-brittle materials, especially when specimen sizes and or the availability of materials are an issue.

Future Work

The CAB and CWB test methods have been used to very successfully characterize the K_{la} in cleavage oriented iron single crystals, between -196 and 0°C [5]. The resulting database is unique and has, for the first time, has clarified the fundamental dynamics and controlling mechanisms of cleavage fracture. This database has also been used to develop a preliminary, but powerful, new semiempirical multiscale model of the macroscopic $K_{lc}(T)$ curve for complex structural steels. Notably, this model predicts an approximately invariant shape of the master toughness-temperature curve for complex steels, as well as the reference temperature shifts in the master curve due to irradiation hardening, that are in agreement with observation. Further analysis of the database and development of the model as well as full documentation of these results, including preparation of manuscripts for journal publication, will be completed during this current reporting period.

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A CHEVRON NOTCHED WEDGE LOADED DOUBLE CANTILEVER BEAM TEST METHOD TO MEASURE THE INITIATION AND ARREST FRACTURE TOUGHNESS OF SEMIBRITTLE MATERIALS WITH SMALL SPECIMENS—G. R. Odette, M. Y. He, and M. L. Hribernik (University of California, Santa Barbara)

OBJECTIVE

The objective of this work was to develop a chevron-notched, wedge-loaded, double-cantilever beam fracture toughness test method, based on a comprehensive finite element analysis that was used to select an effective specimen geometry and to quantify the stress intensity factor. This new test method was used to measure the initiation and arrest toughness of both TiAl at ambient temperature and cleavage oriented single crystal Fe over a wide range of temperatures.

SUMMARY

Our goal was to design a specimen and test procedure that allowed the initiation and arrest of a crack in very small cleavage oriented iron single crystals (< 10 mm). This was accomplished by incorporating iron single crystal slices into composite specimens. The test method described here is based on a chevron-notched, wedge-loaded, double-cantilever beam specimen. Conceptually, slow insertion of the wedge, to load the beam arms, gradually increases the crack mouth opening displacement (Δ), and the corresponding stress intensity factor (SIF), K_I, up to K_{Ic}, thus initiating a propagating cleavage crack. However, due to the combination the wedge loading a double-cantilevered beam and chevron geometry, the K_I decreases very rapidly with increasing depth (a/W), and the crack arrests at a SIF K_I = K_{Ia}, after a short pop-in jump. Thus the crack can be grown in a series of short, and relatively stable, jumps. The initiation and arrest-re-initiation depths can be seen on the fracture surface.

Implementation of this concept required an extensive finite element (FE) analysis, both to select an effective specimen geometry and to quantify the stress intensity factor in terms of its relation to the measured test parameters. In addition to the effects of varying specimen geometry, the FE analysis was used to examine the effects such plastic deformation and slanting of the crack front. Both monolithic and composite 'sandwich' type specimens were modeled, where the effects of the modulus difference between the oriented single crystal Fe and the polycrystalline steel was investigated in the latter case. The K_I was also found to vary along the crack front, with a broad minimum in the center and local maxima at the side-corners of the of chevron wedge. This socalled 'chevron-wedge-beam' (CWB) test method was evaluated with tests on TiAI, that showed a consistent K_{Ic} and K_{Ia} are obtained by assuming that initiation occurs at the chevron corners and arrest near the center of the crack front. The average K_{Ic} $\approx 7.1\pm1$ MPa \sqrt{m} measured with the CWB test method is consistent with the previous measurements of the toughness of fatigue precracked TiAI bend bars with K_{Ic} $\approx 8\pm1$ MPa \sqrt{m} and the results of notched double anvil compression specimen tests with K_{Ip} $\approx 7.1\pm0.7$ MPa \sqrt{m} . Note the CWB test method can also be applied to other brittle and semi-brittle materials.

PROGRESS AND STATUS

Introduction

The new test method described here was specifically developed to provide a way to measure the initiation and arrest toughness, K_{lc} and K_{la} , of small cleavage oriented iron single crystals. Cylindrical rods of unalloyed iron single crystals, slightly less than 1 cm in diameter and 5-6 cm in length, were cut to within 15° of the specified axial orientation. Oriented crystal sections were EDM sectioned and trimmed to ≈ 2 mm thick rectangular slices that were then diffusion bonded to low alloy steel arms that acted to transmit loads and release elastic strain energy. The CWB test method resembles the procedure in ASTM Standard E 1304-97 [1]. However, the CWB test method developed in this study differs from the one in the Standard in three major ways. First, the CWB specimen is much smaller than the E 1304-97 configuration, due to the limited sizes and

amounts of available oriented Fe single crystals. Second, the CWB test method loading is carried out under crack mouth opening displacement (Δ) control, leading to much higher crack growth stability, compared to the grip loading method used in the ASTM Standard. Third, at least in the case of the Fe single crystal measurements, the CWB tests involve composite specimens. Thus an extensive set of FE calculations was required to select the CWB specimen geometry and to quantify the stress intensity factor as a function of the specimen size, Δ , the elastic modulus (E), and the crack lengths at initiation (a_i) and arrest (a_a).

The Finite Element Model

The first set of calculations was carried out for a monolithic CWB specimen under fully elastic loading conditions, as characterized by the elastic modulus (E). The chevron-notched wedge specimen geometry is specified by the dimensions in the sketch of the specimen shown in Fig. 1a. These dimensions include the specimen thickness (B), width (W), the beam height (2h), the depth of the initial chevron point (a_0) relative to the loading line, the crack depths, a_i for initiation, and a_a arrest. The Mode I SIF, K_I, can be specified by the Δ , or the load (P), using the following standard relations:

$$K_I = Y_d E \Delta / \sqrt{B} \tag{1}$$

and

$$K_I = Y_P P / (B\sqrt{a}) \tag{2}$$

The non-dimensional Y_d and Y_p factors are functions of the overall CWB specimen geometry that was selected based on the FE analysis. The Y_d and Y_p represent non-dimensional forms of the SIF that are quantified in this report.

The commercial finite element code ABAQUS/standard was used for the analysis. Twenty-node quadratic isoparametric brick elements were employed to model one quarter of the specimen. A quarter-point crack tip element served to model the inverse square root stress singularity at the crack front. A typical finite element mesh, which contains 4350 elements and 24024 nodes, is shown in Fig. 1b. A half-specimen mesh was also used to evaluate the effects of variations in the crack depth along the crack front.



Fig. 1. a) The CWB specimen showing the key dimensions (not to scale). b) The quarter section the mesh used in the FE model.

The values of J along the crack front were calculated by the domain integral method. Five contours were used, and the scatter of J for the various contours was less than 1% due to the finely focused crack front mesh. The SIF were obtained from J as

$$K_I = \sqrt{\left(\frac{EJ}{\left(1 - \nu^2\right)}\right)} \tag{3}$$

The 3D finite element analysis gave accurate results for SIF, even for the relatively coarse five layer mesh [2]. Based on a careful convergence study, meshes of 9, 14, 30, and 50 layers were used. The 9 layer model was sufficiently accurate to calculate the average SIF. The 30 and 50 layer meshes were used to calculate the SIF at the corner and for the slanted crack front, where higher accuracy was necessary.

The elastic calculations were complemented by elastic plastic modeling of the monolithic specimen using constitutive laws in the form:

$$\frac{\varepsilon_e}{\varepsilon_v} = \left(\frac{\sigma_e}{\sigma_v}\right)^n \quad \text{for } \sigma_e > \sigma_y \tag{4}$$

Where σ_e is effective stress defined by the stress deviator S_{ij} as:

$$\sigma_e = (\frac{3}{2} S_{ij} S_{ij})^{1/2} \tag{5}$$

 \mathcal{E}_{e} is the effective strain defined as:

$$\varepsilon_e = \left(\frac{2}{3}\varepsilon_{ij}\varepsilon_{ij}\right)^{1/2} \tag{6}$$

The results reported here are for a yield stress, $\sigma_y = 500$ MPa, and a Ramberg-Osgood power law hardening exponent of n = 10.

Elastic FE calculations were also carried out for a composite sandwich specimen containing a single crystal chevron shaped slice with modulus E_c that differs from E for the CWB arms. In this case the thickness (t) of the single crystal also slightly influences the SIF.

Finite Element Results

Monolithic Specimens

A main purpose of the FE analysis was to determine the SIF values as a function of crack depth, a/W. Several specimen geometries were selected as candidates for the calculations and specimen design. The two W/B were 1.45 and 2.0, consistent with the recommendations of ASTM E 1304. For W/B = 1.45, FE calculations were carried out for three a_0/W of 0, 0.18, 0.3. For W/B = 2, FE calculations were carried out only for $a_0/W = 0$. The total beam height, including the Fe crystal slice, was fixed a B/2. The SIFs at the mid-plane of the crack front are shown in Fig. 2. Under load control (Fig. 2a), the critical crack length occurs at the CWB specimen's SIF minimum. However, the minimum occurs at a/W = 0 for $a_0/W = 0$, and increases continuously at larger crack depths, as illustrated in Fig. 2a. Increasing a_0/W ultimately results in a very shallow minimum, as shown in Fig. 2a to occur at $a_0/W = 0.3$. However, none of these geometries have a SIF versus a/W curve that would result in crack arrest under load control.

In contrast, under displacement controlled wedge crack mouth opening loading, the CWB specimen SIF rapidly decreases with the increasing a/W, as shown in Fig. 2b. The larger W/B =

2 produces a more rapid decreases, compared to the W/B = 1.45 case. It is also clear that $a_o/W = 0$ is desirable, since this geometry gives larger distances and a wider range of decreasing SIFs for crack initiation and arrest pop-in events. Thus W/B = 2 and $a_o/W = 0$ were selected for further modeling.



Fig. 2. a) The SIF (Y_p and Y_d) as a functions of crack length a/W, for various specimen geometries, normalized by P. b) The SIF (Y_p and Y_d) as a functions of crack length a/W, for various specimen geometries, normalized by Δ .

Three-dimensional effects along the chevron crack front as a function of x/B_a are very important. Here x is the distance from the center plane (x = 0) of the crack front in the thickness direction and B_a is the total crack front length at a crack depth of a. For, $a > a_o$ the crack front has two corners, where it intersects the edges of the chevron wedge at x/B_a = ± 0.5. The corners lead to secondary stress concentrations and higher SIFs than at the crack front center at x = 0. The SIF distributions along the crack front are shown in Fig. 3a for a/W = 0.5 in terms of the K₁(x/B_a)/K₁(0) ratio. The K₁(x/B_a)/K₁(0) ratio is nearly constant for x/B_a < 0.35, but rapidly increases as x/B_a approaches 0.5. The K₁(x/B_a)/K₁(0) ratio depends on a/W. Figure 3b shows the SIF as a function of a/W for both x/B_a = 0 and \approx 0.5. The K₁(a/W) for x/B_a \approx 0.5 is about 30% higher than for x/B_a \approx 0. Note, the K values at x/B_a \approx 0.5, obtained from the domain integrals, are only estimates. A detailed discussion of the corner singularity effects can be found elsewhere [3].



Fig. 3. a) The SIF distribution along the crack front for a/W = 0.5. b) The SIF functions for the crack center and edge.

Since crack initiation requires high stresses over a finite material dimension, the K_I values near $x/B_a \approx 0.5$ are believed to provide the best estimates of the effective SIF for crack initiation, K_{Ic}. Likewise, the lower SIF at $x/B_a = 0$ provides the best K_I estimate of the arrest K_{Ia}. These trends have been observed experimentally in the CWB tests on Fe single crystals, and are discussed further in the section on the calibration of the CWB test method.

The Effects of Slanted Crack Fronts

Figure 4 illustrates the effects of a slanted crack front, as characterized by a slant angle $\alpha > 0$ (see the insert in Fig. 4a), by plotting the SIF for x/B_a between \pm 0.5 at a/W = 0.5. Figure 4a shows the SIF decreases continuously from a maximum at the acute angle of intersection of the crack front with the edge of the chevron with the shallowest depth, at $x/B_a = -0.5$, to a minimum at the corresponding obtuse angle with the largest depth, at $x/B_a = +0.5$. The effect of a slanted crack front increases with α , but only slightly between 10 and 14°. Figure 4b shows that the maximum to minimum SIF ratio, $K_{I}(-0.5)/K_{I}(0.5)$, increases with a/W. However, the K_{I} at the x = 0 crack front midplane, $K_1(0)$ is independent of α . The maximum $K_1(-0.5)$ is also relatively insensitive crack slanting, increasing by only about 7% for α from 10 to 14°, compared to a unslanted, $\alpha = 0$, crack front. Thus the initiation toughness can be approximately evaluated from the unslanted (α = 0) crack curve shown in Fig. 3b. The minimum $K_1(0.5)$ is about 80 to 90% of the SIF for the unslanted crack at $x/B_a = 0$. Thus, the arrest toughness K_{Ia} could be somewhat overestimated using the $x/B_a = 0$ curve in Fig. 3b. However crack slanting has little effect around $x/B_a = 0$ and the minimum SIF at x/B_a = 0.5 only bounds K_{la}. The fact that the arrest must occur over a significant length of the crack front provides an averaging effect that would mitigate any local minimum SIF effects of moderately slanted cracks on K_{ia} . Thus it is also reasonable to use the lower $x/B_a = 0.0$ curve in Fig. 3b to assess K_{la}.



Fig. 4. Effects of slanting of the crack front on the SIF: a) For a/W = 0.5, and α = 0, 10[°] and 14[°]. b) The ratio of SIF of short intersection to the long intersection for α = 10.

The Effects of Plastic Deformation

Plastic deformation generally reduces the <u>elastic</u> crack tip energy release rate and the corresponding elastic SIF at a specified loading, as represented by Δ /B for the CWB test. Figure 5 plots the normalized SIF as a function of Δ /B for the constitutive law described previously, assuming a yield stress of $\sigma_y = 500$ MPa and a Ramberg-Osgood strain hardening exponent of n = 10. The curves are for a/W = 0.2 and 0.5 at various x/B_a points along the crack front. For fully elastic loading, the SIF is proportional to Δ , hence, K/ Δ , is approximately independent of Δ . Figure 4a shows plasticity results in a small initial peak in the SIF for Δ /B between about 0 to 0.006, followed by significant decreases at higher loading. For example for x/B_a = 0, the SIF decreases by more than a factor of 2 between Δ /B = 0.01 and 0.05, roughly scaling as $\sqrt{(B/\Delta)}$. The small peak in the SIF slightly increases with larger x, but the variations with Δ /B are otherwise similar.

The effect of plasticity is much smaller for the deeper crack at a/W = 0.5. In this case, the small peak is shifted to larger Δ/B and plasticity induced reductions of SIF begin at about $\Delta/B > 0.02$, with a decrease between $\Delta/B = 0.01$ and 0.05 of about 25% at $x/B_a = 0$. In summary, effect plasticity depends on a/W, and is modest below about $0.01\Delta/B$ for a/W = 0.2 and $0.025\Delta/B$ for a/W = 0.5.



Fig. 5. Effects of the plastic deformation for a) a/W = 0.2 and b) a/W = 0.5.

Figure 6 plots the elastic plastic loading as a function of Δ /B in terms of the normalized crack tip opening displacement, δ /B, where δ is defined as the distance between the crack faces at the intercept of two symmetric 45° lines from the blunted crack tip. For small scale yielding (SSY) conditions δ is approximately linearly proportional to Δ , after the initial blunting transient, as observed for the a/W = 0.5 case. The curves for the shallower crack with a/W = 0.3 show a slight negative curvature that may indicate some deviations from SSY. Figure 7 shows the relation between δ , σ_y and J, expressed in terms of the standard coefficient, $d_n = \sigma_y \delta/J$; note, the subscript n indicates that d_n depends on the strain hardening behavior of the material. The d_n decreases rapidly with increasing Δ /B during the initial blunting transient and plateaus at a value of $d_n \approx 0.54$ for a/W ≈ 0.3 to 0.6, in good agreement with the previous results obtained by O'Dowd and Shih [4]. The d_n for the shallower a/W = 0.2 crack falls systematically lower by an increment of about 0.05.



Fig. 6. The normalized d/B as a functions of Δ /B for a) a/W = 0.2 and b) a/W = 0.5.



Fig. 7. The $d_n = \delta \sigma_v / J$ coefficient as a function of Δ / B for various a/W.

These results suggest that elastic plastic fracture mechanics can be used to analyze CWB test data, at least slightly beyond the elastic limit. Note, however, we have not carried out a detailed assessment of the crack tip fields for this geometry, including as they are influenced by the combination of plasticity and other potentially significant effects such as T-fields and variations along the crack front. There are likely differences between these fields and classical SSY fields that could be significant in interpreting the K_{lc} and K_{la} measurements from the CWB test, especially as they might relate to more conventional SSY test geometries. It should also be noted that there is local plasticity (plastic zone formation) even when the overall cracked specimen is in the globally elastic loading regime, where the loading can be fully characterized by K_{l} . Further, in the case of semi-brittle cleavage fracture of single crystal iron, the local plasticity is associated with discrete dislocation slip traces, rather than quasi-homogeneous-continuum plastic zones.

Sandwich CWB Specimens

The high cost of iron single crystal and relatively small size of the oriented single crystal slices requires that they be incorporated in a composite specimen as shown in Fig. 1. The initial scoping studies confirmed that the basic geometry CWB of W/B = 2, h/B = 0.5 and a_o/W = 0 provides a large range of K₁ over a/W distances sufficient for pop-in arrest events. The CWB specimens were fabricated by diffusion bonding an oriented single crystal slice to two adjoining low alloy steel arms to form a rectangular three-layer sandwich with a square cross section. This sandwich was then (electro-discharge machined) EDM in from the sides to form the chevron shaped iron single crystal wedge. A shallow 30° notch was also EDM in the arms at the tip of the chevron to provide mating surfaces for the wedge that produce uniform loading along the crack front. The effective loading point for the wedge induced displacements was taken at the $a_0/W = 0$ location in the FE calculations. A shallow \approx 150 µm round notch was EDM into pointed end of the chevron to promote the first crack initiation event and to avoid interference between the single crystal and wedge. The first pop-in event was used to condition the CWB specimen with a sharp pre-crack at a/W > 0. A 1 mm half round notch was EDM on the back of the specimen to mate with a pin on the test fixture to provided precise specimen alignment, and unrestricted rotation of the beam arms. Knife edges were also EDM on the chevron tip end of the specimen for mounting a clip gauge to continuously measure Δ . Evaluation of the stresses in the plastic zone showed that the single crystal thickness of t = 1 mm was sufficient to avoid high interface stresses that might lead to debonding of the iron crystal from the beam arms. The overall dimensions of the CWB specimens were about 8mm wide by 4mm thick by 4 mm high.

The FE analysis was extended to treat the modulus difference of single crystal Fe section, taken as 130 GPa for the [100] direction, and the low alloy steel arms, taken as 200 GPa. The normalized SIF at the mid-plane as a function of crack length is given in Fig. 5a. The result for the monolithic material is also included for comparison, showing a difference approximately 5-10 % between the two cases. This is consistent with the relatively small difference between the volume weighted average modulus of the composite CWB specimen and that for the low alloy steel.

CWB Test Procedure and Evaluation

Evaluation of the CWB tests was performed on monolithic TiAl, first using a small table-top fixture, where the wedge was driven by a high resolution micrometer head. Previous tests on fatigue precracked specimens on this same material measured an average $K_{lc} \approx 8 \pm 1$ MPa \sqrt{m} [6]. A total of 30 CWB benchtop tests on TiAl gave an average $K_{lc} = 7.2 \pm 1.3$ MPa \sqrt{m} , and an average $K_{la} = 3.7 \pm 0.5$ MPa \sqrt{m} [5]. The results are shown in Fig. 8. Figure 8a shows the evaluation for based K_{l} averaged along the crack front for the sandwich specimen. The K_{lc} appear to depend on a/W in this case, while the K_{la} do not. Figure 8b shows the corresponding TiAl toughness evaluation, assuming initiation occurs at the $K_l = K_{lc}$ at $x/B_a = \pm 0.5$ (the edge), while arrest occurs at $K_l = K_{lc}$ at $x/B_a = 0$ (near the center). Using the latter assumption, both K_{lc} and K_{la} are independent of a/W.



Fig. 8. a) Normalized SIF $x/B_a = 0$ as a function of crack length a/W for the monolithic and sandwich specimens.

However, the micrometer wedge fixture was intended only for the initial scoping studies and was far too compliant for actual single crystal testing and was limited to a maximum load of about 400 N. Thus a robust, low compliance crack mouth opening displacement fixture was designed and built for use with a MTS servohydraulic actuator to drive the wedge at a specified rate, typically about 1 µm/s, corresponding to a stress intensity loading rate of about 0.25±0.15 MPa√m/s. The Δ was measured by a clip gage mounted on knife-edges on the outside of the beams. The wedge was stopped immediately after the rapid load drop that accompanied crack initiation and arrest. Crack initiation was also monitored with an acoustic emission detector. The initiation (a_i) and arrest (a_a) depths were easily observed on the fracture surfaces.

The loading fixture and instrumentation described above provided reliable and repeatable results. The TiAl data from a final test procedure calibration are shown in Figs. 9 and 10. Twelve tests gave an average of $K_1 = 6.9 \pm 0.7$ MPa \sqrt{m} and $K_{1a} = 3.7 \pm 0.5$ MPa \sqrt{m} [5]. The overall average of $K_{1c} \approx 7.1 \pm 1$ MPa \sqrt{m} for all 42 TiAl tests is reasonably consistent with previous measurements with fatigue pre-cracked bend bars of 8 ± 1 MPa \sqrt{m} and the results of compression anvil notched

beam tests of K₁ \approx 7.1 ± 0.7 MPa \sqrt{m} [5,7]. The arrest toughness in the latter case was K_{1a} \approx 2.8 ± 1.4 MPa \sqrt{m} [5,7].



Fig. 9. a) The TiAl K_{lc} and K_{la} values from the table top chevron-wedge technique showing a dependence on crack length (a/W) based on the average K_{l} . b) The TiAl K_{lc} and K_{la} assuming that initiation is controlled by $K_{l}(a_{i}/B_{a} = \pm 0.5)$ and arrest is controlled by $K_{l}(a_{a}/B_{a} = 0)$, where both are independent of a/W.



Fig. 10. The final TiAl calibration data showing consistent scatter bands of K_{lc} (upper) and K_{a} (lower) toughness values.

Summary Discussion and Concluding Remarks

A chevron notched, wedge loaded double cantilever beam (CWB) test method to measure the initiation and arrest fracture toughness of brittle and semi-brittle materials using very small composite specimens and that can be fabricated using minimal amounts of critical materials has been developed. This report focuses on finite element (FE) simulations that were used to select a specimen geometry that is effective, and to quantify the stress intensity factor (SIF) for the CWB specimen. An effective geometry to facilitate initiation and arrest events was found to be a thickness ratio, W/B = 2, a height to thickness, h/B = 0.5, and an initial crack depth to width ratio, $a_o/W = 0$. The SIF for this geometry decreases rapidly with increasing a/W between 0 to 1. Combined with the wedge loading, this configuration results in stable crack growth, manifested as a series of short pop-in events. The FE solutions provide the basis to evaluate K_{Ic} and K_{Ia} for a specified CWB specimen size (B), the elastic modulus (or moduli) of the fixture and specimen material(s) (E), the critical crack mouth (load line) displacement (Δ_c) and the crack depths (a_i/W and a_a/W) at initiation and arrest.

Notably, the SIF varied by approximately 30% along the crack front between a broad minimum at the center and a local maximum at the chevron edges. Thus we believe proper analysis of CWB data requires the use of two SIF versus a/W curves. The curve for the edge specifies the $K_I = K_{Ic}$ at initiation, while the curve for the center specifies the $K_I = K_{Ia}$ at arrest. The variation in the SIF is larger if the crack front is slanted. In this case, the SIF is highest where the crack front forms an acute angle with the side of the chevron and lowest where it forms an obtuse angle with the chevron side. However, the maximum SIF is only slightly higher than that for an unslanted crack front, while the minimum is about 10-20% lower than for the corresponding SIF at the middle of an unslanted crack. Since the fracture may initiate at a one point, but must arrest over an appreciable length of crack front, use of the SIF functions for unslanted cracks to evaluate K_{Ic} and K_{Ia} from CWB tests is a reasonable approximation.

Plastic deformation reduces the SIF relative to a fully elastic condition. The effect plasticity depends on a/W, and is modest below about $0.01\Delta/B$ for a/W = 0.2 and $0.025\Delta/B$ for a/W = 0.5. This assessment is based only on continuum elastic loading criteria and does not account for difference in the local crack tip fields due to a variety of factors, ranging from T-fields effects, to detailed variations in local deformation patterns.

Tests on cleavage oriented iron single crystals were carried out on composite sandwich specimens, with thin (t) crystal slices diffusion bonded to low alloy steel arms. The FE simulations were used to assess the corresponding interfaces stresses as a function t. A thickness of t = 1 mm was found to be sufficient to avoid high normal interface stresses that could lead to debonding. The effects of elastic modulus differences on the SIF between the single crystal Fe and the steel arms were also evaluated; while this effect was minimal, the sandwich SIF as function of a/W was used in the Fe single crystal K_{lc} and K_{la} evaluations.

Implementation of the CWB test method was carried out on a precision-machined wedge loading crack mouth opening displacement fixture, driven by a MTS servohydraulic load frame. The test was instrumented with a clip gauge to measure Δ . The CWB method was evaluated by testing TiAl specimens, with previously reported $K_{I_p} \approx 7.1 \pm 0.7$ to $K_{I_c} \approx 8 \pm 1$ MPa \sqrt{m} , for a notched CAB and fatigue precracked three point bend specimens, respectively. The CWB tests, including the scoping studies with a simpler loading device, gave a corresponding average $K_{I_c} \approx 7.1 \pm 1$ MPa \sqrt{m} , in good to excellent agreement with the previous results. The average K_{I_a} for the CWB tests on TiAl was 3.7 MPa \sqrt{m} , compared to an average of 2.8 ± 1.4 MPa \sqrt{m} measured by the CAB tests.

Static CWB tests at -196°C gave an average of $K_{lc} = 11.4 \pm 3.8$. This compares well with a corresponding value of 12.5 ± 2.7 MPa \sqrt{m} measured by CAB tests, but is much higher than the 5.8 ± 0.6 MPa \sqrt{m} measured in static sharp pop-in crack 4-point bend tests. This difference may be partly due to the fact that the CWB tests are conducted at a slightly lower effective loading rate than the static 4-point bend tests. However as noted in a companion report [7], the K_{lc} from the CAB tests are believed to be overestimates of the actual initiation toughness for a variety of reasons. Further, initiation may not always be exactly at the chevron-crack front corner. Thus it is recommended that the lower grouping of the CWB data be averaged to estimate the actual K_{lc}, with a minimum of at least 2-4 data points. Alternately the highest, or few highest, K_{lc} data point(s) could be eliminated in the averaging, especially if they differ appreciably from the other data. The former method gave an average K_{lc} of $8.55 \pm MPa\sqrt{m}$ for the iron single crystals, which is more consistent with the 4-point bend test data extrapolated to the lower loading rates.

In summary, CWB tests on polycrystalline TiAl and Fe single crystals were successfully carried out using small specimens with dimensions of 8x4x4 mm. Thus the CWB test method offers a powerful new tool to measure the fracture toughness of brittle and semi-brittle materials, especially when specimen sizes and or the availability of materials are an issue.

Future Work

The CAB and CWB test methods have been used to very successfully characterize the K_{Ia} in cleavage oriented iron single crystals, between -196 and 0°C [5]. The resulting database is unique and has, for the first time, has clarified the fundamental dynamics and controlling mechanisms of cleavage fracture. This database has also been used to develop a preliminary, but powerful, new semi-empirical multi-scale model of the macroscopic $K_{Ic}(T)$ curve for complex structural steels. Notably, this model predicts an approximately invariant shape of the master toughness-temperature curve for complex steels, as well as the reference temperature shifts in the master curve due to irradiation hardening, that are in agreement with observation. Further analysis of the database and development of the model as well as full documentation of these results, including preparation of manuscripts for journal publication, will be completed during this current reporting period.

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10. DOSIMETRY, DAMAGE PARAMETERS, AND ACTIVATION CALCULATIONS

No contributions.

11. MATERIALS ENGINEERING AND DESIGN REQUIREMENTS

No contributions.

12. IRRADIATION FACILITIES AND TEST MATRICES

No contributions.