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**FUSION MATERIALS
SEMIANNUAL PROGRESS REPORT
FOR THE PERIOD ENDING**

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FOREWORD

This is the forty-eighth in a series of semiannual technical progress reports on fusion materials science activity supported by the Fusion Energy Sciences Program of the U.S. Department of Energy. It covers the period ending June 30, 2010. This report focuses on research addressing the effects on materials properties and performance of exposure to the neutronic, thermal and chemical environments anticipated in the chambers of fusion experiments and energy systems. This research is a major element of the national effort to establish the materials knowledge base for an economically and environmentally attractive fusion energy source. Research activities on issues related to the interaction of materials with plasmas are reported separately.

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

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

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US and Japanese pressurized tubes of V-4Cr-4Ti contained in the HFIR 17J irradiation experiment at 600°C to 3.7 dpa have been examined by transmission electron microscopy. Analysis was intended to determine Burgers vector anisotropy in order to provide understanding of dislocation development resulting from irradiation creep. Both materials were found to have developed precipitation in reactor at 600°C, the US heat probably containing TiO₂ and the Japanese heat forming oxy-carbo-nitrides, but precipitation did not prevent satisfactory dislocation imaging. Also, it was found that V-4Cr-4Ti develops both $a_2\langle 111 \rangle$ and $a\langle 100 \rangle$ Burgers vectors during irradiation, with the $a\langle 100 \rangle$ dislocation densities similar to those with $a_2\langle 111 \rangle$ for an unstressed condition but lower as a result of applied stress. However, Burgers vector anisotropy measurements in V-4Cr-4Ti did not show the large variations found in ferritic steels.

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 (¹Oak Ridge National Laboratory; ²Electric Power Research Institute and ³ORNL, Retired)

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We have performed atomistic simulations of helium behavior in iron using a new 3-body Fe-He inter-atomic potential combined with the Ackland iron potential. With the ORNL potential, interstitial helium is very mobile and coalesces to form interstitial clusters. If the He cluster is sufficiently large the cluster can push out an Fe interstitial, creating a Frenkel pair. The resulting helium-vacancy cluster is not mobile. The ejected SIA is mobile, but is weakly trapped by the He-V cluster. If more helium atoms join the He-V cluster, more Fe interstitials can be pushed out, and they combine to form an interstitial dislocation loop. In the reverse process, multiple helium atoms can be trapped in a single vacancy, and if there are few enough, the vacancy can recombine with an Fe interstitial to create a helium interstitial cluster. These mechanisms are investigated together in larger simulations that examine the nucleation of He defects. Helium bubbles of sizes 1–6 nm are also studied. In order to estimate the amount of helium present from an observed bubble size distribution, it is necessary to understand the relationships between bubble size, pressure and helium content. Extensive atomistic simulations of such bubbles are compared to show effect of temperature, interatomic potentials used and helium concentration.

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Roger E. Stoller¹ and David M. Stewart^{1,2} - ¹Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6138, USA; ²Center for Materials Processing, The University of Tennessee, Knoxville, TN 37996-0750, USA

The evolution of gas-stabilized bubbles in irradiated materials can be a significant factor in the microstructural processes that lead to mechanical property and dimensional changes in structural materials exposed to high-energy neutrons. Helium generation and accumulation is particularly important under DT fusion irradiation conditions. Although the process of ballistic resolution of gas from bubbles has been long-discussed in the literature, there have been few computational studies of this mechanism. Resolution could limit bubble growth by ejecting gas atoms back into the metal matrix. A detailed atomistic study of ballistic He resolution from bubbles in bcc iron has been carried out using molecular dynamics. A newly-developed Fe-He interatomic potential was employed, with the iron matrix described by the potential of Ackland and co-workers from 1997. The primary variables examined were: irradiation temperature (100 and 600K), iron knock-on atom energy (5 and 20 keV), bubble radius (~0.5 and 1.0 nm), and He-to-vacancy ratio in the bubble (0.25, 0.5 and 1.0) in order to obtain an assessment of this dynamic resolution mechanism. The results presented here focus on the 5 keV cascades which indicate a modest, but potentially significant level of He removal by this process.

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EXAMINATION OF IRRADIATED V-4Cr-4Ti PRESSURIZED CREEP TUBES - D. S. Gelles*, K. Fukumoto (Graduate School of Nuclear Power and Energy Safety Engineering, University of Fukui, Fukui 910-8507, Japan), T. Muroga (National Institute for Fusion Science, Oroshi, Toki, Gifu 509-5292, Japan) and R. J. Kurtz* (Pacific Northwest National Laboratory)*

OBJECTIVE

The objective of this effort is to quantify microstructural response in irradiated V-4Cr-4Ti pressurized tubes in order to better understand irradiation creep mechanisms.

SUMMARY

US and Japanese pressurized tubes of V-4Cr-4Ti contained in the HFIR 17J irradiation experiment at 600°C to 3.7 dpa have been examined by transmission electron microscopy. Analysis was intended to determine Burgers vector anisotropy in order to provide understanding of dislocation development resulting from irradiation creep. Both materials were found to have developed precipitation in reactor at 600°C, the US heat probably containing TiO₂ and the Japanese heat forming oxy-carbo-nitrides, but precipitation did not prevent satisfactory dislocation imaging. Also, it was found that V-4Cr-4Ti develops both $\frac{a}{2}\langle 111 \rangle$ and $a\langle 100 \rangle$ Burgers vectors during irradiation, with the $a\langle 100 \rangle$ dislocation densities similar to those with $\frac{a}{2}\langle 111 \rangle$ for an unstressed condition but lower as a result of applied stress. However, Burgers vector anisotropy measurements in V-4Cr-4Ti did not show the large variations found in ferritic steels.

PROGRESS AND STATUS

Introduction

It is now well understood that irradiation creep for practical applications is a consequence of radiation induced dislocation loop nucleation, growth, intersection with matrix dislocations, and evolution into dislocation networks due to an applied stress. It is also well established that both dislocation nucleation and climb (or motion) are affected by the applied stress called Stress Induced Preferential Nucleation (SIPN) and Stress Induced Preferential Absorption (SIPA) so that certain Burgers vectors are favored. This results in what can be termed Burgers vector anisotropy, and when deformation is entirely due to dislocation evolution, the induced creep strain is simply a measure of the anisotropy in dislocation motion so that

$$\dot{\epsilon} = \sum_i \rho_i \bar{b}_i \bar{v}_i \quad (1)$$

where $\dot{\epsilon}$ is the plastic strain rate, i defines each of the possible Burgers vectors, $\bar{b}$, ρ is the dislocation density and $\bar{v}_i$ is the average dislocation velocity for each Burgers vector [1]. Therefore, as irradiation induced deformation proceeds under stress, dislocations with Burgers vectors optimally oriented will develop enhanced densities and as point defects are absorbed, they will move at least as far as unfavorably oriented Burgers vectors, resulting in a net change in shape. However, it can be noted that once an anisotropy is established by an imposed stress state, then that anisotropy will continue to increase unless a mechanism is imposed to stabilize the anisotropy.

The present effort is intended to quantify this Burgers vector anisotropy. Burgers vector anisotropy is difficult to quantify because a procedure is required that is able to identify all Burgers vectors in a field of view. In fact, procedures have now been developed to identify all Burgers in austenitic [2,3] and ferritic steels [4]. However, in both cases, the analysis is complicated by development of two types of Burgers vectors. For example, austenitic steels develop Frank loops as well as perfect dislocations, and ferritic steels are found to develop $a\langle 100 \rangle$ Burgers vectors during irradiation along with the usual $\frac{a}{2}\langle 111 \rangle$. It was anticipated that

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

vanadium alloys would have the advantage that only one Burgers vector would be present, of the type $\frac{a}{2}\langle 111 \rangle$, and therefore only four variants had to be examined. In a previous report, pressurized tubes of V-4Cr-4Ti were examined following irradiation at 425°C, but it was found to be impossible to identify dislocation structures in those conditions due to heavy precipitation of oxy-carbo-nitrides [5]. The present effort instead examines conditions irradiated at 600°C where the effects of precipitation are not expected.

The present effort has the added advantage that two heats of V-4Cr-4Ti were irradiated side by side in the HFIR 17J test, the US heat 832665 and the Japanese heat NIFS-heat2. These heats differ primarily in impurity levels, with the US heat having higher oxygen and the Japanese heat with higher nitrogen. The present experiment therefore consists of examinations of six conditions: zero, intermediate and high stress levels for each of the heats. A condition that had failed was also examined. Results of diameter change following irradiation for the Japanese tubes have been reported [6] and the behavior of the US tubes has been analyzed [7].

Experimental Procedure

The results of diameter change measurements for V-4Cr-4Ti pressurized tubes from the HFIR 17J test have been kindly provided by Meimei Li and are listed in Table 1 [7]. Those specimens selected for destructive examination are marked with a star, but selection of UN02 was made before creep strain information had been obtained. As noted in the table, specimen UN02 was found to contain a residue believed to be a lithium compound and indicating that the low strain value was due to leakage. Therefore, specimens UN05 and UN12 also probably leaked, and UB-19 is confirmed to have leaked [7]. Furthermore, as diameter change is expected to be linear with time and the strain for UN02 is approximately 27% for that of UN17, it is expected that UN02 failure occurred after about a quarter of the irradiation cycle, and most likely as a result of a weld failure. Detailed information on specimen preparation has been reported previously [3,4], but in summary, tubes were sectioned and then punched using a curved mandrell producing curved disks which were then electropolished in a Tenupol polishing apparatus with a solution of 10% sulfuric acid in methanol at dry ice temperature. Microscopy was performed using a JEOL 2010 transmission electron microscope operating at 200 KeV and images were recorded digitally and processed using Photoshop. The orientation of the disk curvature in the microscope was set so that the longitudinal direction of the tube corresponded to the x-tilt axis and therefore the stress state was known. Tilt conditions were recorded for each image. Stereo measurements were used to determine specimen thickness and a line intersection method was used to determine dislocation density for each Burgers vector of interest.

Table 1. Test conditions for specimens of interest irradiated in the 17J test at 600°C to 3.7 dpa [7].

Tube ID	Heat	Midwall Effective Stress (MPa)	Effective mid-wall strain (%)	Comments
UB00*	US heat: 832665	0.5	0.004	
UB15	US heat: 832665	29.6	0.054	
UB08	US heat: 832665	57.4	0.109	
UB03	US heat: 832665	127.2	0.266	
UB12*	US heat: 832665	113.1	0.221	
UB06*	US heat: 832665	166.8	0.503	
UB19	US heat: 832665	165.2	0.012	leak
UN19*	NIFS-Heat2	0.5	0.011	
UN08	NIFS-Heat2	30	0.118	
UN13*	NIFS-Heat2	58.7	0.286	
UN05	NIFS-Heat2	115.6	0.026	
UN12	NIFS-Heat2	114.4	0.104	
UN02*	NIFS-Heat2	172.5	0.330	Contained lithium
UN17*	NIFS-Heat2	172.5	1.228	

* Specimen sectioned for examination.

The procedure used to identify Burgers vectors matched that used previously [5], requiring six images of the same area and involving tilts of approximately 45°. An image using $\bar{g}=\langle 200 \rangle$ is expected to show all of the $\frac{a}{2}\langle 111 \rangle$ dislocations present, whereas any $\bar{g}=\langle 110 \rangle$ such as $[01\bar{1}]$ should only show two of the four possibilities and allow separation of the dislocation populations into two groups of two Burgers vectors. A second $\bar{g}=\langle 110 \rangle$ such as $[\bar{1}10]$ will in fact allow separation of each of these groups. However, comparison of images to unambiguously identify those dislocations that appear is very difficult given the large tilts between images and therefore the procedure uses stereo imaging, and two images separated by about 10° of tilt are needed for each $\bar{g}$ used. However, only images approaching weak beam conditions proved satisfactory for $\bar{g}=\langle 200 \rangle$ in thicker specimens, and those images have been inverted for analysis.

Stereo images are presented as anaglyphs, requiring the standard red-blue or red-green glasses for viewing. In order to maximize the depth of the stereo for a given anaglyph, the image must be rotated so that the operating $\bar{g}$, indicated by an arrow, appears vertical. All micrographs contain a 200 nm magnification marker appearing as a white bar.

Results

Examinations revealed differences between the US and Japanese heats. No voids were observed but both were found to contain uniform distributions of precipitates following irradiation at 600°C, but precipitate densities were much lower than those observed following irradiation at 425°C [5], and precipitation did not appear to affect the dislocation structures. Examples are provided in Figure 1, showing the US heat in (a) and the Japanese heat in (b), both imaged using $\bar{g}=\langle 110 \rangle$ near (001). The US heat contains small circular platelets ~40 nm in diameter on {100} planes, with two orientations showing in this image, one approximately vertical and the other approximately horizontal, both viewed on edge, and the Japanese heat shows a similar density of smaller equiaxed precipitates ~10 nm in diameter. Therefore, precipitation response was different for the two materials.

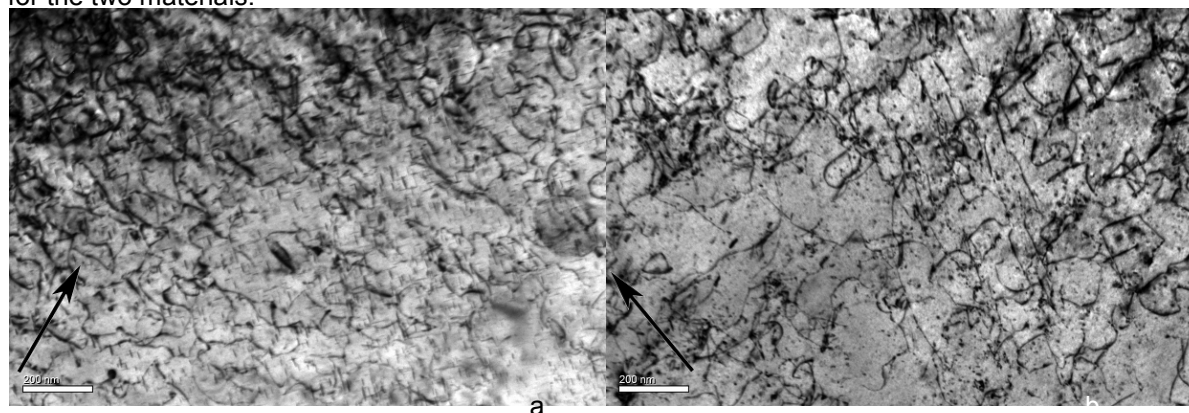


Figure 1. Dislocations and precipitation in pressurized tubes UB06 (a) and UN17 (b) irradiated at 600°C to dpa at midwall effective stress levels of ~170 MPa.

Examination of images revealed a problem with the starting assumptions for this project. It was assumed that all Burgers vectors would be of type $\frac{a}{2}\langle 111 \rangle$ but comparison of images raised questions with that assumption. If all Burgers vectors were of type $\frac{a}{2}\langle 111 \rangle$, then all dislocations would be visible in $\bar{g}=\langle 200 \rangle$ contrast. Figure 2 provides comparison of images using $\bar{g}=[01\bar{1}]$, $\bar{g}=[200]$, and $\bar{g}=[\bar{1}10]$, respectively, for specimen UN19, the unstressed Japanese tube. Careful examination reveals images, particularly in $\bar{g}=[\bar{1}10]$ contrast but also in $\bar{g}=[01\bar{1}]$ contrast that do not appear in $\bar{g}=[200]$ contrast. They tend to be straight dislocation segments, whereas most of the dislocations in $\bar{g}=[200]$ contrast appear as loops or arcs. As no stacking faults are apparent, and examples will be shown where variations in intensity occur for different dislocation segments, it is anticipated that $a\langle 100 \rangle$ Burgers vectors have been produced during irradiation in V-4Cr-4Ti. Fortunately, the problem of determining Burger's vector anisotropy for ferritic steels has been developed [4]. For that

case, where both $\frac{a}{2}\langle 111 \rangle$ and $a\langle 100 \rangle$ exist, the procedure uses the same images as were collected for this study, but the analysis is more complex.

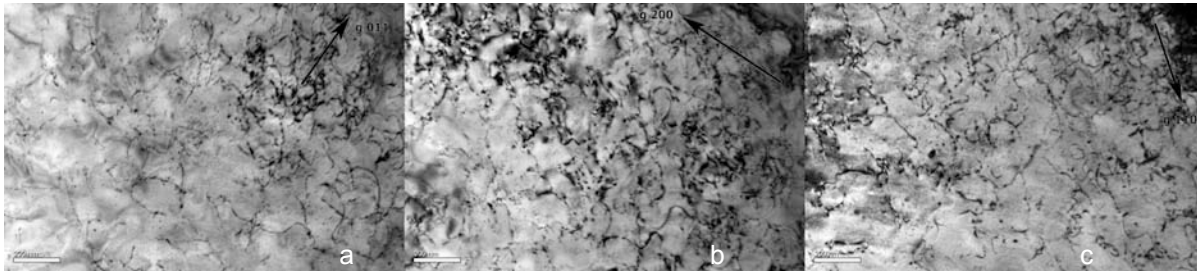


Figure 2. Comparison of images for $\bar{g}=[01\bar{1}]$ in (a), $\bar{g}=[200]$ in (b), and $\bar{g}=[\bar{1}10]$ in (c) for condition UN19, an unstressed tube of the Japanese heat of V-4Cr-4Ti.

The dislocation structures as stereo pairs for the conditions examined are shown in Figures 3 through 9. However, in order to optimize resolution, these images have been rotated (counterclockwise) with respect to all other images in this report so that the longitudinal direction of the tube is now towards one o'clock. In each case, the $\bar{g}=\langle 200 \rangle$ image is in the center (b) and the corresponding $\bar{g}=\langle 110 \rangle$ images are on either side at (a) and (c). Each image contains an arrow indicating the direction for $\bar{g}$, so that to maximize the stereo effect, the viewer should rotate the image so the arrow points away. However, note that to invert the top and bottom of the stereo image, one need only rotate the picture 180° . The stress axis can be envisioned as follows: the length of the tube is in approximately the vertical direction but actually rotated $\sim 25^\circ$ clockwise or towards one o'clock as shown inset, the radial tube direction is orthogonal, and the tube thickness is in the direction of the stereo effect (ideally with the sample at zero tilt).

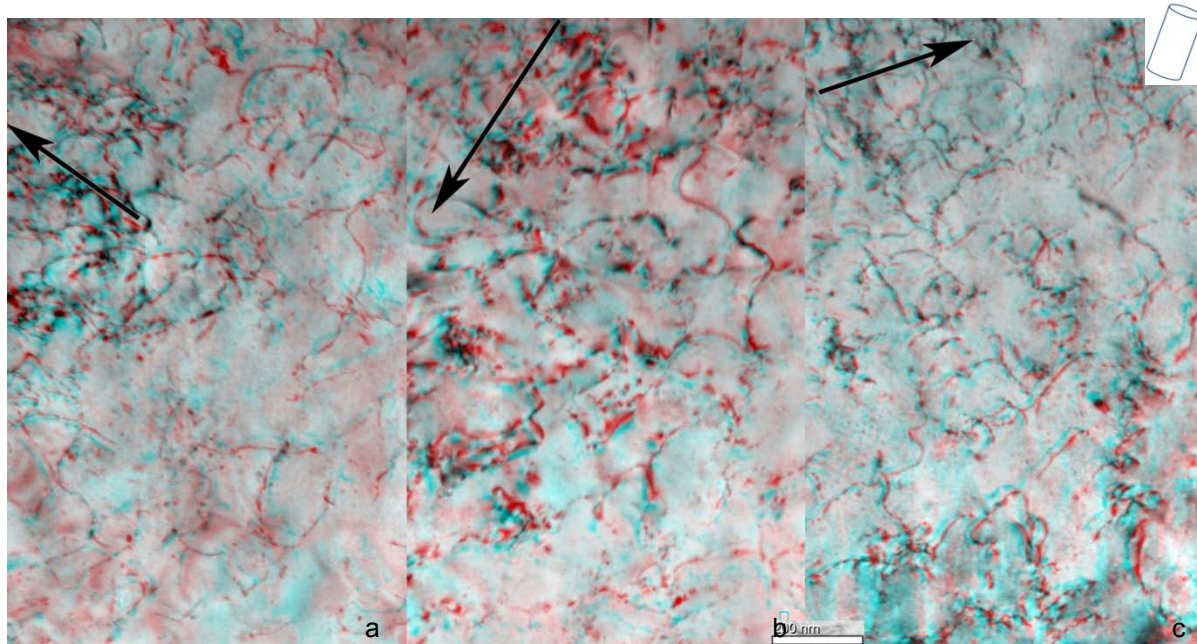


Figure 3. Anaglyph stereo images of dislocation structure in Japanese heat specimen UN19 unstressed with $\bar{g}=[01\bar{1}]$ contrast in (a), $\bar{g}=[200]$ contrast in (b) and $\bar{g}=[\bar{1}10]$ contrast in (c).

It should first be noted that the images for Figures 7, 8 and 9 are for much thicker samples than those for Figures 3, 4, 5 and 6. This is a result of examining the US specimens first, and not yet understanding how difficult it would be to analyze such images for Burgers vector anisotropy. For example, thicker samples required weak beam dark field imaging to successfully see all dislocations in $\langle 200 \rangle$ contrast, whereas for thinner samples, bright field imaging was adequate.

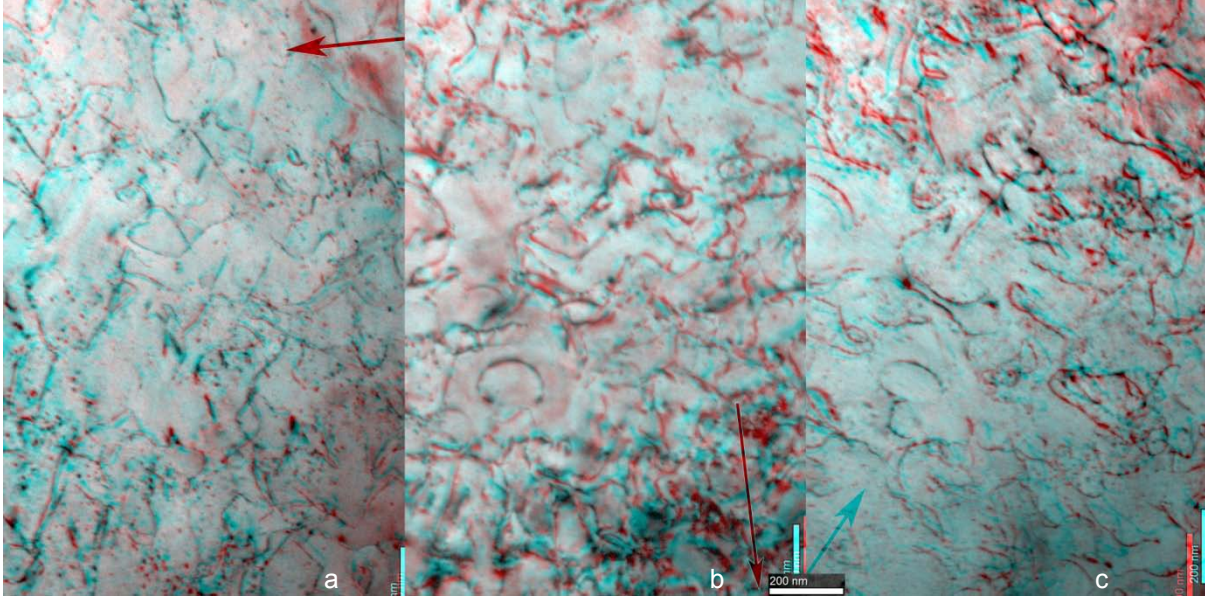


Figure 4. Anaglyph stereo images of dislocation structure in specimen UN13 at 58.7 MPa with $\bar{g}=[01\bar{1}]$ contrast in (a), $\bar{g}=[200]$ contrast in (b) and $\bar{g}=[\bar{1}10]$ contrast in (c).

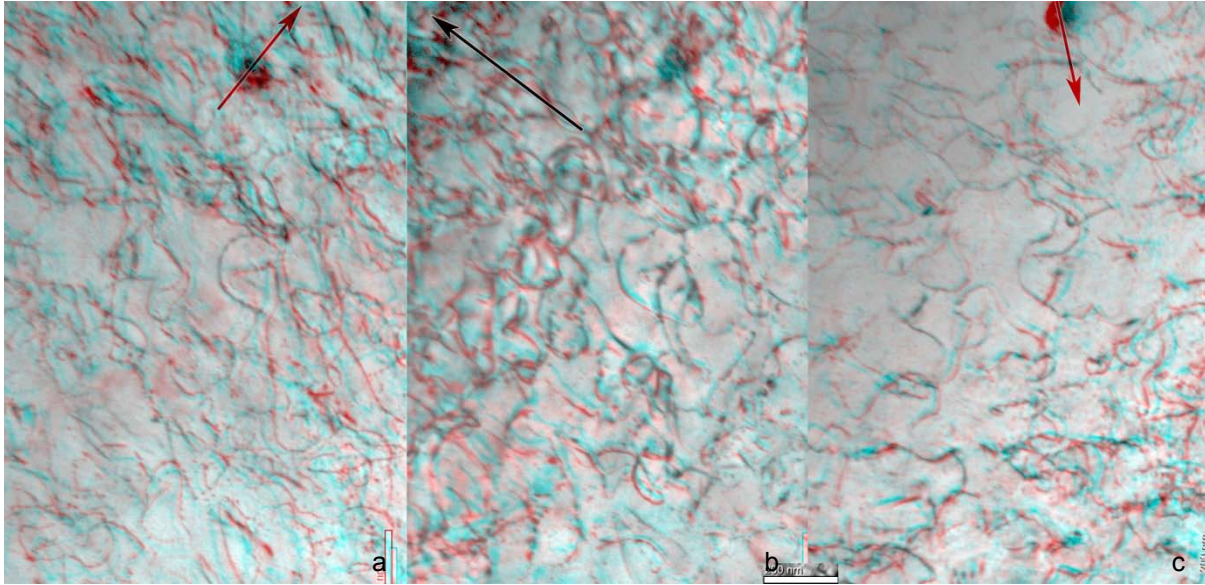


Figure 5. Anaglyph stereo images of dislocation structure in specimen UN17 at 172.5 MPa with $\bar{g}=[01\bar{1}]$ contrast in (a), $\bar{g}=[200]$ contrast in (b) and $\bar{g}=[\bar{1}10]$ contrast in (c).

Therefore, the images for the Japanese tube conditions were analyzed first. The procedure can be best envisioned based on Figure 10 showing three of the six imaging conditions used; $\bar{g}=[01\bar{1}]$, $\bar{g}=[200]$ and $\bar{g}=[\bar{1}10]$. A truth table defining dislocation contrast conditions for the various possible imaging conditions is given in Table 2. (The $\bar{g}=[101]$ imaging condition is included, but happens not to apply to any of the imaging sequences used in this study.) From Table 2, it can be determined that for $[200]$ imaging, all the $\frac{a}{2}\langle 111 \rangle$ as well as $a[100]$ Burgers vectors should be visible. For $\bar{g}=[01\bar{1}]$ imaging, only half the $\frac{a}{2}\langle 111 \rangle$ as well as $a[010]$ and $a[001]$ Burgers vectors should be visible. Therefore, the $\bar{g}=[01\bar{1}]$ and $\bar{g}=[200]$ images can be compared to

identify those which appear only in $\bar{g}=[01\bar{1}]$ contrast, only in $\bar{g}=[200]$ contrast or both, to separate the dislocations into three groups. Likewise, the $\bar{g}=[200]$ and $\bar{g}=[\bar{1}10]$ images can be compared to separate the dislocations into three somewhat different groups. Then, comparison of these groups can uniquely determine which Burgers vector corresponds to each dislocation image.

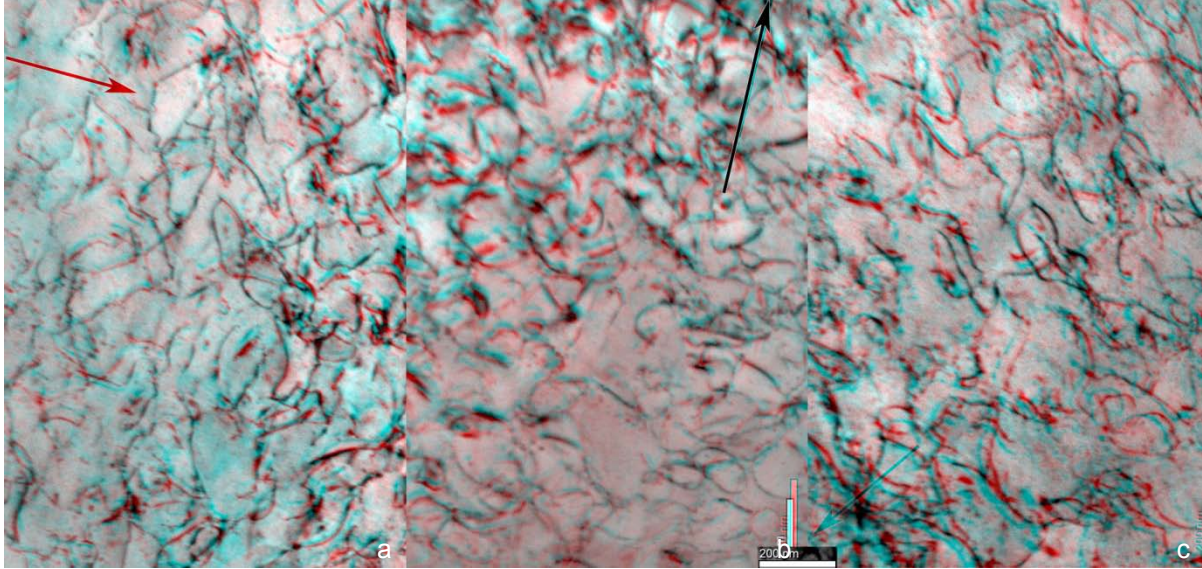


Figure 6. Anaglyph stereo images of dislocation structure in specimen UN02 at 172.5 MPa but believed to have failed at ~25% of the strain of specimen UN17 with $\bar{g}=[01\bar{1}]$ contrast in (a), $\bar{g}=[200]$ contrast in (b) and $\bar{g}=[\bar{1}10]$ contrast in (c).

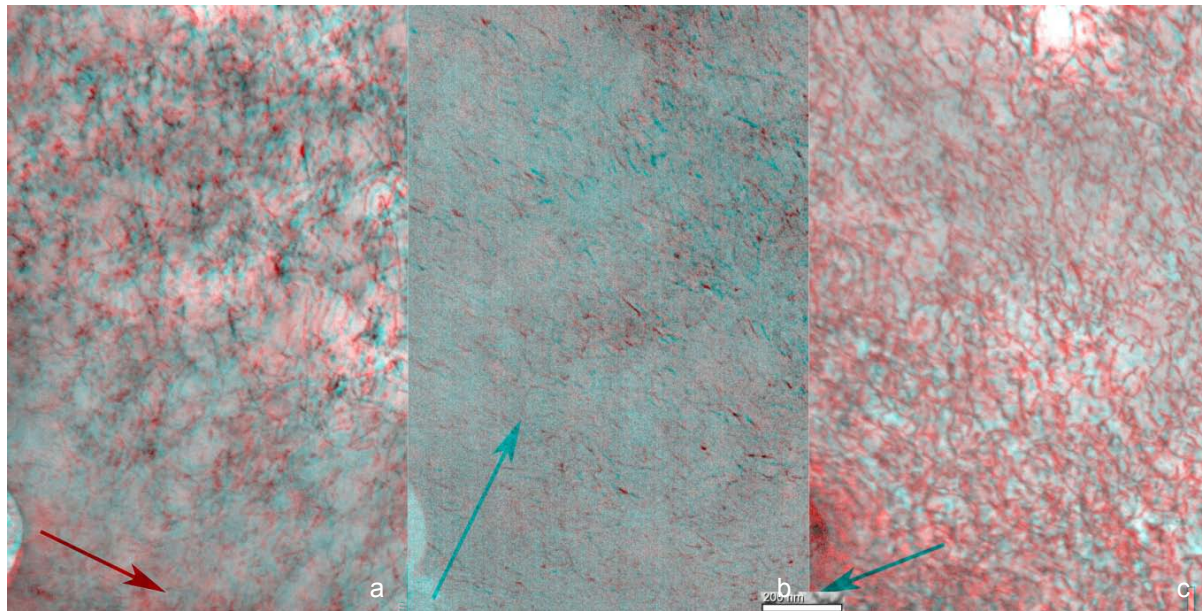


Figure 7. Anaglyph stereo images of dislocation structure in US heat specimen UB00 unstressed with $\bar{g}=[01\bar{1}]$ contrast in (a), $\bar{g}=[200]$ contrast in (b) and $\bar{g}=[\bar{1}10]$ contrast in (c).

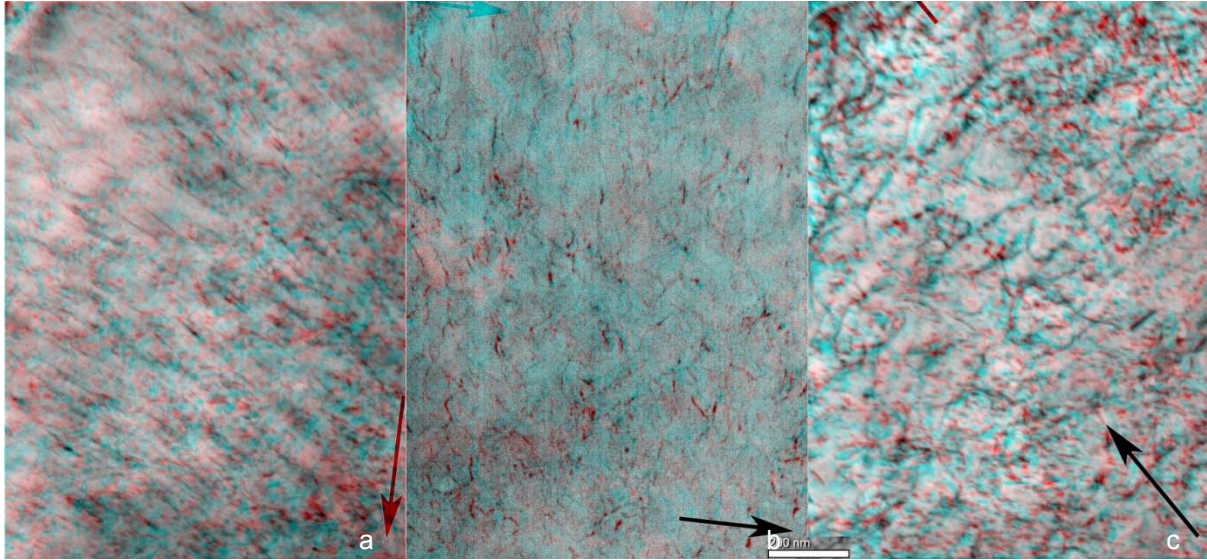


Figure 8. Anaglyph stereo images of dislocation structure in specimen UB12 at 113.1 MPa with $\bar{g}=[01\bar{1}]$ contrast in (a), $\bar{g}=[200]$ contrast in (b) and $\bar{g}=[\bar{1}10]$ contrast in (c).

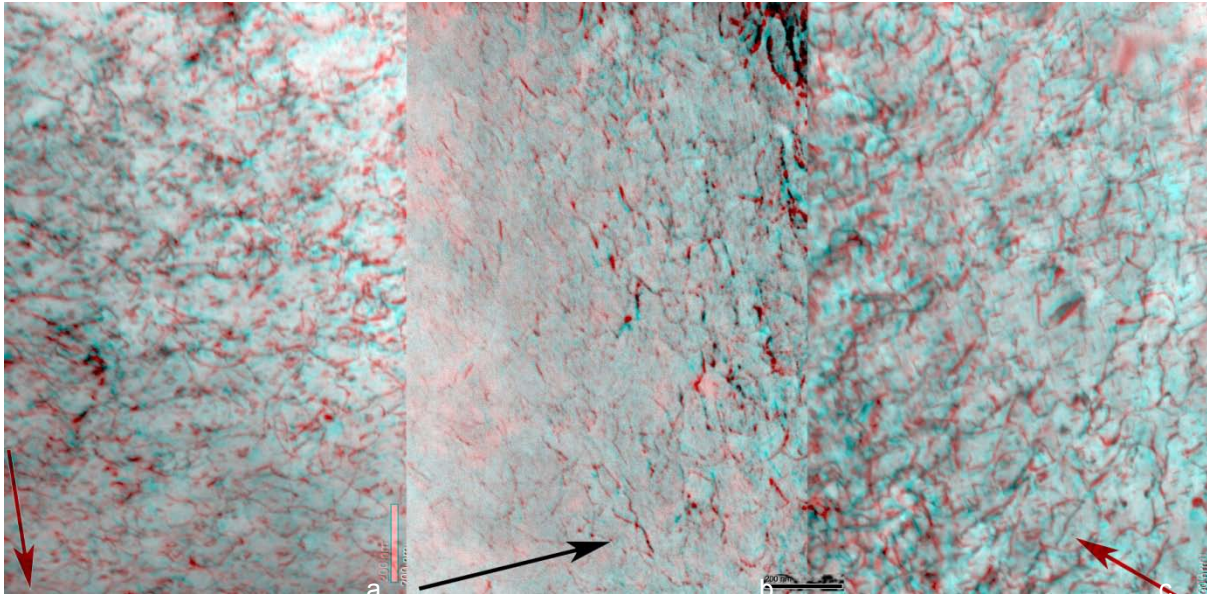


Figure 9. Anaglyph stereo images of dislocation structure in specimen UB06 at 166.8 MPa with $\bar{g}=[01\bar{1}]$ contrast in (a), $\bar{g}=[200]$ contrast in (b) and $\bar{g}=[\bar{1}10]$ contrast in (c).

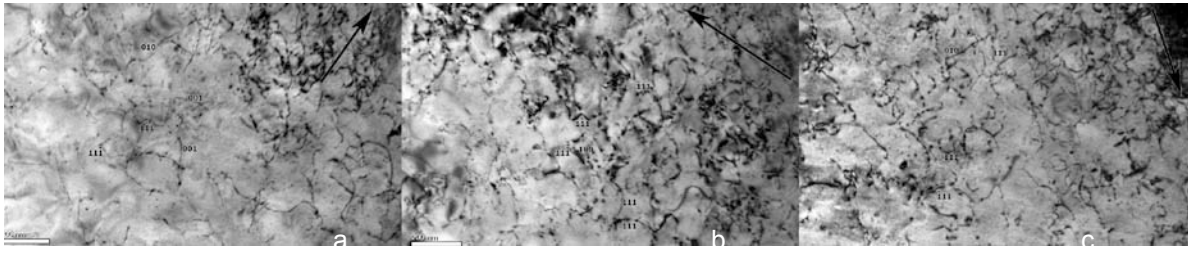


Figure 10. Images of UN19 to identify different Burgers vectors in $[01\bar{1}]$ contrast in (a), $[200]$ contrast in (b) and $[\bar{1}10]$ contrast in (c), using indices to mark the different Burgers vectors.

Table 2. Truth table for $\bar{g} \cdot \bar{b}$ imaging contrast for the various imaging and Burgers vector conditions used in this study, taken from [4].

Condition	Dislocation Burgers vector						
$\bar{g}$	$\frac{a}{2}[111]$	$\frac{a}{2}[\bar{1}\bar{1}1]$	$\frac{a}{2}[\bar{1}\bar{1}\bar{1}]$	$\frac{a}{2}[11\bar{1}]$	$a[100]$	$a[010]$	$a[001]$
$[200]$	1	1	1	1	2	0	0
$[01\bar{1}]$	0	0	1	1	0	1	1
$[\bar{1}10]$	0	1	1	0	1	1	0
$[\bar{1}01]$	0	1	0	1	1	0	1

Figure 10 is intended to provide insight into the dislocation configurations in V-4Cr-Ti following irradiation at 600°C. The three contrast conditions have been marked to provide examples of the different Burgers vectors listed in Table 2. For example, a dislocation image marked “100” representing $a[100]$ only appears in $\bar{g}=[200]$ imaging but is in strong contrast, whereas a dislocation image marked “111” representing $\frac{a}{2}[111]$ only appears in $\bar{g}=[200]$ imaging with weaker contrast; a dislocation image marked “ $11\bar{1}$ ” representing $\frac{a}{2}[11\bar{1}]$ appears in $\bar{g}=[200]$ and $\bar{g}=[01\bar{1}]$ contrast; and so on. Of particular note are dislocation images marked “ $\bar{1}\bar{1}1$ ” representing $\frac{a}{2}[\bar{1}\bar{1}1]$, one toward the top and the other towards the bottom of the images in Figures 10b) and c). Based on the surface traces that are barely perceptible towards the top of Figure 10b), it is expected that the upper example is in fact a slip dislocation that has moved following specimen preparation. Another example of such behavior can be identified on the right in Figure 1b).

Following the procedure outlined above, dislocation images for the NIFS-Heat2 pressurized tubes were compared and marked as best as possible so that Burgers vectors were determined for each dislocation. This was very difficult in areas containing dislocation tangles at high density. The dislocation densities for each of the seven Burgers vectors present was then determined and results of measurements presented in Table 3. Analysis for the US heat pressurized tube images will be attempted at a later time. Measurements were based on intersections of the dislocation array in an image with a superimposed grid of lines. The grid line length times the thickness represents a surface in the foil so that intersections of a given Burgers vector with that surface divided by the surface area is equivalent to dislocation length per unit volume.

Table 3. Measurements of dislocation density in cm^{-2} for all possible Burgers vectors in the irradiated Japanese pressurized tubes under examination.

Specimen	Dislocation Burgers vector						
	$\frac{a}{2}[111]$	$\frac{a}{2}[\bar{1}11]$	$\frac{a}{2}[1\bar{1}1]$	$\frac{a}{2}[\bar{1}\bar{1}\bar{1}]$	$a[100]$	$a[010]$	$a[001]$
UN19	3.6×10^8	3.6×10^8	2.7×10^8	2.2×10^8	1.8×10^8	3.1×10^8	3.6×10^8
UN13	4.2×10^8	3.6×10^8	3.1×10^8	8.1×10^8	1.4×10^8	1.6×10^8	2.4×10^8
UN17	5.0×10^8	4.2×10^8	5.9×10^8	6.8×10^8	0.88×10^8	1.5×10^8	1.9×10^8
UN02	6.3×10^8	3.6×10^8	4.0×10^8	5.3×10^8	2.0×10^8	2.0×10^8	2.9×10^8

The results given in Table 3 should probably be considered estimates given the difficulty of the analysis and the time available to perform it. Also, it has not yet been possible to relate the applied stress to the Burgers vector directions. It can be noted from these results that the $\frac{a}{2}\langle 111 \rangle$ dislocation density for the unstressed condition appears to be lower than that for the stressed conditions, indicating that stress promotes increases in dislocation density. Also, dislocation densities for $a\langle 100 \rangle$ Burgers vectors tend to be lower than those for $\frac{a}{2}\langle 111 \rangle$ Burgers vectors when stress is applied, except for the unstressed case where the $a\langle 100 \rangle$ densities are higher. Also, the $a\langle 100 \rangle$ dislocation density appears to decrease with increasing stress. However, the results obtained for UN17, the high stress condition, show anisotropy of only about 50% both for $\frac{a}{2}\langle 111 \rangle$ and $a\langle 100 \rangle$ Burgers vectors whereas similar variations are found for UN19, unstressed, and for UN02, at high stress for only about 25% of lifetime.

Discussion

It can be noted that Burgers vectors other than $\frac{a}{2}\langle 111 \rangle$ have only once been previously identified in V-4Cr-4Ti [9]. This can in part be attributed to the fact that few examinations have been conducted following irradiation at 600°C, and examinations at lower irradiation temperatures are complicated by extensive oxy-carbo-nitride precipitation. It can be noted that we examined a series of vanadium alloys (excluding V-4Cr-4Ti) following irradiation at 600°C, and it was concluded that only $\frac{a}{2}\langle 111 \rangle$ Burgers vectors were found [8]. It therefore may be possible that V-4Cr-4Ti is the exception, but more likely, the effects of precipitation again complicated analysis in that work. Also, it can be noted that our recent post-irradiation work assumed only $\frac{a}{2}\langle 111 \rangle$ Burgers vectors [10], but interpretation was confusing, probably as a result of the presence of the $a\langle 100 \rangle$ Burgers vectors. However, Nakasaka and co-workers recently had the opportunity to examine weldments of the NIFS-HEAT-2 following irradiation at 290°C to 0.08 dpa in JMTR, and identified black spot damage that did not correspond to an $\frac{a}{2}\langle 111 \rangle$ Burgers vector [9]. The low irradiation temperature in that experiment was probably not detrimental to imaging because the dose was too low to cause extensive precipitation.

Figure 10 does provide the opportunity to demonstrate that the Burgers vector differing from $\frac{a}{2}\langle 111 \rangle$ is indeed $a\langle 100 \rangle$. The dislocation marked “001” in Figure 10a) does not appear in Figures 10b) or c). Therefore, the two necessary $\bar{g} \cdot \bar{b} = 0$ invisibility criterion are met and the Burgers vector must be $a[001]$. Considerable discussion has appeared in the literature, trying to explain the observation of $a\langle 100 \rangle$ Burgers vectors in ferritic steels, and, in fact, vanadium was predicted to have a higher probability for $a\langle 100 \rangle$ loop formation than was ferritic steel, 5.5×10^{-5} versus 5.7×10^{-9} [11]. Those probability predictions ranked niobium slightly higher than vanadium and tungsten much lower, at 1.4×10^{-27} .

The dislocation configurations found in unstressed and stressed V-4Cr-4Ti irradiated pressurized tubes can be summarized as follows. After irradiation at 600°C to 3.7 dpa in HFIR, a dislocation network develops that includes $\frac{a}{2}\langle 111 \rangle$ and $a\langle 100 \rangle$ burgers vectors. The complex network is difficult to envision unless all dislocation line segments in a field of view can be understood; individual line segments often appear in individual images. Therefore, the network can be defined by the dislocation nodes or points where line segments meet. However, many examples can be shown both for stressed and unstressed samples where

the line segments are bowed into arcs, indicating that considerable stress develops during irradiation by the preferential absorption of interstitials, and the nodes restrain the dislocation motion.

Application of stress is expected to preferentially influence those Burgers vectors that are favorably oriented with respect to the stress axis. This is the case both during loop nucleation and dislocation climb. As a consequence, those Burgers vectors favorably oriented are expected to develop high populations and densities, and this study was intended to quantify that behavior in V-4Cr-4Ti. The procedure has been hindered by the observation that dislocations are found to slip in the foil either during preparation, loading or examination, changing the apparent populations. However, it was a relatively simple matter to restrict quantification to areas where no apparent slip had occurred.

As the Burgers vector anisotropy develops, it is expected that the anisotropy will continue to increase unless there is a process restraining it. This is because any favored Burgers vector is expected to climb more rapidly than an unfavored Burgers vector as predicted by SIPA, resulting in even more line length and further increases in anisotropy. The restraining process is likely to be a result of the internal stress that results from the presence of the anisotropy. The sum of all dislocation stress fields will produce an internal stress state, the larger the anisotropy, the larger the non-hydrostatic portion of the internal stress state. It is anticipated that the internal stress state will increase until it matches the externally applied stress, and then the Burgers vector anisotropy will stabilize, reaching a steady state.

However, the present attempt to measure the consequences of irradiation creep as Burgers vector anisotropy is not definitive. Anisotropy measurements for the high stress condition were similar to those at lower stress. Comparison with previous results show that for ferritic steels,[4] anisotropies for samples at hoop stresses of 86 and 60 MPa irradiated at 420°C produced higher dislocations densities and higher anisotropies, on the order of a factor of 7 variation for $\frac{a}{2}\langle 111 \rangle$ Burgers vectors and 3 to 5 for $a\langle 100 \rangle$ Burgers vectors. Also, the densities for $a\langle 100 \rangle$ Burgers vectors were comparable to those for $\frac{a}{2}\langle 111 \rangle$. Our results are surprising because the anisotropy found was small compared to those other materials. However, the creep coefficient measured at 600°C for the US heat of V-4Cr-4Ti was $5 \times 10^{-6} \text{ MPa}^{-1} \text{ dpa}^{-1}$, compared to $\sim 0.5 \times 10^{-6} \text{ MPa}^{-1} \text{ dpa}^{-1}$ for ferritic/Martensitic steels and $\sim 1 \times 10^{-6} \text{ MPa}^{-1} \text{ dpa}^{-1}$ for austenitic stainless steels [7]. The consequences are not yet understood.

When a pressurized tube fails, it can be anticipated that the anisotropic Burgers vector populations will continue to evolve for some time before the anisotropy dissipates. To study this response, images were collected for specimen UN02. Based on the diameter change for UN02 in comparison with UN17, it is likely that UN02 failed after about 27% of goal fluence. Therefore, anisotropy measurements in UN02 will give insight into the dose needed to return the dislocation structure to an isotropic condition. Given the observation that the dislocation structure is a network defined by nodes, returning the structure to an isotropic condition can be envisioned as a process that simply shifts the nodal positions, and therefore isotropy could be reached quickly. Interestingly, the anisotropy observed in UN02 is similar to UN17 suggesting that an isotropic condition was not attained, but it should also be also noted that the same level of anisotropy is present in all of the specimens examined regardless of applied stress.

Conclusions

Seven V-4Cr-4Ti pressurized tubes from the HIFR 17J irradiation experiment, three of US heat 832665 and four of heat NIFS-heat2, have been examined by transmission electron microscopy in order to measure Burgers vector anisotropy produced during irradiation creep and subsequent growth after tube failure. It was found that both materials developed precipitation in reactor at 600°C, the US heat probably containing TiO_2 and the Japanese heat forming oxy-carbo-nitrides, but precipitation did not prevent satisfactory dislocation imaging. Also, it was found that V-4Cr-4Ti develops both $\frac{a}{2}\langle 111 \rangle$ and $a\langle 100 \rangle$ Burgers vectors during irradiation, with the $a\langle 100 \rangle$ dislocation densities similar to those with $\frac{a}{2}\langle 111 \rangle$ for an unstressed condition but lower as a result of applied stress. However, Burgers vector anisotropy measurements in V-4Cr-4Ti did not show the large variations found in ferritic steels.

Future Work

Anisotropy measurements will be continued and it is hoped that this work will shift to modeling Burgers vector anisotropy in order to estimate the internal stress state generated by Burgers vector anisotropy and to dislocation interactions during post-irradiation deformation. Also, issues will be considered regarding growth response when stresses relax.

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THE ELECTRICAL CONDUCTIVITY OF SiC_f/SiC – EFFECTS OF PYROCARBON FIBER COATING THICKNESS AND CONTACT RESISTANCE – G. E. Youngblood and E. Thomsen (Pacific Northwest National Laboratory)* and R. J. Shinavski (Hyper-Therm HTC, Inc.)

OBJECTIVE

The primary objectives of this task are: (1) to assess the properties and behavior of SiC_f/SiC composites made from SiC fibers (with various SiC-type matrices, fiber coatings and architectures) before and after irradiation, and (2) to develop analytic models that describe these properties as a function of temperature and dose as well as composite architecture. Recent efforts have focused on examining the electrical conductivity properties of SiC_f/SiC composites considered for application in FCI-structures in support of the U.S. dual-coolant lead-lithium (DCLL) fusion reactor blanket concept.

SUMMARY

The previous report examined in-plane and transverse electrical conductivity (EC) data from RT to 800°C for several forms of two-dimensional silicon carbide composites made with a chemical vapor infiltration (CVI) matrix (2D-SiC/CVI-SiC). A fairly substantial correction due to contact resistance at the sample-electrode interface was required to arrive at transverse EC-values, an important quantity needed for the design of a flow channel insert (FCI). In this report, the dependence of in-plane and transverse EC-values for 2D-SiC/CVI-SiC on the total thickness of the pyrocarbon (PyC) fiber coating is examined. As previously hypothesized, both in-plane and transverse EC-values for 2D-SiC/CVI-SiC strongly depend on the total thickness of the PyC fiber coating, and the interconnectivity and alignment of the carbon-coated fiber network. Our “3-layer series” model predicts that transverse EC-values for a seal-coated 2D-SiC/CVI-SiC with a monolayer PyC fiber coating of ~50 nm thickness will be <20 S/m for all temperatures up to ~800°C, as desired for the FCI-application.

PROGRESS AND STATUS

Introduction

New EC data for 2D-SiC/CVI-SiC made with Nicalon™ Type S 0/90 woven fabric coated with a relatively thin ~50 nm monolayer of pyrocarbon (PyC) are reported. These data are analyzed together with the previously reported results for a similar composite prepared with multi-layer PyC/SiC fiber coating with a thicker ~200 nm total PyC thickness. All of these experimental results were acquired in support of a DOE-sponsored SBIR contract (DE-FG02-07ER84717) with Hyper-Therm HTC, Inc. The EC measurement systems and protocol as well as the previous results for 2D-SiC/CVI-SiC composite, and for dense, monolithic CVD-SiC are described in Fusion Material Semiannual Progress Reports (FMSPR) [1-5].

In FMSPR [4], a simple model was introduced that describes the transverse EC(T) of a 2D-SiC/CVI-SiC plate in terms of the EC of the interior, carbon net-worked SiC fabric-layered region in series with outer “seal coat” layers of densely adherent, single phase CVD-SiC (in our case). The transverse EC(T) for such a three-layered composite can be expressed by:

$$EC(T) = EC_{int}[1 - 2f(1 - R)]^{-1} \quad [1]$$

In Eq. [1], T is temperature, $f = t/L$ where t is the average thickness of a seal coat layer, L is the composite plate thickness (including the seal coat layers) and EC_{int} is the transverse EC for only the interior region of a 2D-SiC/CVI-SiC. EC_{int} was determined by making EC measurements on a disc sample with each surface ground down well into the fabric layer region. Also, R is the ratio EC_{int}/EC_{sc} , where EC_{sc} was

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calculated for a CVD-SiC seal coat of known thickness using values of EC measured for representative samples of pure, monolithic CVD-SiC [2]. Note that $EC(T)$ is NOT an intrinsic property of 2D-SiC/SiC, but rather an “effective” transverse electrical conductivity useful for comparing designs for FCI-structures subject to potentially a deleterious MHD pressure drop in a DCLL blanket.

As previously shown, electrical conduction in the interior region of a high quality 2D-SiC/SiC composite with carbon-coated fibers is dominated by the amount of high conductivity carbon, even though the amount of carbon is only a few percent. Importantly, the continuity of the fiber coatings with parallel alignment control the in-plane EC, while the amount or lack of interconnectivity of the carbon fiber coating network through touching fiber coatings is important in determining the conduction in the transverse direction of a 2D-composite [5].

When using a simple 2-probe measurement method (no guard ring attachments), which is preferred when measuring the transverse EC and its temperature dependence of a relatively thin disc-shaped sample, the measured $EC(T)$ -values must be corrected for contact resistance. This is not trivial as the contact resistance is very dependent on sample surface preparation and type of electrodes used as well temperature. Usually the contact resistance at the interior region/electrode interface is much less than that at the pure SiC seal coat/electrode interface. The interior region/electrode contact resistance is less because numerous, highly conductive carbon coating pathways penetrate this interface and make direct electrical contact with the metal electrodes. Nevertheless, the current density at the electrode-interior region interface is far from uniform; there will always be at least some contact resistance due to current constrictions at this interface. Thus, the actual contact resistance will depend upon the carbon network configuration as well as the number of carbon-electrode contacts at the interface. At lower temperatures, SiC acts more like an electrical insulator (actually SiC is a wide band gap semi-conductor and exhibits a relatively steep temperature dependence) and the contact resistance for a SiC-metal contact may become very large. At higher temperatures, SiC becomes more conducting; the electrical current is more uniformly spread across a SiC-metal interface and contact resistance decreases dramatically. This is the reason that the preferred method to estimate the transverse $EC(T)$ -values for 2D-SiC/CVI-SiC with a SiC seal coat is to measure $EC_{int}(T)$ directly with a 2-probe method that at least minimizes contact resistance, and then calculate $EC(T)$ using Eq. [1].

In this report the specific contact resistance as function of temperature will be estimated for three types of electrodes (Au and thin and thick layers of porous Ni) applied to 2D-SiC/CVI-SiC with the same weave patterns but different carbon fiber coating thicknesses. Then, using Eq. [1] our 2-probe $EC_{int}(T)$ -data will be used to obtain an estimate of the transverse $EC(T)$ for 2D-SiC/CVI-SiC with a relatively thin CVD-SiC seal coat for each case.

Experimental Procedure and Results

Two bar and two disc samples of 2D-SiC/CVI-SiC with 8HS-0/90 weave (referred to as Batch 3 samples) and with a monolayer carbon fiber coating of purposely-reduced thickness were obtained from Hyper-Therm, HTC. Except for the fiber-coating step, these new samples were produced in the same manner as the samples with thicker, multilayer (ml) PyC/SiC fiber coatings examined in the previous report (Batch 1 and 2 samples) [5]. As before, bar samples (40 x 5.3 x 3.1 mm) were used for 4-probe in-plane EC measurements; disc samples (10 mm diameter x ~2 mm thick.) were used for measurements normal to the plane of the woven SiC fabric layers, i.e., the transverse direction. Measurements were made as a function of temperature during a heating-cooling cycle up to ~800°C in ~40°C steps. The EC of disc samples was measured first for as-received samples with the SiC seal coat intact, then again after the SiC seal coat was removed. For the latter case, ~0.1 mm was ground from each disc surface to expose a surface cut well into the carbon net-worked interior region. The disc faces were polished before reapplying the electrodes; however it was difficult to prepare an undamaged in-plane surface. The small diameter SiC fibers lying parallel and exposed near the cut surface sometimes broke and dislodged during polishing. Porous nickel electrodes (reduced NiO) were used for all disc sample EC-measurements except for the 2D-GE sample, where evaporated gold was used [5].

Because our main concern in this report is the effect of the thickness and configuration of the carbon fiber coating on both the specific contact resistance and EC(T), only representative samples from the previous report with 0/90 weave orientation are considered here. Therefore, in Tables 1-2 sample codes, batch designation, weave-type, carbon layer thickness(es) as well as the individual sample bulk density values are listed only for the Hyper-Therm fabricated bar and disc samples selected for this study, respectively. A bar and a disc reference sample of 2D-SiC/CVI-SiC made by General Electric with a ~150-nm monolayer PyC fiber coating also are listed [5].

Table 1. Bar Samples (4-probe in-plane EC)

Code	Type	thickness PyC (nm)	Bulk Density (g/cc)
B1	Batch 1, 5HS weave	180 + 4(20), C/SiC ml	2.77
B2	" " "	" " "	2.78
B7	Batch 2, 8HS weave	230 + 4(20), C/SiC ml	2.75
B9	" " "	" " "	2.85
B17	Batch 3, 8HS weave	50, monolayer	2.80
B18	" " "	" " "	2.73
2D-GE	Ref., 5HS weave	150, monolayer	2.69

Table 2. Disc Samples (2-probe transverse EC)

Code	Type	thickness PyC (nm)	Bulk Density (g/cc)
D1	Batch 1, 5HS weave	180 + 4(20), C/SiC ml	2.71
D8	Batch 2, 8HS weave	230 + 4(20), C/SiC ml	2.79
D12	Batch 3, 8HS weave	50, monolayer	2.73
2D-GE	Ref., 5HS weave	150, monolayer	2.69

In Figures 1(a-d), an optical micrograph of a polished transverse cross-section of the Hyper-Therm 2D-SiC/CVI-SiC composite with 50-nm monolayer PyC fiber coatings shows the general spacing of the fabric-layered interior region and the adherent, ~50 μ m thick outer SiC seal coat layers (1a); and SEM views that show details of a damaged polished surface cut into the interior fabric-layered region (1b) and the continuous PyC interconnectivity along individual fibers or an intermittent PyC interconnectivity between neighboring fibers within the yarn bundles (1c) or between neighboring fibers (1d). In particular, (1b) shows that a serious amount of surface damage occurred to the surface cut into the fabric-layered interior region even though extreme care was taken during final polishing. When the SiC matrix covering an in-plane fibers became too thin it sometimes broke away from the underlying fiber. Nevertheless, a number of direct Ni metal-PyC fiber coating contacts occurred at such an interface.

In Figure 2, the in-plane EC(T)-values from RT to ~800°C measured using the 4-probe method for the bar samples listed in Table 1 are given. The slight deviation from a smooth curve observed for sample discs B7 and B9 is thought to be an artifact due to the automated data acquisition system. Also, the cooling legs of each 800°C temperature cycle were reproducible with the heating legs for all of the samples, so for clarity only the values determined for the decreasing temperature leg are presented here.

In Figure 3, the measured electrical resistance values, R(T), in the transverse direction for the disc samples listed in Table 2 with and without SiC seal coat are given. For each disc sample, the two curves represent total resistances (including contact resistances) across the samples with the SiC seal coat intact (dashed) and with the seal coat removed (solid).

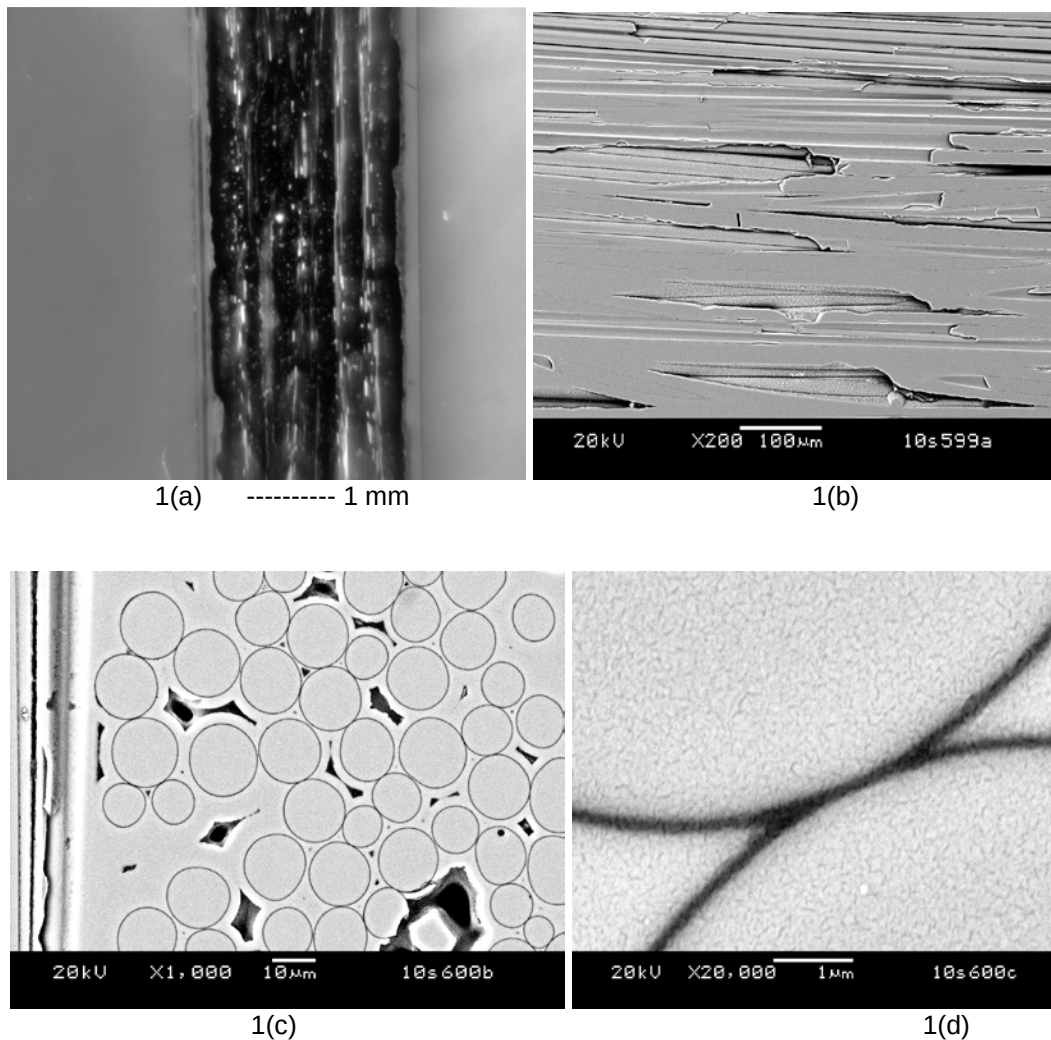


Figure 1(a-d). An optical micrograph of a polished transverse cross-section of the Hyper-Therm 2D-SiC/CVI-SiC composite with the thin monolayer PyC fiber coatings that shows the general spacing of the fabric-layered interior region and the adherent SiC seal coat layers (a); and SEM views that show details of a damaged polished surface cut into the interior fabric-layered region (b) and the continuous PyC interconnectivity along individual fibers or intermittent PyC interconnectivity between neighboring fibers within the yarn bundles (c) or between neighboring fibers (d). Backscatter electrons were used for the SEM views, so the carbon layers are dark and a little fuzzy. The CVI-SiC matrix and fiber components (Nicalon™ type S fiber is ~99% polycrystalline SiC) appear light grey.

In Figure 2, the in-plane $EC(T)$ -values from RT to ~800°C measured using the 4-probe method for the bar samples listed in Table 1 are given. The slight deviation from a smooth curve observed for sample discs B7 and B9 is thought to be an artifact due to the automated data acquisition system. Also, the cooling legs of each 800°C temperature cycle were reproducible with the heating legs for all of the samples, so for clarity only the values determined for the decreasing temperature leg are presented here.

In Figure 3, the measured electrical resistance values, $R(T)$, in the transverse direction for the disc samples listed in Table 2 with and without SiC seal coat are given. For each disc sample, the two curves

represent total resistances (including contact resistances) across the samples with the SiC seal coat intact (dashed) and with the seal coat removed (solid).

Analysis and discussion

The in-plane EC(T)-data in Fig. 2 appear to exhibit three general features: (1) the in-plane EC-value curves all lie roughly parallel to each other and exhibit a similar temperature dependence with the EC-values gradually increasing as temperature increases; (2) the in-plane EC-values for each pair of bar samples with the same PyC fiber coating total thickness were reproducible within a few percent; and (3) a marked decrease in EC-values occurred as the PyC fiber coating thickness decreased from 310 nm down to 50 nm (at RT, ~800 S/m for 310-nm PyC, 450 S/m for 260-nm PyC, 325 S/m for 150-nm PyC, and 150 S/m for 50-nm PyC, respectively). The in-plane EC(T)-values for all the bar samples were higher than observed for monolithic CVD-SiC (see Fig. 5), and exhibited a much shallower temperature dependence than CVD-SiC (~100 S/m at 800°C down to 1 S/m at RT). As previously hypothesized [5], the in-plane EC(T) for 2D-SiC/CVI-SiC primarily depends on the thickness of the relatively continuous, high conductivity PyC coatings on the fiber bundles aligned parallel to the conduction direction even though the amount of carbon is only a few percent, and not so much on the electrical conductivity of the CVI-SiC matrix.

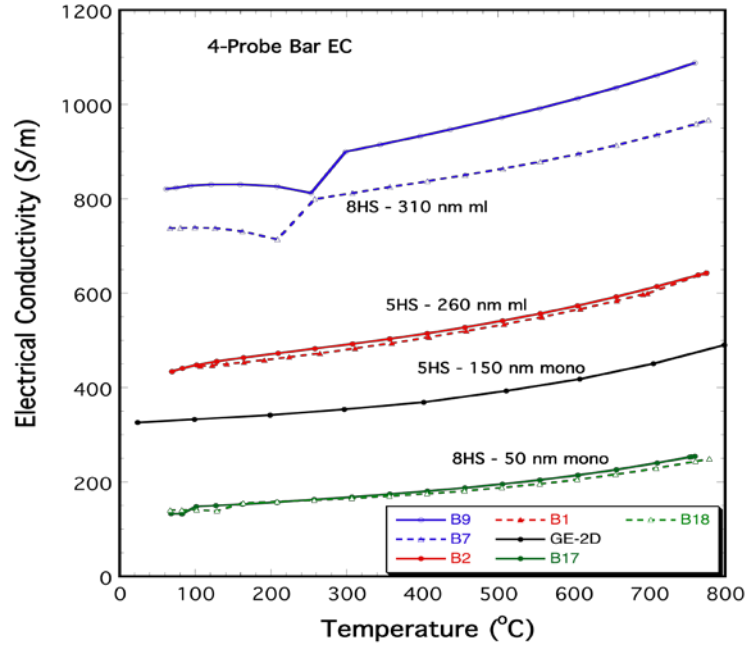


Figure 2. In-plane EC(T)-values for representative 2D-SiC/CVI-SiC bar samples (see Table 1) with 0/90 weave. The total PyC thicknesses for each grouping were 310 nm (multilayer), 260 nm (multilayer), 150 nm (monolayer), and 50 nm (monolayer), in descending order. A 4-probe dc method was used.

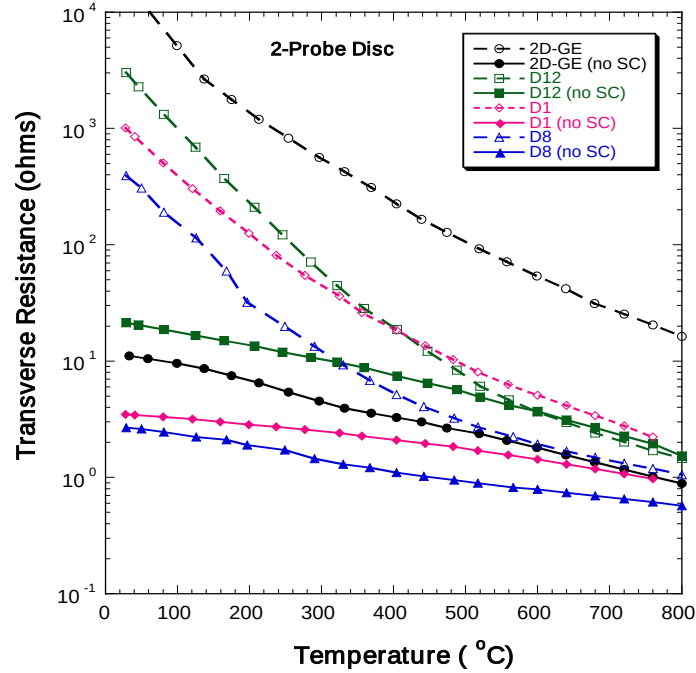


Figure 3. Transverse electrical resistance values as a function of temperature for the 2D-SiC/CVI-SiC disc samples listed in Table 2 with the SiC seal coat intact (open symbols) and removed (closed symbols). A simple 2-probe dc method was used.

In Figure 3, at room temperature the absolute transverse electrical resistance values for the representative disc samples with different total PyC fiber coating thicknesses (see Table 2) and with their SiC seal coats intact (dashed lines, open symbols) were much higher than corresponding values for the same samples with their seal coats removed (solid lines, closed symbols). Also, the high values ($\sim 10^4$ - 10^3 ohms) decreased dramatically with temperature increasing up to 800°C until the resistance values were only slightly more than the values observed for the samples with seal coats removed (~ 1 -10 ohms).

This difference is attributed to a large contact resistance, especially at lower temperatures, inherent when using a 2-probe dc measuring method. In our case, use of a 2-probe method is dictated by the small size of the disc samples used (~ 1 cm dia.) and the inhomogeneous nature of 2D-SiC/SiC made with stacked layers of woven fabric. A 4-probe method could not possibly be connected to measure uniform potential drops across such a thin, inhomogeneous disc-shaped sample. Because of the inhomogeneous nature of these samples, even a guarded ring method would be subject to the influence of non-uniform current distribution and contact resistance.

Apparently, grinding off the dense SiC seal coat into the fabric-layered interior region of the composite considerably reduced the contact resistance by exposing the carbon networked interior region. Then the applied porous Ni electrodes made good electrical contact through the exposed carbon network. Although the thin SiC seal coat itself contributes a small amount to this difference in resistance, most of the separation is due to contact resistance at the electrode-SiC interface. If the small contact resistance for the “no SC” case is ignored (estimated previously to be $\sim 1 \Omega\text{cm}^2$), the contact resistance (R_c) can be estimated for resistances in series as

$$R_c \sim R_{\text{tot}} - R_{\text{int}} - 2r$$

q. [2]

where R_{tot} and R_{int} are the measured resistances across a disc sample with seal coat intact or ground off, respectively; and r is the calculated resistance for the thin SiC seal coat layer on each disc.

We calculated r for a seal coat layer 50 microns thick when using $EC(T)$ -values measured in our lab for high-purity CVD-SiC [3]. The specific $R_c(T)$ -values (in Ωcm^2) estimated from Eq. [2] are shown in Fig. 4.

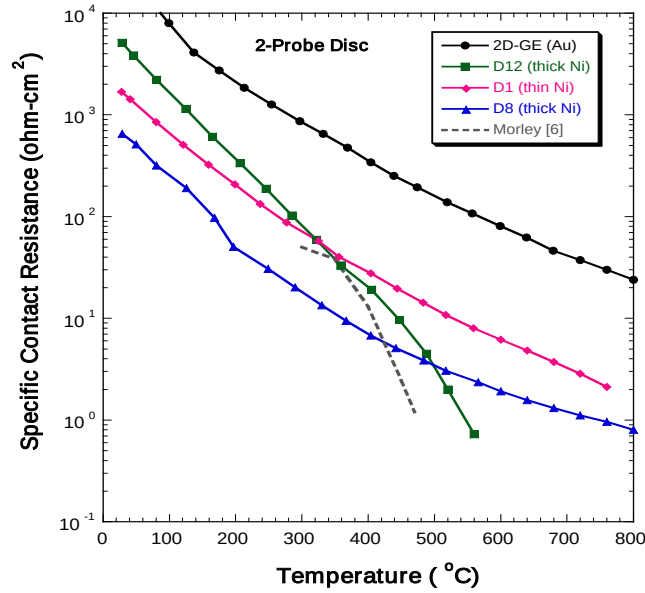


Figure 4. Estimated $R_c(T)$ from Eq. [2] for 2D-SiC/SiC disc samples: 2D-GE (evaporated Au electrodes), D1 (thin porous Ni electrodes), and D8 and D12 (thick porous Ni electrodes). For comparison, the data from Morley [6] for a liquid Pb-Li electrode on monolithic CVD-SiC are shown in dashed gray.

In Figure 4, the specific $R_c(T)$ -values decrease rapidly with increasing temperature from $> 10^4 \Omega\text{cm}^2$ at RT to $\sim 1\text{-}20 \Omega\text{cm}^2$ at 800°C . Also, the R_c -values depended sensitively on the type of electrodes used with values for the evaporated Au electrodes being significantly larger than those for porous Ni electrodes, and the values for thin porous Ni electrodes larger than those for thicker electrodes (except for sample D12, see below). Obviously, the contact resistance is large for samples with metal electrode-pure SiC interfaces, especially at low temperatures, and will seriously affect $EC(T)$ -values when using a 2-probe method.

The specific $R_c(T)$ -values depicted in Fig. 4 are subject to error, especially at lower temperatures, as the actual values for $EC(T)$ for the SiC seal coat are not known. More importantly, at higher temperatures the contact resistance at the electrode-carbon networked interior region was ignored in Eq. [2]. Even though small it is possible that its absolute value is about the same magnitude as the sample resistance and should not be ignored. The latter situation appears to have occurred for disc sample D12 where the surface of the cut region was damaged due to pullouts during final polishing (see Fig. 1b), and likely accounts for the larger than expected $R_c(T)$ -values observed at lower temperatures and the unusually steep downward sloping temperature dependence at higher temperatures. For this damaged surface condition, the number of actual direct contacts of the thin (~ 50 nm) PyC coating layers with the porous Ni electrodes likely were reduced, and a larger than normal contact resistance due to current restrictions at the electrode interfaces developed. For the disc samples with thicker PyC coating layers, the final

polished surfaces did not exhibit such extensive damage; the corresponding contact resistance values for the metal-carbon networked interior region likely were small enough so that Eq. [2] was valid.

Also, shown in Figure 4 are some estimated specific $R_c(T)$ -values observed by Morley for 2-probe dc measurements on CVD-SiC with molten lead-lithium eutectic (LLE) electrodes, as would be the case for an operating FCI-structure [6]. Morley made measurements for three similar set-ups and observed significant contact resistances ranging from 1-100 Ωcm^2 when samples first came into contact with LLE near its melting point, the contact resistances decreased as the samples were further heated, and the resistances varied markedly from sample to sample, presumably depending on small variations in disc preparation. The magnitude of our values of $R_c(T)$ compare reasonably well with those values reported by Morley. Unlike Morley's observations with liquid metal electrodes, our $R_c(T)$ -values for solid Au or porous Ni electrodes generally were reproducible with temperature cycling from RT-800°C. Initially, we made measurements for three successive heating-cooling temperature cycles. We observed reproducibility of the $EC(T)$ -values, so made measurements for a single temperature cycle thereafter. The reproducibility continued to be observed for each leg of the heating-cooling cycle. For the liquid Pb-Li metal electrodes, the contact resistance was time dependent; it likely depended on the degree of wetting with the SiC surface. For our porous Ni (or Au) electrodes, the contact resistance was time independent; it depended on the physical nature of a metal/semi-conductor interface as well as the quality of the SiC seal coat and its surface condition.

As stated earlier, the easiest way to obtain effective transverse $EC(T)$ -values is to measure $EC_{\text{int}}(T)$ by a 2-probe dc method, hopefully with a minimum influence of contact resistance, and use Eq. [1]. In Figure 5, the estimated $EC(T)$ -values from Eq. [1] (solid curves, closed symbols) are compared to the measured $EC_{\text{int}}(T)$ -values (dashed curves, open symbols) for the four samples with different thicknesses of PyC fiber coating (D8 with 310-nm PyC, D1 with 260-nm PyC, 2D-GE with 150-nm PyC, and D12 with 50-nm PyC). For reference, the measured $EC(T)$ -values for a high-purity monolithic CVD-SiC (values used to estimate the effects of the SiC seal coat) also are included in Fig. 5. Figure 5 in this report is the same as Fig. 5 in Ref. [5], except the new data for disc sample D12 has been added.

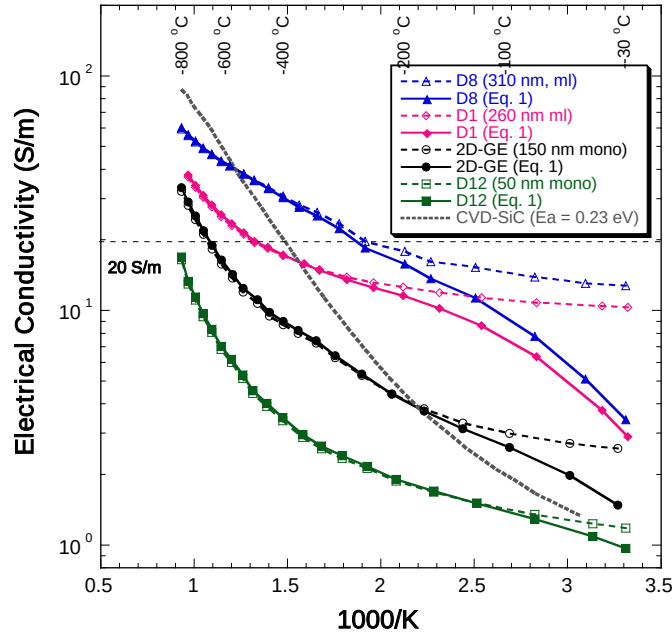


Figure 5. Transverse $EC(T)$ predicted by using Eq. [1] (solid lines) and measured $EC_{\text{int}}(T)$ with minimum contact resistance (dashed lines) for four types of 2D-SiC/CVI-SiC. Samples D8 (8HS weave) and D1

(5HS weave) had multilayer PyC/SiC fiber coatings (~310-nm and 260-nm total PyC thickness, respectively), and 2D-GE and D12 (5HS and 8HS weave, respectively) had single layer PyC fiber coatings (~150-nm and 50-nm PyC thickness, respectively). EC(T)-values measured for a high-purity monolithic CVD-SiC with effective activation energy of 0.23 eV also are shown (grey dashed line).

As before [5], for $T > \sim 300^\circ\text{C}$ the predicted EC(T)-values are approximately the same as the measured $EC_{\text{int}}(T)$ -values for each corresponding sample. For $T < \sim 300^\circ\text{C}$, predicted EC(T)-values begin to deviate more and more below the corresponding sample $EC_{\text{int}}(T)$ -values as the temperature decreases. Also, at high temperatures the temperature dependence (slopes of the EC(T)-curves) approaches but remains somewhat less than that of CVD-SiC, at moderate temperatures the slopes are less and deviate more from those of CVD-SiC, and at low temperatures the temperature dependence again approaches that of CVD-SiC. These observations are interpreted: at high temperatures electrical conduction through the SiC matrix and fiber components dominates, at moderate temperatures conduction through the interconnected PyC fiber coating network dominates, and at sufficiently low temperatures conduction becomes limited by the SiC seal coat.

Also, suggested as a possibility in Ref. [5], the predicted transverse EC-values for a 2D-SiC/CVI-SiC composite with a relatively thin (50 nm) PyC fiber coating were below the FCI-application design limit of 20 S/m for all temperatures up to 800°C .

It is instructive to examine the dependence of the rate of increase of the transverse EC on the total PyC fiber coating thickness. In Figure 6, the ratio of the transverse EC-value for each disc (solid lines) and bar (dashed lines) sample with the corresponding EC-values of the disc or bar sample with a 50-nm thick PyC coating is plotted against the ratio of the total PyC coating thickness for each sample type to 50 nm for two temperatures, a high 700°C (shown in red) and a low 200°C (shown in blue).

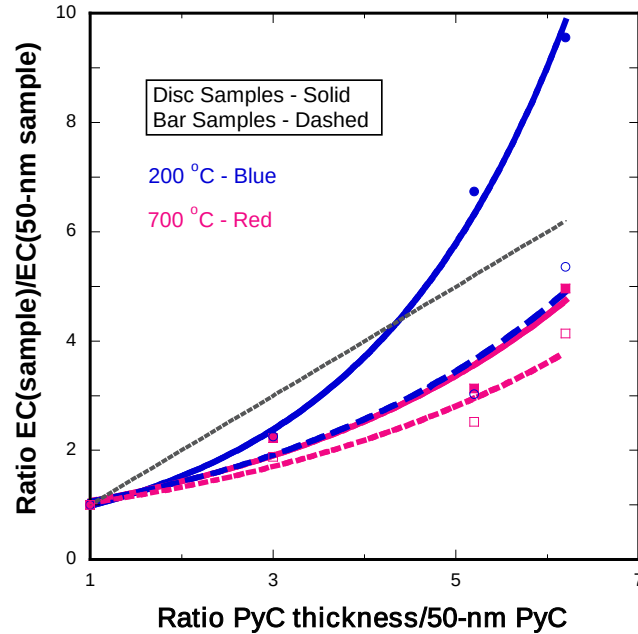


Figure 6. Dependence of transverse (solid lines) and in-plane (dashed lines) EC of 2D-SiC/CVI-SiC on total PyC fiber coating thickness at two temperatures (200°C in blue and 700°C in red). The dashed gray line indicates direct proportionality. For guidance, an exponential curve was fit to the data points.

In Figure 6, at either the representative low (200°C) or high (700°C) temperatures, the bar sample EC-ratio curves lie below the direct proportionality line. This is because the almost continuous CVI-SiC matrix, which amounts to ~90% of the composite volume, also contributes to the over all in-plane EC. Also, the 700°C curve lies above the 200°C curve, which indicates that the SiC matrix EC contribution becomes more important at higher temperatures, as expected for semi-conducting SiC. For the disc sample EC-ratios, the low temperature curve lies below the direct proportionality line, while the high temperature curve starts out below the proportionality line but increasingly tends to exceed the proportionality line as the total PyC thickness increases above 150 nm or so. Apparently, the interconnectivity of the PyC coating network plays an increasingly more important role as the coating thickness increases. Of course, the multilayer PyC/SiC coatings may also result in additional interconnectivity of the carbon network.

CONCLUSIONS

1. The contact resistance is large when using a 2-probe method to measure transverse EC(T) through a 2D-SiC/CVI-SiC plate with a SiC seal coat. The simplest way to estimate these EC(T)-values is to use the 2-probe method to measure $EC_{int}(T)$ of disc samples with seal coat ground off and then calculate EC(T) using Eq. [1]. The effect of contact resistance will be minimized when measuring $EC_{int}(T)$ because now the metallic electrodes make good electrical contact with the highly conductive PyC fiber-coating network with numerous intersections at the ground surfaces. However, to actually minimize the contact resistance for 2D-SiC/CVI-SiC composite with its SiC seal coat ground off extreme care is necessary when preparing the cut interior surfaces to minimize polishing surface damage.
2. The newly predicted transverse EC(T)-values for a 2D-SiC/CVI-SiC composite with a relatively thin 50 nm monolayer PyC fiber coating were below the desired FCI-application limit of 20 S/m for all temperatures up to 800°C.
3. The in-plane EC(T)-values for the 2D-SiC/CVI-SiC composites with similar fabric weaves but with different PyC fiber coating thicknesses ranged from ~100 to 1000 S/m for total PyC thickness ranging from 50 to 310 nm, respectively. Furthermore, the temperature dependences were much shallower than observed for pure SiC over the RT to 800°C temperature range (~0.1-100 S/m, respectively). This occurs because the in-plane EC is dominated by conduction along the continuous PyC fiber-coating network lying mostly parallel to the in-plane conduction direction. Also, in-plane EC-values were 10-100 times larger than transverse EC-values, as expected for these 2D materials.
4. The EC in the transverse direction for 2D-SiC/CVI-SiC with PyC fiber coatings is strongly controlled by conduction through the interconnections of the carbon network within and between fiber bundles, especially at moderate temperatures (~300°C to 700°C). For higher temperatures, the EC of the SiC matrix plays an increasingly more important role; while at lower temperatures the low EC-values for the SiC seal coat become important.
5. The in-plane EC(T)-values for 2D-SiC/CVI-SiC depend primarily on the high conductivity PyC network pathways, however the almost continuous parallel conduction pathways through the CVI-SiC matrix also contribute. The magnitude of the transverse EC(T)-values depends more on the interconnectivity of the PyC network between fabric layers and within the fiber bundles. The degree of interconnectivity increases for composite with thicker PyC fiber coatings or with multilayer SiC/PyC coatings.

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COMPARATIVE STUDY OF TENSILE PROPERTIES OF UNI-DIRECTIONAL SINGLE-TOW SiC-MATRIX COMPOSITES REINFORCED WITH VARIOUS NEAR-STOICHIOMETRIC SiC FIBERS

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OBJECTIVE

A procedure for evaluating mechanical properties of SiC/SiC mini-composite samples was established, with specific consideration of minimizing the personnel exposure during testing of radiological samples. In the course of the test procedure development, unirradiated CVI SiC matrix mini-composite samples reinforced with four different near-stoichiometric SiC fibers were evaluated.

SUMMARY

Four types of mini-composites (with variations in fiber and interphase but with the same SiC matrix) were evaluated for tensile and fiber/matrix interfacial properties. The composites reinforced with Hi-Nicalon™ Type-S (HNLS), Tyranno™-SA3 (SA3), experimental Sylramic™ and Sylramic-iBN fibers exhibited ultimate tensile stresses equivalent to ~77, ~53, ~69, and ~81% of the single fiber strength at 25 mm, respectively. The ultimate tensile stress appeared to increase with the estimated interfacial sliding stress, with the exception of the HNLS composite. The sliding stress increased with increasing fiber surface roughness. The HNLS composite exhibited the high tensile strength, likely because the very low interfacial sliding stress enabled global load sharing. The SA3 and Sylramic composites exhibited premature failure, attributed to the very high interfacial sliding stresses due primarily to the physical roughness of the fiber surfaces. More compliant interphases would optimize these fiber composites with unidirectional architecture.

PROGRESS AND STATUS

Introduction

Silicon carbide (SiC) -based ceramics and composites (SiC/SiC) are considered for applications in various components of fusion and advanced fission reactor systems and fuel assemblies, due primarily to their superior irradiation performance and thermo-physical, -chemical, and -mechanical properties [1, 2]. Continuous SiC-fiber, SiC-matrix composites are of particular importance for applications which require reliability, toughness, and near-net shape fabrication.

One focus of irradiation studies of SiC/SiC composites in the past few decades has been determination of the fundamental response of the materials produced with various constituent options and processing routes. Through this effort, composites containing near-stoichiometric SiC fibers, such as Tyranno™-SA3 (SA3) and Hi-Nicalon™ Type-S (HNLS), and high crystallinity SiC matrices produced by chemical vapor infiltration (CVI) or nano-infiltration and transient eutectic-phase (NITE) processes are found to possess acceptable irradiation stability. However, a design scheme for the optimum interphase for radiation service remains unresolved due primarily to the lack of understanding of the irradiation effects on the fiber/matrix interfacial properties.

The use of mini-composites, which are composites uni-directionally reinforced with a single fiber tow, is an appropriate approach for evaluating the interfacial properties [3]. The general advantages of the mini-composite approach are as follows: 1) due to its simple uni-directional fiber architecture, the in-situ fiber strength and interfacial properties can be determined in relatively simple ways [4, 5], and 2) a large number of specimens can be fabricated at a low cost in relatively a short time. Moreover, the very small volume of the mini-composite samples is attractive for irradiation studies due to the very high unit-volume cost of irradiation and the radiological concerns associated with the evaluation of irradiated material.

In the present work, a procedure for evaluating mechanical properties of SiC/SiC mini-composite samples was established at Oak Ridge National Laboratory, with specific consideration of minimizing the personnel exposure during testing of the radiological samples. In the course of the test procedure development, CVI SiC matrix mini-composite samples reinforced with four different near-stoichiometric SiC fibers were evaluated in the unirradiated condition.

Experimental Procedure

Materials

Table I describes the mini-composites; optical micrographs of polished cross sections of each mini-composite are shown in Fig. 1. In brief, four types of unidirectional single-tow mini-composites were prepared in this study. Tyranno-SA3, Hi-Nicalon Type-S, experimental Sylramic™ and experimental Sylramic™-iBN SiC fibers were used as reinforcement. The Sylramic-iBN, made from Sylramic, is a fiber with the excess boron used as a sintering aid removed from the fiber bulk. This boron formed a thin in-situ BN coating on the fiber surface, in order to improve thermo-structural and -chemical properties [6]. The unidirectional mini-composites were fabricated by the CVI process at Hyper-Therm High-Temperature Composites, Inc. (Huntington Beach, California). During the CVI process, the fiber bundle was held so that the cross sectional area of a mini-composite was minimized and the shape of the cross section was close to a circle, as shown in Fig. 1. The fiber/matrix (F/M) interphase was single layer pyrolytic carbon (PyC) with a nominal thickness of 150 nm. The PyC interphase coating was not applied to the experimental Syl-iBN composite. Hereafter, the IDs indicated in Table I (SA3 for Tyranno-SA3 (UD)/150nm-PyC/CVI, HNLS for Hi-Nicalon Type-S (UD)/150nm-PyC/CVI, Syl-PyC for experimental Sylramic (UD)/150nm-PyC/CVI, and Syl-iBN for experimental Sylramic-iBN (UD)//CVI mini-composite) are used in this paper.

Table I: Properties of mini-composites used in this study. Nominal mechanical properties of SiC fibers are also listed as supplied by the manufacturers.

ID	Fiber	Int.	Matrix	r [μm]	N	f [%]	σ_f [GPa]	E_f [GPa]	ε_f [%]
HNLS	Hi-Nicalon Type-S	150 nm PyC	CVI	12	500	45-50	2.6	420	0.6
SA3	Tyranno-SA3	150 nm PyC	CVI	7.5	1600	42-47	2.8	409	0.7
Syl-PyC	Exp-Sylramic	150 nm PyC	CVI	10	800	43-50	3.0	380	0.8
Syl-iBN	Exp-Sylramic-iBN	n/a	CVI	10	800	44-47	3.0	380	0.8

Int. denotes interphase, r the fiber diameter, N the number of filaments in a tow, f the fiber volume fraction, σ_f the single fiber strength at 25 mm, E_f the fiber modulus, ε_f the fiber elongation, *PyC* pyrolytic carbon, *CVI* chemical vapor infiltration, and *exp* experimental.

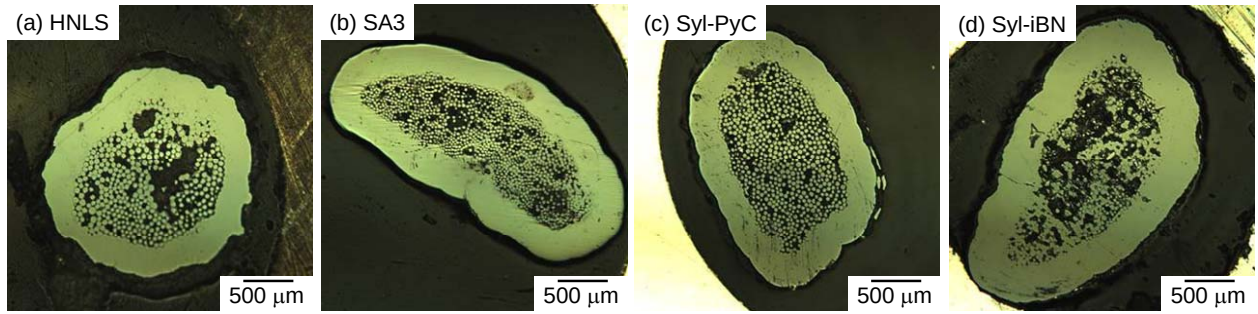


Figure 1: Optical micrographs of polished cross sections of (a) HNLS, (b) SA3, (c) Syl-PyC, and (d) Syl-iBN mini-composites.

Tensile Tests

The test apparatus is shown in [Fig. 2](#). The tensile tests were conducted using an electromechanical testing machine (Insight 10, MTS Systems Co., Eden Prairie, Minnesota) with a load capacity of 10 kN. Strain was measured by a pair of linear variable differential transducers, LVDTs (Lucas Schaevitz GCA-121-125, Hampton, Virginia). We adopted an alignment system similar to the one used in single fiber tensile testing standardized in ASTM C 1557 in order to assure specimen alignment.

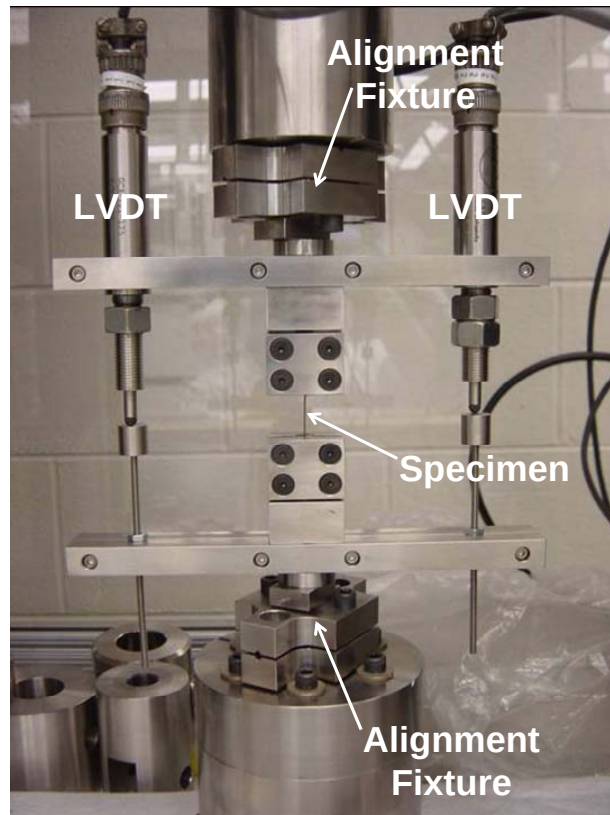


Figure 2: Mini-composite tensile test apparatus used in this study.

Figure 3 is a drawing of a specimen and aluminum tabs. A pair of aluminum tabs was fastened to the ends of a mini-composite sample using an epoxy adhesive dispersed by a syringe. In order to assure specimen alignment, the specimen to be glued was fixed in a V-notched fixture with flathead screws, as shown in Fig. 4. A polyethylene spacer sheet and/or the combination of a silicon release spray and a silicone remover were used to remove the specimen from the fixture after epoxy curing. This fixture including the specimen was cured at 110°C for more than 3 hours in an air furnace in order to develop the adhesive's maximum bonding strength. The gauge length of the specimens is 18 mm, defined by the distance between the inner ends of the aluminum tabs. Figure 5 shows the gripping fixture and the guide rail provided for alignment. The specimen was clamped into the simple V-notched fixtures with flathead screws. The guide rail was used to confirm specimen alignment and to avoid damaging the specimen during handling.

The tests were conducted at ambient conditions under crosshead displacement control at 0.1 mm/min. Unloading/reloading cyclic tensile tests were conducted to evaluate interfacial properties. Previous to the tensile tests, compliance of the grip assembly was determined using a set of tungsten wires with various gauge lengths. As a result, the system compliance of $1.32 \times 10^2 \mu\text{m/N}$ was obtained as shown in Fig. 6. Tensile strain is determined by the following equation, $\varepsilon = (\Delta L - C_s P)/L_0$, where ε is the tensile strain, ΔL the average cross-head displacement recorded by LVDTs, C_s the system compliance, P the applied load, and L_0 the gauge length. The fiber volume fraction (f) of the mini-composites was determined by a combination of optical microscopy and image analysis. It is noted that some errors may have been introduced due to surface damage during polishing. The mini-composite tensile stress (σ) is defined by $\sigma = P/(\pi r^2 N/f)$, with r the average fiber radius, and N the number of filament in a tow. The proportional limit load or proportional limit stress (PLL or PLS) was defined as the stress at 0.5% deviation from the extrapolated fit of the slope by the least squares method for the initial loading.

After the tensile tests, the fracture surfaces of the specimens were examined using a scanning electron microscope (SEM, Topcon SM-510, Paramus, New Jersey). Fiber pull-out length and matrix crack spacing were also measured, in order to estimate the interfacial sliding stress. This study included only tensile tests on unirradiated composites, but identical procedures will be used in experiments on irradiated material.

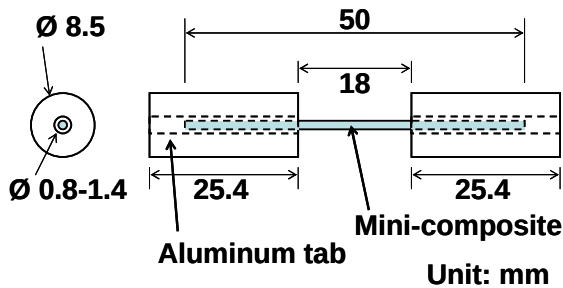


Figure 3: Dimension of a mini-composite and a pair of aluminum tabs.

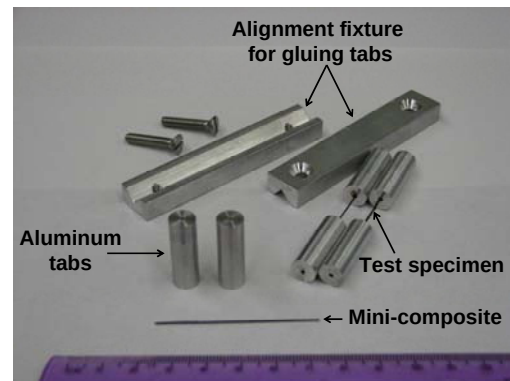


Figure 4: Mini-composite, aluminum tabs and alignment fixture for gluing tabs.

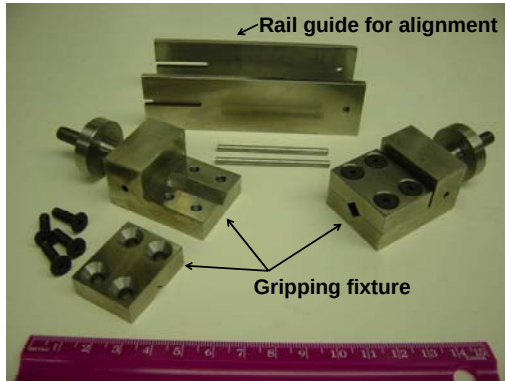


Figure 5: Gripping fixture and rail guide for specimen alignment.

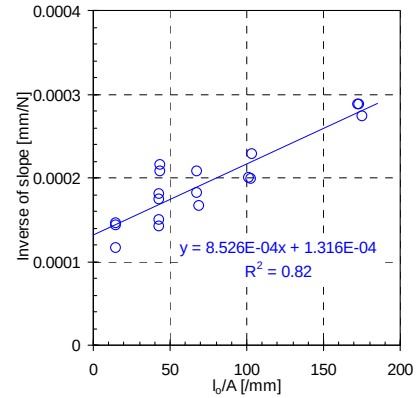


Figure 6: Machine compliance of the mini-composite tensile system. l_0 and A denote the gauge length and the cross-sectional area of the specimen.

Results and Discussion

Tensile Load-Strain Responses

Representative load-tensile strain curves for the four mini-composites are shown in Fig. 7, and the mechanical properties of the mini-composites are listed in Table II. As shown in Fig. 7 (a), the HNLS mini-composites exhibited a typical pseudo-ductile fracture behavior; there was an initial steep linear region in the load-strain curve, with a second, nearly linear region at higher strains, repeated during tensile loading with multiple unloading-reloading sequences. The initial linear portion corresponds to the linear elastic deformation of the mini-composite, whereas the second linear portion corresponds to a process of progressive development and opening of multiple matrix micro-cracks. The SA3 mini-composites exhibited more brittle behavior, with narrower hysteresis loop width ($\sim 0.02\%$) and smaller elongation after the PL (an average of 0.174% for the fracture strain), compared to the HNLS mini-composites. The Syl-PyC and Syl-iBN composites exhibited rather brittle failure. The overall behavior of these mini-composites is similar to the SA3 mini-composite, implying fiber properties comparable to Tyranno-SA3 at room temperature. Of importance is the fiber strength (the RS values in Table II.). In the overall composite strength, 69% of Sylramic and 81% of Sylramic-iBN fiber strength was achieved in the mini-composite system; this compares the HNLS (77%) and the SA3 (53%). This result indicates that the experimental fibers are capable of bearing loads similar to the two near-stoichiometric SiC fibers which are currently commercially available.

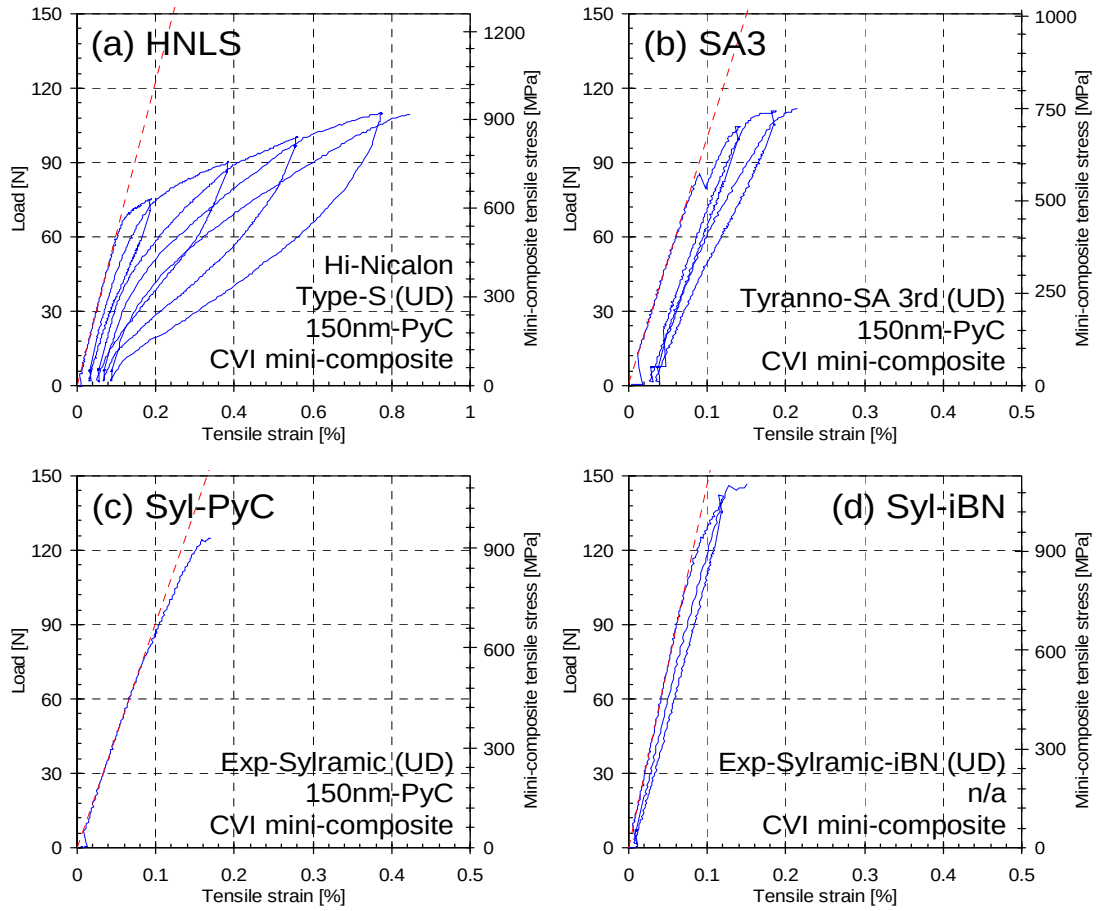


Figure 7: Representative tensile load-strain curves for (a) HNLS, (b) SA3, (c) Syl-PyC, and (d) Syl-iBN mini-composites. Note that the tensile strain axis is different for each mini-composite.

Table II: Tensile test results for the mini-composites. Numbers in parenthesis show standard deviations.

ID	Fiber	Int.	Matrix	P_f [N]	P_p [N]	ε_{fr} [%]	ε_p [%]	σ_U [MPa]	σ_p [MPa]	σ^T [MPa]	RS [%]	#
HNLS	Hi-Nicalon Type-S	150 nm PyC	CVI	113 (5)	67 (4)	0.877 (0.029)	0.152 (0.011)	923 (31)	552 (34)	-303 (75)	77 (3)	4
SA3	Tyranno-SA3	150 nm PyC	CVI	105 (6)	80 (8)	0.270 (0.072)	0.114 (0.041)	676 (52)	513 (51)	-110 (121)	53 (3)	4
Syl-PyC	Exp-Sylramic	150 nm PyC	CVI	130 (7)	91 (11)	0.201 (0.044)	0.121 (0.006)	958 (40)	675 (91)	-73 (-)	69 (4)	2
Syl-iBN	Exp-Sylramic-iBN	n/a	CVI	153 (10)	112 (18)	0.174 (0.033)	0.099 (0.012)	1115 (17)	819 (168)	0 (-)	81 (5)	2

P_f denotes the load at fracture, P_p the load at proportional limit (PL), ε_{fr} the strain at fracture, ε_p the strain at PL, σ_U the ultimate tensile strength, σ_p the PL stress, σ^T the misfit stress, RS the relative strength of the mini-composite to the single fiber strength, and # the number of tests.

SEM observation

Figure 8 shows SEM images of the fracture surface of each mini-composite. Table III lists the result of the

average fiber pull-out length determination. Shorter pull-out lengths ($\sim 100\ \mu\text{m}$) were measured in SA3 and Syl-PyC compared to the HNLS ($\sim 300\ \mu\text{m}$), while very short pull-out length ($\sim 15\ \mu\text{m}$) was obtained in Syl-iBN (HNLS > SA3 $\sim$ Syl-PyC > Syl-iBN). In order to measure the matrix crack spacing, the fractured specimen was mounted on a glass platen with an epoxy adhesive and polished longitudinally, but unfortunately typical matrix crack spacing could not be detected for all specimens using an optical microscope. It is believed that such typical transverse matrix cracks were not seen along the whole specimen due to the premature failure before the matrix loading reached saturation in these composite systems. Therefore, the matrix crack spacing in a fiber bundle or the distance of crack deflection near a fracture surface were used as the matrix crack spacing in this study. Examples of these determinations are shown in Fig. 9.

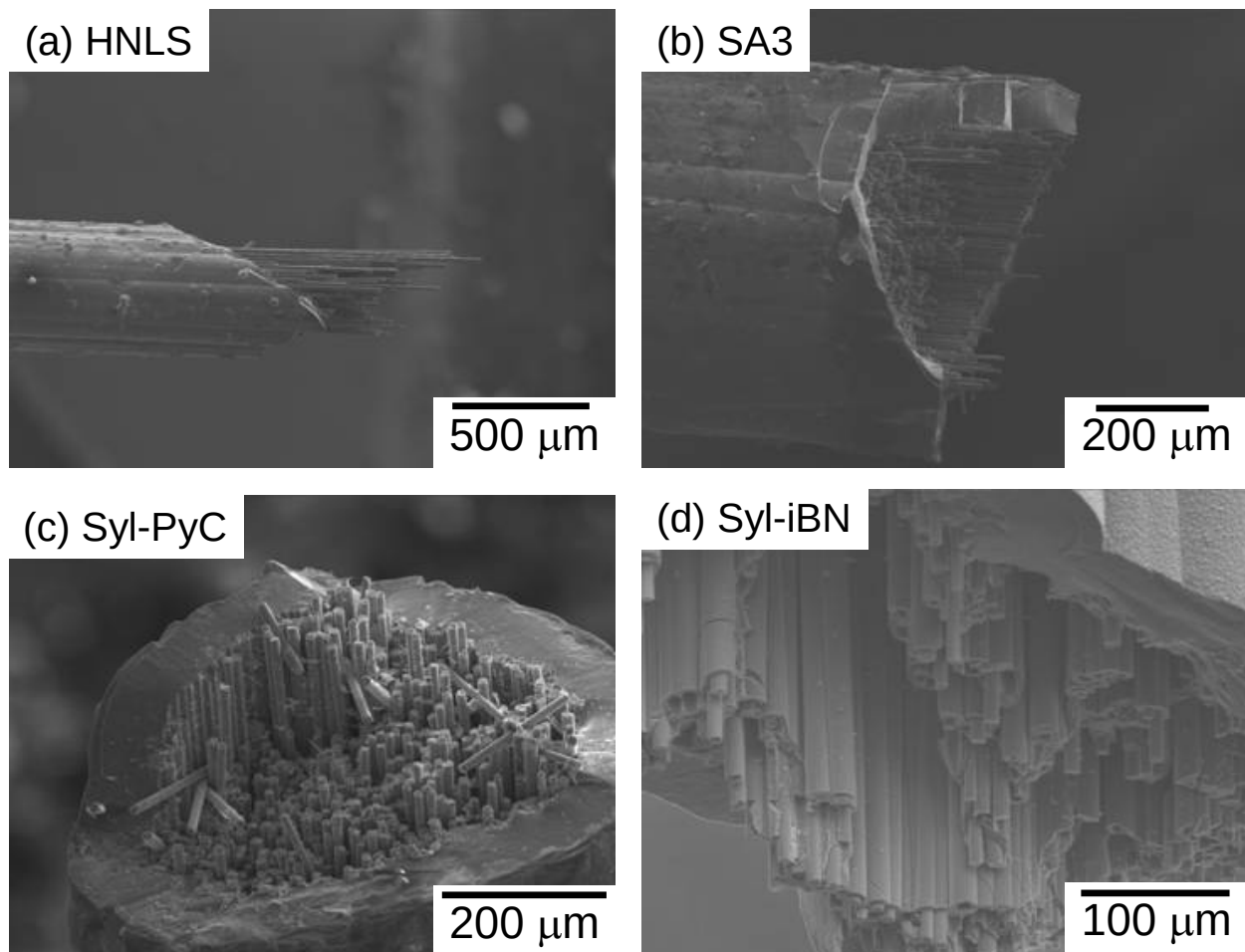


Figure 8: SEM micrographs of the fracture surfaces of the (a) HNLS, (b) SA3, (c) Syl-PyC, and (d) Syl-iBN mini-composites.

Table III: Results of the average fiber pull-out length, the average matrix crack spacing, and the interfacial sliding stress from the hysteresis loop analysis for the mini-composites.

	l_p [μm]	d [μm]	τ from Eq. (1) [MPa]	τ from Eq. (2) [MPa]	τ from Eq. (3) [MPa]
HNLS	300	~400	5	8	11-14
SA3	100	~100	85	15	15-20
Syl-PyC	100	~200	170	16	28-37
Syl-iBN	15	~50	950	73	219-287

l_p , d , τ denote the average fiber pull-out length, the average matrix crack spacing, and the interfacial sliding stress, respectively.

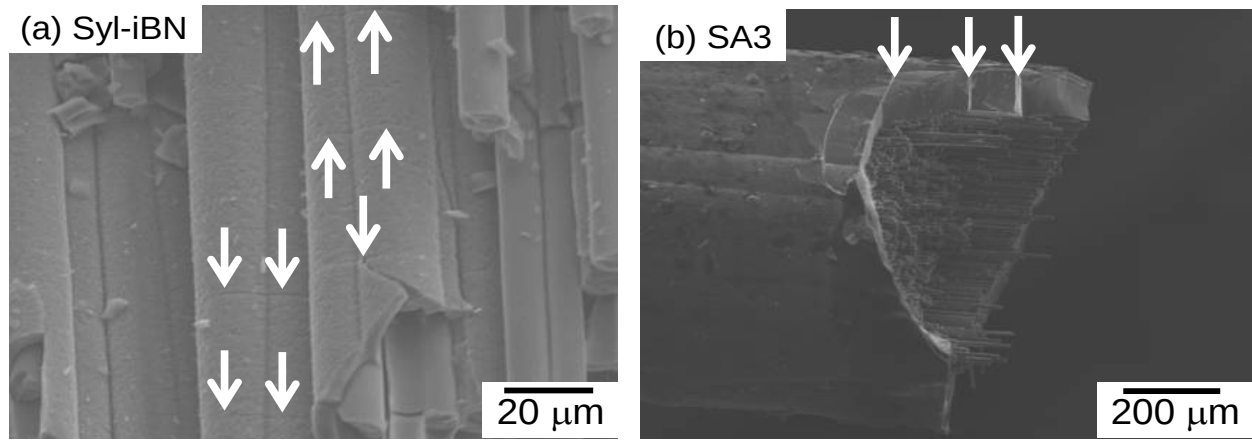


Figure 9: Examples of matrix crack spacing determination. (a) Matrix crack spacing in the fiber bundle for Syl-iBN, and (b) distance between the crack deflection at outer SiC layer for SA3.

Interfacial Sliding Stress

The interfacial sliding stress (τ) was estimated from the hysteresis loop width, the matrix crack spacing, and the fiber pull-out length. First, in the hysteresis loop analysis by Lamon *et al.* [4] and Vagaggini *et al.* [5], the interfacial sliding stress (τ) can be obtained from the following equation [4]:

$$\tau = \frac{b_2(1-a_1f)^2}{2f^2E_m} \left(\frac{r}{d} \right) \left(\frac{\sigma_p^2}{d\varepsilon} \right) \left(\frac{\sigma}{\sigma_p} - \frac{\sigma_{\min}}{\sigma_p} \right) \left(1 - \frac{\sigma}{\sigma_p} \right) \quad (1)$$

where a_1 and b_2 are the Hutchinson-Jensen parameters [7], E_m the matrix modulus, d the average matrix crack spacing, $d\varepsilon$ the hysteresis loop width, σ_p the peak stress of the hysteresis loop, σ the stress where $d\varepsilon$ is measured, and $\sigma_{\min}$ the minimum stress of the hysteresis loop. τ was determined from the hysteresis loop immediately prior to failure, assuming the same matrix crack spacing at the failure of the composite systems.

τ is also estimated using the matrix crack spacing, expressed as [8]:

$$\tau = \frac{\sigma_s r E_m (1 - f)}{2 d E f} \quad (2)$$

where σ_s is the applied stress at matrix cracking saturation. The observed result of the matrix crack spacing suggests that the mini-composites fractured before reaching matrix crack saturation, therefore the ultimate tensile stress was taken as σ_s for convenience.

The third method for estimating τ is to use the fiber pull-out length. Curtin derived the following equation to estimate the interfacial sliding stress [9]:

$$\tau = \frac{r \lambda(m) \sigma_c}{4 l_p} \quad (3)$$

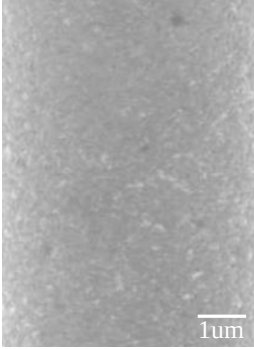
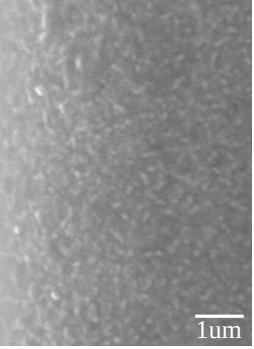
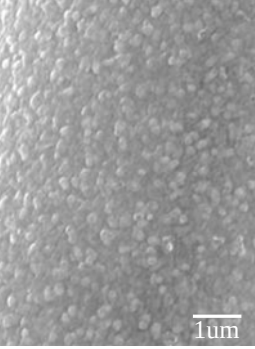
where l_p is the average fiber pull-out length, σ_c and m the in-situ fiber fracture strength and the Weibull modulus, respectively, and $\lambda(m)$ is the known function of Weibull modulus as $\lambda(m) \approx 0.716 + 1.36/m^{0.6}$ for $m \geq 1$ [10]. In this paper the fiber strength at fracture is used for the in-situ fiber fracture strength. There is limited data about the Weibull modulus of in-situ SiC fiber strength, but $m=3-9$ is assumed in Eq. (3), according to the references on in-situ strength of similar SiC fibers [10, 11].

All results for the interfacial sliding stress are shown in Table III. A relatively low value of τ is obtained for the HNLS composite and very high τ values were derived for the three other composites. Because of the relatively brittle failure experienced by these composites, it is likely that the τ values were not correctly determined. However, it is noted that the ranking of the τ values seems to be qualitatively reasonable as they are inversely correlated with the fiber pull-out length (HNLS < SA3 ~ Syl-PyC < Syl-iBN).

The three analytical methods gave very major differences in τ values. During the unloading-reloading processes in the tensile testing, as seen in Fig. 7, the stable interfacial sliding was not achieved with the exception of the HNLS composite. In such a case, it is known that the hysteresis loop analysis gives an unrealistically large sliding stress value. In the matrix crack spacing analysis, the ultimate tensile strength was used to estimate the sliding stress instead of using the stress for matrix crack saturation. Because the matrix crack saturation was obviously not achieved at the failure of the non-HNLS composites, this may have caused a slight underestimation of the sliding stress values. For the method based on the fiber pull-out length, the estimated sliding stress values may suffer substantial errors due to uncertainty in the pull-out length determination. Thus, the τ values in Table III are considered to have only qualitative significance, although those determined from the matrix crack spacing seem to be most realistic.

The interfacial sliding stress (τ is essentially the frictional stress at the sliding interface, thus should macroscopically be a product of the clamping stress and the interfacial frictional coefficient, which is closely related to the fiber surface roughness. The experimental observations with on τ values and the fiber surface roughness are summarized in Table IV. The relative value of τ is clearly dependent on the micro-topological features of the fiber surface.

Table IV: The relationship between microstructure, fiber roughness, and interfacial sliding stress of near-stoichiometric SiC fibers.

Fiber	Hi-Nicalon Type-S	Tyranno-SA3	Exp-Sylramic	Exp-Sylramic-iBN
Surface Micro-structure				
R_q [nm]	•0.87, Hinoki (2001) •2.33, Sauder <i>et al.</i> (2010) •<10, Yun <i>et al.</i> (2001)	•1.71, Hinoki (2001) •8.04, Sauder <i>et al.</i> (2010)	•~10, Yun <i>et al.</i> (2001) •17.561, Brennan (2000)	•~27, Yun <i>et al.</i> (2001)
τ [MPa]	•8, This work •14.46, Sauder <i>et al.</i> (2008)	•15, This work •223, Sauder <i>et al.</i> (2008)	•16, This work	•73, This work
Interphase	•150 nm PyC	•150 nm PyC	•150 nm PyC	•n/a (Sylramic-iBN)

R_q denotes the root mean square fiber surface roughness. References are from [6, 12-14] for the fiber roughness, and from [15] for the interfacial sliding stress.

The clamping stress, or the compressive radial stress at the interface, generally results from a combination of the mismatch in coefficient of thermal expansion (CTE) between the fiber and the matrix (possibly involving the interphase), the physical roughness of the interface, and the compliance and strength of the interphase. We have considered the clamping stress in each mini-composite system qualitatively. The clamping stress (σ_{CL}) is expressed by the following equation [16],

$$\begin{aligned}\sigma_{CL} &\sim \sigma_{CTE} + \sigma_R \\ &= \sigma_{CTE} + \frac{E_m E_f}{E_f(1+\nu_m) + E_m(1-\nu_f)} \left(-\frac{A}{r} \right)\end{aligned}\quad (4)$$

where σ_{CTE} and σ_R are the residual stress induced by CTE mismatch and the contribution of fiber roughness, the ν_m , ν_f are the Poisson's ratios of the matrix and fiber, E_f the Young's modulus of a fiber, and A the characteristic amplitude of roughness along the debonded interface. Figure 10 shows the calculated results for the residual stress of each composite system, and Table V gives the calculated result for the clamping stress in each composite system. The four phase model [17] was used to estimate σ_{CTE} . For calculation, ν_m , ν_f and A were assumed to be 0.2, 0.2 and $2R_q$, where R_q is the root mean square fiber surface roughness. The thickness of the BN layer on the Sylramic-iBN fiber was assumed to be 200 nm [6]. As shown in Table V, the contribution of fiber surface roughness is much larger than the CTE mismatch. Additionally, the clamping stress is strongly affected by the fiber surface roughness. This trend of the calculated clamping stress qualitatively corresponds to the misfit stress as described below. Therefore, it is concluded that the relationship of the tensile properties of the mini-composites studied is mainly attributed to the difference in the fiber surface roughness.

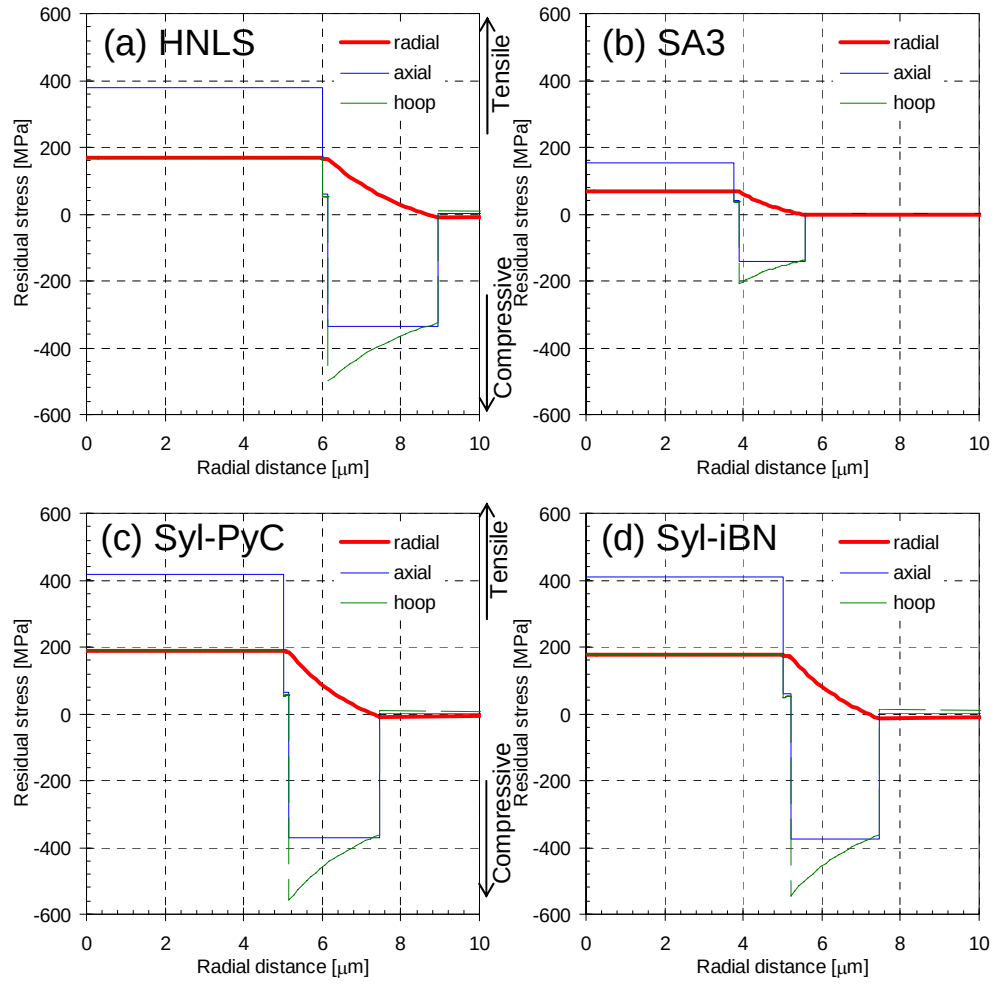


Figure 10: Residual stress analysis result for (a) HNLS, (b) SA3, (c) Syl-PyC, and (d) Syl-iBN composite, using the four phase model.

Table V: Calculated results of the radial residual stress by CTE mismatch (σ_{CTE}), the compressive stress caused by fiber surface roughness (σ_R), and the clamping stress (σ_{CL}). Note that negative value ($\sigma < 0$) denotes compressive stress.

	σ_{CTE} [MPa]	σ_R [MPa]	σ_{CL} [MPa]
HNLS	167	-172	-5
SA3	69	-939	-871
Syl-PyC	188	-1490	-1302
Syl-iBN	175	-2291	-2116

Misfit Stress (σ^J)

The misfit stress of each mini-composite was also measured using regression analysis of the tensile reloading segments, using the method derived by Steen *et al.* [18] (Table II). It is noted that negative misfit stress ($\sigma^J < 0$) denotes compressive axial residual stress in the matrix and tensile residual stress in the radial direction. As shown in Table II, the larger σ^J values were obtained for the SA3, Syl-PyC, and Syl-iBN composites compared to the HNLS composites (HNLS < SA3 < Syl-PyC < Syl-iBN ~ 0).

Ultimate Tensile Strength (UTS)

The tensile properties of a unidirectional composite system are strongly affected by the Weibull modulus (m), the characteristic strength (σ_0) of the fibers, and the interfacial sliding stress (τ). Under the assumption of the global load sharing (GLS) theory of Curtin [19], the fiber-averaged UTS ($\sigma_{U,f}$) in a unidirectional composite system is expressed as follows:

$$\sigma_{U,f}^{GLS} = \left(\frac{\sigma_0^m \tau L_0}{r} \right)^{\frac{1}{m+1}} \left[\frac{2(m+1)}{(m+2)m} \right]^{\frac{1}{m+1}} \left(\frac{m+1}{m+2} \right) \quad (5)$$

Figure 11 compares the fiber-averaged UTS results accompanied by the $\sigma_{U,f}^{GLS}$ strength calculated according to this theory. The interfacial sliding stress from the matrix crack spacing was used for τ . The Weibull modulus was assumed to be ~ 6.2 for HNLS [15, 20], 8.2 for SA3 [15], and 4.21 for the two experimental Sylramic fibers [21]. The fiber-averaged UTS of HNLS appeared to agree with the value calculated from the GLS theory. In contrast, this theory largely overestimates the fiber-averaged UTS for the three other composites. It is likely that, in these composites, the global load sharing is not achieved before fracture but the fracture is governed by the local load sharing (LLS), due to their relatively high interfacial sliding stress (Hence the use of Sylramic-iBN fiber without any interfacial coating in unidirectional architecture is generally not recommended due to the high fiber surface roughness (Ref. [6] and Table IV)). Based on one of the simplest LLS models, Zweiben derived the following relationship for the fiber-averaged UTS of uni-directional composites [22]:

$$\sigma_{U,f}^{LLS} = \sigma_0 \left(\frac{L_0(m-1)}{LNm} \right)^{\frac{1}{m+1}} \quad (6)$$

where L is also the gauge length of the mini-composite. In this model, the early fiber failures tend to initiate catastrophic failure of the composite. Hence it is noted that this can be regarded as a lower bound on the composite strength. Figure 11 also shows the $\sigma_{U,f}^{LLS}$ calculated using Eq. (6). These values underestimate the experimental data. However, the difference between the fiber-averaged UTS and the $\sigma_{U,f}^{LLS}$ may be reasonable since the fracture mode is different. The calculated $\sigma_{U,f}^{LLS}$ are the values under the assumption of catastrophic (brittle) fracture. However, the three composites actually fractured with pseudo ductile behavior as shown in Fig. 8. The part of the specimen where this pseudo ductile fracture has occurred should contribute to the increase of the composite strength.

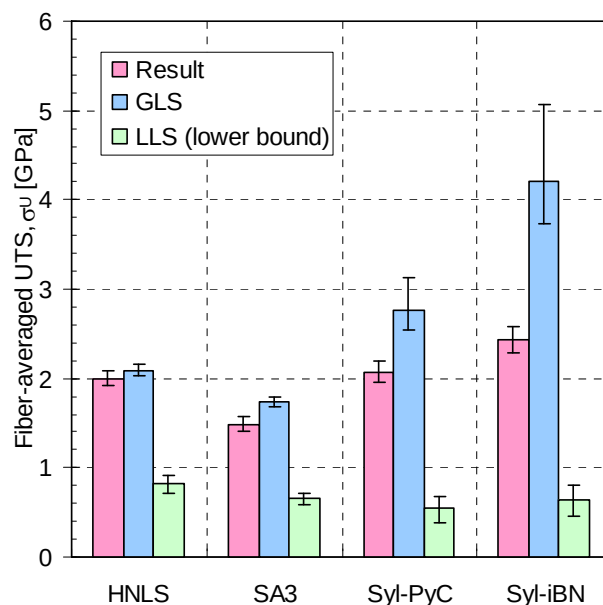


Figure 11: Fiber-averaged UTS compared with the two models. The error bars indicate the standard deviation for the result and ± 1 change in the Weibull modulus for the GLS and the LLS.

Acknowledgement

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STABILITY OF HIGH PURITY SILICON CARBIDE AND STOICHIOMETRIC SILICON CARBIDE FIBER COMPOSITES AT HIGH NEUTRON FLUENCES —Y. Katoh, L.L. Snead, K. Ozawa (Oak Ridge National Laboratory), T. Nozawa, H. Tanigawa (Japan Atomic Energy Agency)

OBJECTIVE

The objective of this work was to demonstrate the high neutron fluence stability of both monolithic SiC and the current nuclear grade SiC/SiC composite. Materials have been evaluated under a United States Department of Energy (US DOE) / Japan Atomic Energy Agency (JAEA) collaboration in a range of dose up to ~40 displacement per atom (dpa) in the High Flux Isotope Reactor (HFIR).

SUMMARY

High purity chemically vapor-deposited silicon carbide and near-stoichiometric SiC fiber, chemically vapor-infiltrated SiC matrix composite were evaluated following neutron-irradiation to ~28 dpa at 300 and 650°C and to ~41 dpa at 800°C, respectively. The irradiated swelling, thermal conductivity, and elastic modulus indicated no change of these properties at high fluences after the initial saturation. With a statistically meaningful sample population, no change in flexural strength of CVD SiC was observed after 300°C irradiation. A slight decrease in strength was observed after 650°C irradiation but was attributed to an experimental artifact; specifically, a reaction between samples and the capsule components. The Hi-Nicalon™ Type-S, CVI SiC composite retained the pre-irradiation strength and the non-linear fracture mode. The electrical resistivity measurement revealed a relatively minor effect of irradiation. Overall, irradiation-insensitivity of the high purity SiC ceramics and composite to neutron irradiation to doses 30-40 dpa at temperatures 300-800°C was demonstrated.

PROGRESS AND STATUS

Introduction

Monolithic silicon carbide (SiC) has been studied for fuel applications in gas cooled reactors for several decades, and for the past two decades as the base material for SiC fiber-reinforced SiC-matrix (SiC/SiC) composites, a potential high-temperature, low-activation structural material for fusion and fission power applications.[1-4] The primary focus of study for the composite material has been the development of a radiation stable material, given the poor as-irradiated performance of early materials.[5-7] Over the past decade significant progress has been made towards this goal with the development of what is now considered a nuclear grade SiC/SiC composite composed of high purity, near-stoichiometric, and dense fibers and matrix. However, these composite materials, and in fact the monolithic chemically vapor-deposited (CVD) SiC which are a critical element of gas-cooled reactor fuels, have not been demonstrated to retain such fundamental properties as strength and dimensional stability under the high-dose irradiation typical of their application. In fact, vast majority of the irradiation effect data published for CVD SiC are those for dose levels below 10 dpa, with some data suggesting a significant degradation in crystalline CVD SiC for doses exceeding 10 dpa.[8] Similarly, the highest neutron dose so far experienced by high purity, near-stoichiometric SiC/SiC composites is 12.5 dpa, although no significant irradiation-induced property modification other than thermal conductivity decrease has ever been reported for these composites by neutron irradiation.[9]

When SiC is irradiated with energetic neutrons, self defects are produced and accumulate in the matrix until the saturation is reached, typically by a few dpa.[3] At the temperatures of common interest for nuclear applications, self-interstitial atoms (SIA) of both types (C and Si) are sufficiently mobile, while the vacancies and SIA clusters are immobile. Therefore, if SIA's are not able to before recombine with vacancies they will remain in the matrix causing volumetric expansion (swelling) and decreased thermal conductivity. Antisite defects are also believed to build up with dose and tend to saturate in concentration, contributing to the observed irradiation effect phenomena. The mechanisms for the saturation in various irradiation-induced changes are not sufficiently understood but are speculated to be related with the

cascade-resolution and the defect interactions with very high concentrations of various type defects and clusters. [10] In this context, whether such irradiation effect phenomena such as swelling and thermal conductivity decrease truly saturate or undergo further gradual evolutions is a question which has not been answered. [3]

The purpose of this work is to report on an irradiation program whose aim is to demonstrate the high-dose stability of both monolithic SiC and the current nuclear grade SiC/SiC composite. Materials have been evaluated under a United States Department of Energy (US DOE) / Japan Atomic Energy Agency (JAEA) collaboration in a range of dose up to 40 displacement per atom (dpa) in the High Flux Isotope Reactor (HFIR).

Experimental Procedure

The monolithic material examined was CVD SiC produced by Rohm and Haas (presently Dow Chemical). This material is of standard resistivity grade and the manufacturer-claimed chemical purity >99.9995%. The composite material used was chemically vapor-infiltrated SiC (essentially CVD SiC) matrix and reinforced with two-dimensional (2D), 5-harness satin-weave Hi-Nicalon™ Type-S (HNLS) SiC fiber fabric in a 0/90° stacking configuration. The fiber fabrics were coated with a ~20 nm-thick pyrolytic carbon (PyC) and ~100 nm-thick SiC alternating multi-layer coating as the fiber-matrix interface. Details of the interfacial coating is found elsewhere.[11]

Rectangular flexure beams measuring 50.2 x 6.35 x 2.63 (mm) of these materials were irradiated in HFIR at Oak Ridge National Laboratory (Oak Ridge, Tennessee, USA) using the flux trap fixed rabbit tube facility, where the typical fast neutron flux is $\sim 1 \times 10^{19}$ n/m²/s. The fluences and irradiation temperatures were 27.8 dpa at 300°C and 28.2 dpa at 650°C for the CVD SiC and 40.7 dpa at 800°C for the HNLS composite. The equivalence of 1 dpa with 1×10^{25} n/m² ($E > 0.1$ MeV) was assumed for conversion of neutron fluence into displacement damage level. The irradiation temperature was determined by post-irradiation annealing of room temperature electrical resistivity of dedicated CVD SiC thermometry samples.[12]

The post-irradiation examination (PIE) items included flexural strength, dynamic Young's modulus, mass density, thermal diffusivity, and electrical conductivity. Measurements were performed at room temperature with the exception of electrical conductivity. Dynamic Young's modulus was estimated based on determination of fundamental resonant frequency by impulse excitation and vibration method, per ASTM C1259-08. Mass density and swelling was determined by means of a density gradient column technique for the monolithic material. Swelling of the composite was determined by the apparent density measurement. Thermal diffusivity was measured using a flash diffusivity technique, ASTM E 1461-07. Electrical conductivity was measured in a four-probe configuration for the in-plane orientation and in a two-probe configuration for the through-thickness orientation.[13]

Flexural strength of the monolithic material was evaluated by a three-point flexure test using miniature samples laterally machined from the beam samples. The support span and the specimen dimensions were 5 mm and measuring 6.35 x 2.63 x 0.5 mm³, respectively. The original flexure beam samples have reacted with stainless steel springs, with which they had been irradiated in contact, and heavily damaged on one side and have metal slightly deposited from the holder material on the other side. The rationale behind the selection of these small beam specimens was two-fold. First, the relatively large CVD SiC beams irradiated to high dose underwent surface reaction with the holder material (likely a chromium vapor plating from the V-4Cr-4Ti holder) and a chemical reaction with the stainless steel springs which were used to ensure thermal contact between the SiC bar and the vanadium holder. The resulting reaction pits, and some resulting cracking compromised the surface of the sample and the possibility of 4 pt. testing of the larger bar. For this reason the microbeam (lateral slices from the larger beam) technique was developed for these specimens. The second reason for utilizing these small samples was that a large number of samples were achieved from each irradiated bar, and previously irradiated bars could be sliced and retested for comparison.

The composite samples did not experience a severe pitting reaction observed for the CVD SiC bars as molybdenum springs were used. However, vapor residue from the V-4Cr-4Ti holder did occur for the composite. To examine the influence of metallic deposition on strength and to best utilize the very limited number of samples available, the original composite beams were machined into four smaller flexure beams of 24.8 x 6.35 x 1.1 mm³. Testing the sub-sized beams revealed no significant difference in flexural strength or fracture behavior for samples with and without the deposition, thus the potential effect of metallic vapor deposition was ignored in the analysis.

Results and Discussion

Swelling, thermal conductivity, and Young's modulus

The results of PIE are summarized in Table I along with the irradiation conditions. The swelling values at ~28 dpa for the CVD SiC were determined to be ~1.65% and ~0.97% at 300 and 650°C, respectively, to a high accuracy using a density gradient column. Swelling of the composite material at ~41 dpa was determined to be ~0.68% at 800°C with less accuracy as it was deduced through standard dimensional measurement. These values appear to be consistent with the literature data for saturation swelling of high purity SiC, most of which had been taken at the doses of a few dpa.[3] Based on this result, we conclude that the true saturation in swelling of SiC in this temperature range had been achieved at much lower doses.

Table I: Summary of irradiation conditions and unirradiated and irradiated properties. Numbers in parentheses are one standard deviations.

	CVD SiC Rohm&Haas			2D-HNLS/ ML/CVI-SiC	
Irradiation Temperature [°C]		300	650		800
Fast Fluence [dpa]	Unirr.	27.8	28.2	Unirr.	40.7
Mass Density [g/cm ³]	3.210	3.157	3.179	~2.4	~2.4
Swelling [%]	n/a	1.65 (0.04)	0.97 (0.02)	n/a	0.68 (0.01)
RT Thermal Conductivity [W/m-K]	>~300	9.4 (1.1)	12.7 (0.8)	~9.8	~2.7
Young's Modulus [GPa]	450	407 (11)	426 (3)	212 (10)	210 (8)
Number of Flexural Tests	67	24	21	8	7
Proportional Limit Stress [MPa]	n/a	n/a	n/a	317 (27)	330 (20)
Ultimate Stress [MPa]	514 (98)	506 (177)	429 (153)	444 (34)	461 (48)

n/a: not applicable

The monolithic CVD SiC thermal conductivity values at room temperature were determined to be ~9.4 and ~12.7 W/m-K for irradiation temperatures of 300 and 650°C, respectively, using the measured thermal diffusivity and mass density values and the specific heat data for pure SiC.[3] The composite thermal conductivity in through-thickness direction was determined to be ~2.7 W/m-K, in the same way, with a significant specimen-to-specimen scatter. These data points again coincide with the typical thermal conductivity values anticipated after a few to 10 dpa irradiation at those temperatures, although it is hard to confirm whether or not saturation is truly achieved due to the typically greater relative error in thermal diffusivity measurement.

Both the swelling and the thermal conductivity values obtained are plotted against fluence in Fig. 1, along with the previous data acquired in the identical experimental equipment and procedures. The trend lines were drawn upon assumptions that the both swelling and reciprocal thermal conductivity build up with the 2/3 power of fluence followed by true saturations. [14] The plots of the present data confirm the above observations. The previously speculated gradual increase in swelling and the gradual decrease in thermal conductivity in the saturation swelling regime appear to be negative or very minor if true.

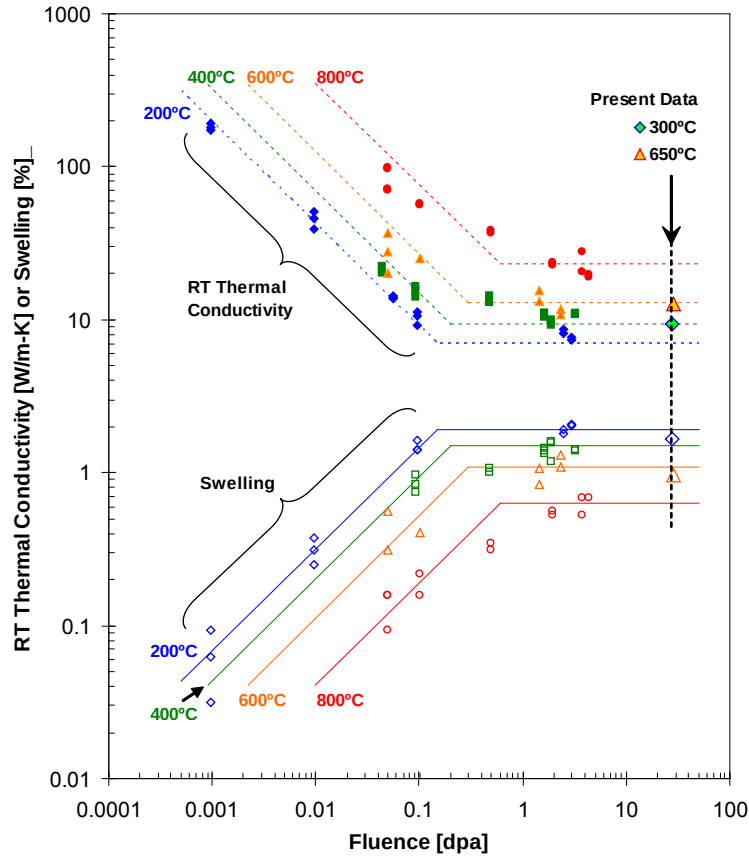


Figure 1: Fluence-dependent evolutions of swelling and thermal conductivity of CVD SiC.

The dynamic Young's modulus exhibited a modest decrease for the irradiated CVD SiC, ~9.5% after 300°C irradiation and ~5.3% after 650°C irradiation, and an insignificant change for the composite. The temperature dependency of Young's modulus of the irradiated CVD SiC is consistent with the literature data; however the relative decrease appears to be greater than anticipated from the magnitude of swelling, or approximately three times that of the volumetric swelling.[3] This discrepancy may be reasonably attributed to the lateral cracks introduced by the metallic reaction.

CVD SiC flexural strength

Results of the flexural strength tests are summarized in Table 1. The Weibull plots of the flexural strength are compared in Fig. 2 for unirradiated and irradiated conditions. An example of 650°C-irradiated specimen, broken during disassembly, before machining into microbeams is shown in the inset. These pits The average strength remained practically unchanged for the case of 300°C irradiation but decreased by ~17%

after 650°C irradiation. The Weibull modulus (m in Fig. 2) decreased from unirradiated value of 6.6 to ~ 3 . Reductions in Weibull modulus have been reported for neutron-irradiated CVD SiC: it decreased from the typical unirradiated values 9 - 10 to 7 - 8 in average with larger specimens.[11, 15] Compared to these results, the unirradiated Weibull modulus 6.6 appears significantly low, and the irradiated m values of ~ 3 appear to be very low. Moreover, Weibull moduli for flexural strength of irradiated CVD SiC tested in the exactly same way were 5.9 and 5.3 for ~ 2.3 dpa at 500°C and ~ 4.5 dpa at 800°C, respectively, where as those obtained through four-point-1/4 flexural test using full size specimens were 5.5 and 8.7 for ~ 2.0 dpa at 500°C and ~ 2.0 dpa at 800°C, respectively.[11] This indicates that the result of the present three point flexural test is likely affected by the very small specimen size and/or the associated test procedure.

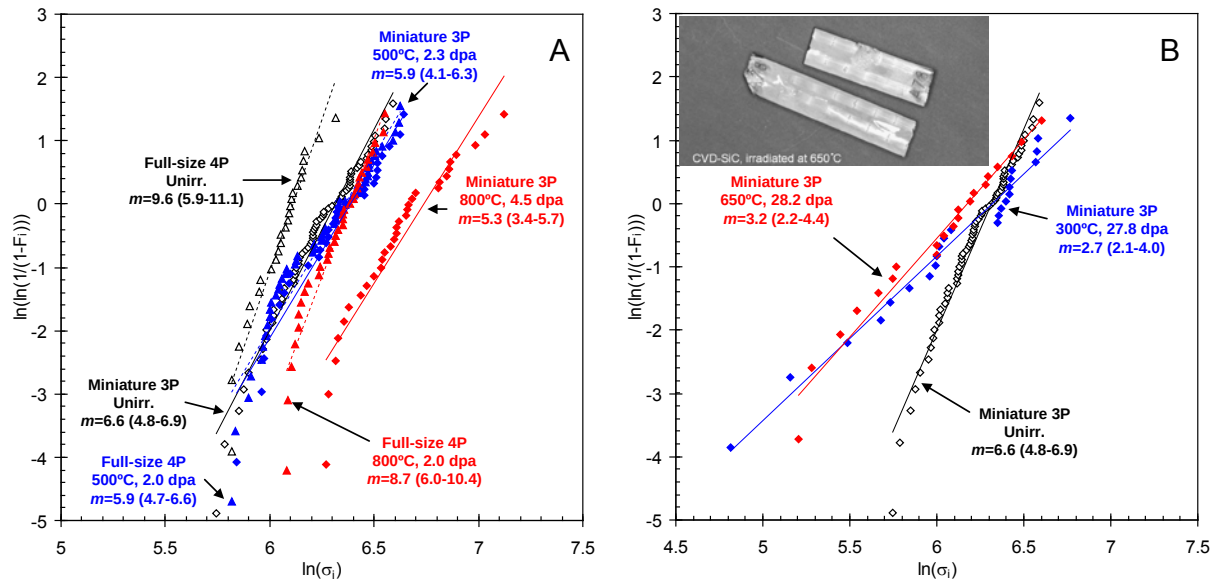


Figure 2: Weibull statistical plot of flexural strength of unirradiated and irradiated CVD SiC; A) Comparison of full-size four-point-1/4 (4P) and miniature three-point (3P) flexural configurations for unirradiated and irradiated conditions, and B) Result from miniature 3P flexural test of high dose-irradiated samples. m denotes Weibull shape parameter and range in parenthesis indicates 95% confidence bound for m value. Full-size 4P data were taken from Ref. [11] The inset photo shows appearance of sample irradiated at 650°C in contact with stainless steel springs showing severe reaction which has lead to failure.

A closer observation of the Weibull plot reveals that presence of the low strength populations which seem to be somewhat disconnected from the higher strength populations are effectively lowering the m values for the high dose irradiated samples. This likely bi-modal strength distribution implies that the weaker populations had been affected by an additional weakening mechanism, which in this case is the reaction with the metallic springs.

Figure 3 plots the irradiated flexural strength of CVD SiC normalized to the unirradiated strength in the present and previous published work as a function of neutron fluence. The irradiation temperatures for the data points vary in a range 300 - 1300°C. The plot indicates that the unirradiated strength of high purity CVD SiC retains its strength at least to a dose of 30 dpa, in contradiction to the precipitous decline at >10 dpa suggested by the work by Dienst.[8, 16-17] The current data further supports the suggestion of previous authors [3, 11] that the Dienst work may have been compromised by inadequate statistics, off-stoichiometric material, or mishandling of the materials during capsule disassembly, all of which were discussed by Dienst and co-authors.

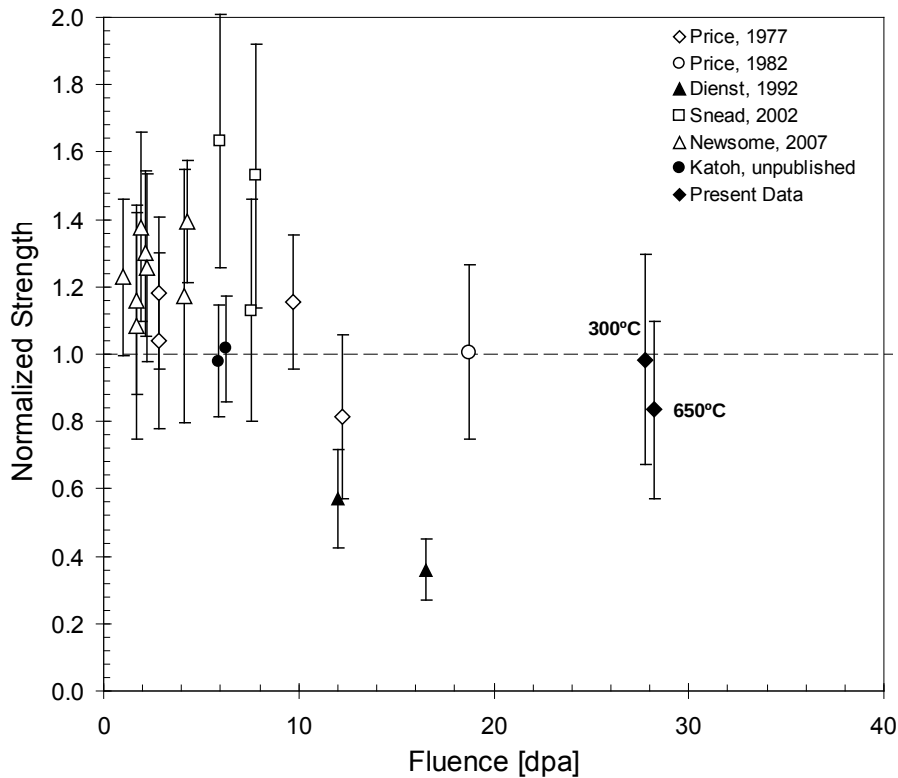


Figure 3: Strength of irradiated CVD SiC, normalized to unirradiated strength, plotted against neutron fluence. Irradiation temperatures for literature data are in a range 300-1300°C. Error bars represent one standard deviation.

Composite flexural strength

The composite material retained its unirradiated ultimate and the proportional limit stresses after irradiation to 40.7 dpa at 800°C, [Table 1](#). Moreover, no significant increase in data scatter was observed for either property. Slight increases in both the ultimate and proportional limit stresses may have been the case, but this increase is not statistically significant. Examples of the recorded load – crosshead displacement curves are presented in [Fig. 4](#), showing no noticeable difference between the unirradiated and irradiated conditions. From these observations and accepted composite theory[18] it can be reasonably concluded that no significant effect of irradiation on either the fracture energy of the matrix material, C VI SiC (essentially the same structure as the CVD material discussed herein), or the statistical strength properties of the reinforcing fibers. The fact that the matrix material retained the original strength implies that the apparent strength reduction observed for CVD SiC irradiated to a lower dose at a slightly lower temperature does not represent the neutron irradiation effect but is likely related to the reaction with the steel springs.

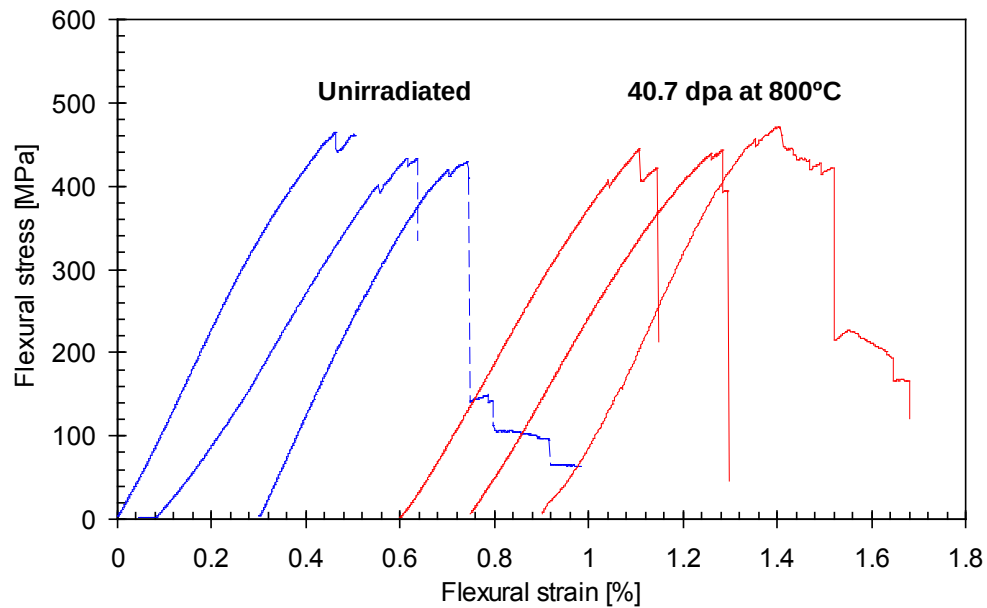


Figure 4: Examples of four-point flexural load – crosshead displacement curves for unirradiated and irradiated Hi-Nicalon™ Type S, CVI SiC matrix composites. Charts are offset for visibility purpose.

Fracture surfaces images of the broken samples are shown in [Fig. 5](#). The higher magnification composite fracture surfaces and the fiber fracture surfaces shown are those in locations under tensile stress during testing. The composite fracture surfaces are characterized by the generally very short yet finite fiber pull-out length and the debond/slide at the interface of the fiber and the interphase whether or not the material has been irradiated. Both the unirradiated and irradiated fiber surfaces appear to be typical of the intact Hi-Nicalon™ Type-S fibers presenting river-like patterns originating from indefinite mirrors around the fracture origins either on the surface or at the fiber interior. No significant difference in the fracture surfaces, irradiated and unirradiated, is observed.

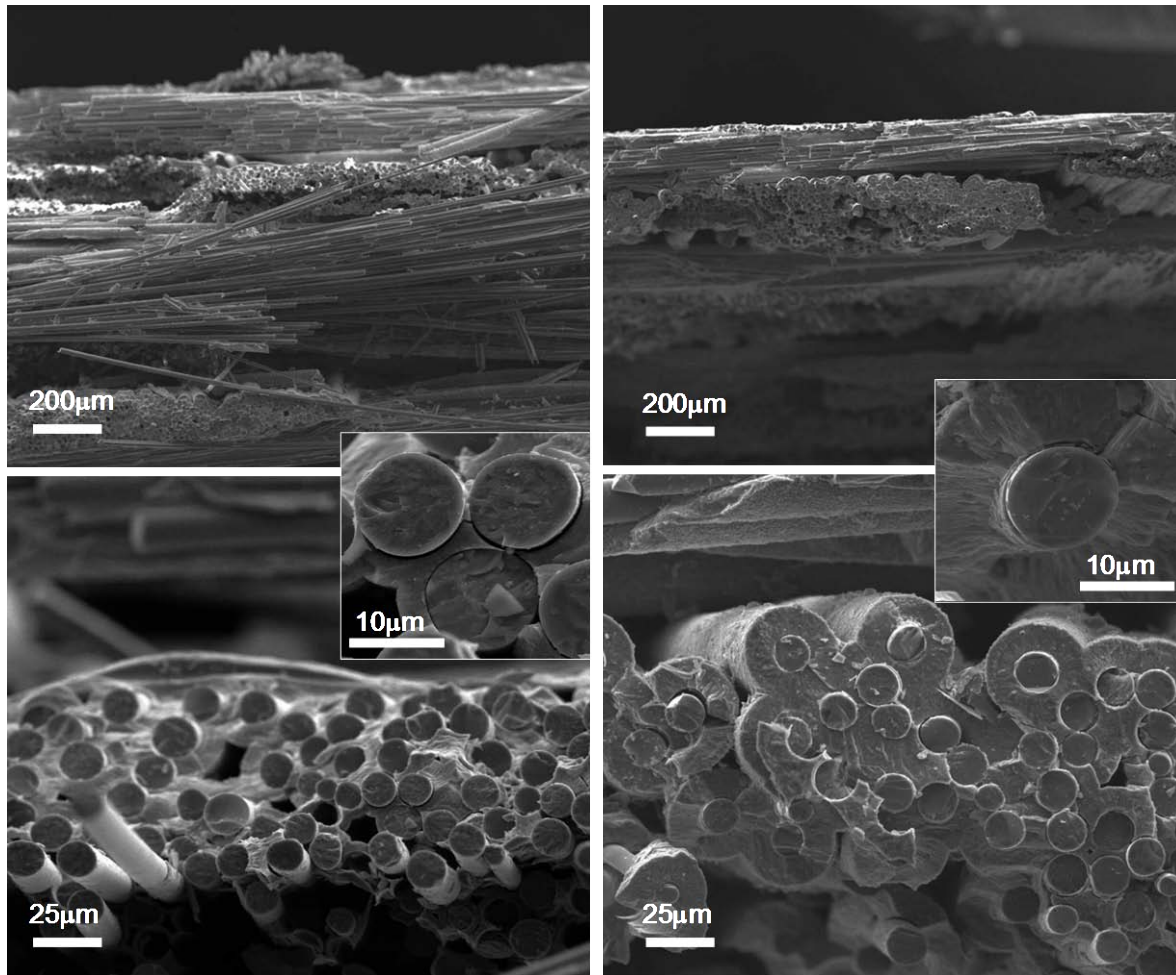


Figure 5: Scanning electron micrographs of fracture surfaces of unirradiated and irradiated Hi-Nicalon™ Type S, CVI SiC matrix composites.

Composite electrical conductivity

The direct current electrical conductivities for the in-plane (one of the fiber directions) and the through-thickness directions are plotted in Fig. 6 as a function of the measurement temperature. The temperature dependence for the unirradiated composite in both directions indicates the dominance of pyrocarbon interphase conduction, until conduction through the matrix SiC starts to contribute at $\sim 500^\circ\text{C}$, in a parallel circuit of pyrocarbon and SiC. The pyrocarbon is much more conductive than SiC and exhibits very weak temperature dependence, practically offering an electrical short circuit. The unirradiated in-plane conductivity 160 S/m at room temperature appears consistent with the previous works [13, 19-20] and indicates the effective conductivity $\sim 3 \times 10^4$ S/m for pyrocarbon. The trans-thickness conductivity 5.5 S/m at room temperature indicates the effective transverse bypass efficiency $\sim 3.4\%$ for the pyrocarbon interphase network, again consistent with results for multilayer interphase composites in the previous work.[13]

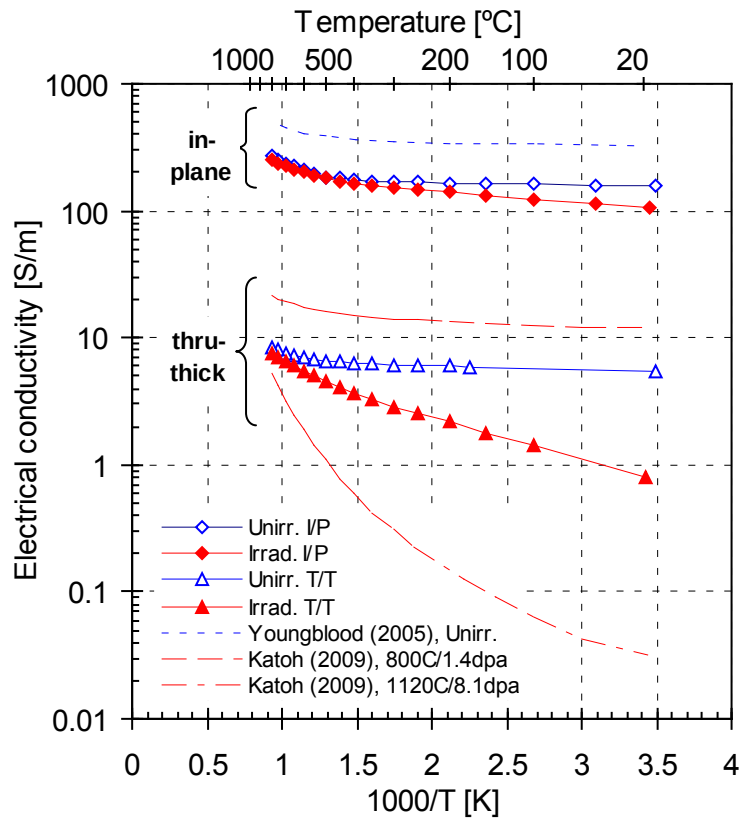


Figure 6: Electrical conductivity of unirradiated and irradiated Hi-Nicalon™ Type S, CVI SiC matrix composites.

The irradiated in-plane conductivity appears to be slightly lower than the unirradiated conductivity, to some extent consistent with the previous data after irradiation to 7.7 dpa at 800°C.[19] The reduced in-plane conductivity at relatively low temperatures indicates the reduction in pyrocarbon conductivity to the same fraction, because the conduction is dominated by the pyrocarbon interphase. This leads to an interesting implication that the pyrocarbon conductivity, constant over a broad temperature range before irradiation, becomes temperature dependent after irradiation. The through-thickness electrical conductivity of the irradiated composite confirms the same trend with more pronounced effect of irradiation lowering the electrical conductivity at relatively low temperatures. Regardless of the orientation, the effect of irradiation on electrical conductivity at high temperatures appeared not to be very significant.

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DOSE DEPENDENCE OF FRACTURE TOUGHNESS OF F82H STEEL - M. A. Sokolov (Oak Ridge National Laboratory), G.R. Odette and T. Yamamoto (University of California, Santa Barbara), H. Tanigawa and N. Okubo (JAEA)

OBJECTIVE

The objective of this work is to evaluate the fracture toughness of F82H RAFM steel irradiated to different doses in several capsules in the High-Flux Isotope Reactor (HFIR).

SUMMARY

A large number of 3-point bend and DC(T) specimens of F82H RAFM steel were irradiated at 250-500°C in capsules RB11, RB12, JP26 and JP-27 to doses from 3.5 to 22 dpa. These specimens were tested in the hot cell and results are reported here.

TEST RESULTS

This report summarizes fracture toughness data determined after testing fracture toughness specimens that were irradiated in different capsules in the HFIR reactor. Two capsules, RB-11J and RB-12J, were irradiated in the HFIR removable beryllium positions with europium oxide (Eu_2O_3) thermal neutron shields in place for neutron spectrum tailoring. Specimens were irradiated up to 5 dpa at design temperatures of 300°C (RB11J) and 500°C (RB12J). Details of the irradiation conditions and the loading of the capsules can be found elsewhere [1].

The bottom and top sections of these capsules were loaded with disk-shaped compact tension [DC(T)] specimens that were used for fracture toughness characterization. These small (12.5 mm diameter and 4.6 mm thick) specimens were irradiated in each "low-" and "high-" irradiation temperature capsule to ~3.8 dpa. Irradiation temperatures were measured by thermocouples. In the low-temperature capsule, specimens were irradiated at an average temperature of 250°C; temperature variation during irradiation was within $\pm 19^\circ\text{C}$ for a given specimen. In the high-temperature capsule, all six specimens were irradiated at an average temperature of 377°C in the bottom part of the capsule; temperature variation during irradiation was within $\pm 30^\circ\text{C}$ for any given specimen.

In addition to DC(T) specimens, 1/3-size Charpy specimens both with regular V-notch (CVN) and precracked (PCVN) to a/W ratio of ~0.5 were irradiated in both capsules. Dimensions of the CVN/PCVN specimens were $3.3 \times 3.3 \times 25.4 \text{ mm}^3$ with a 0.51 mm deep 30°C V-notch and a 0.05 to 0.08 mm root radius. Charpy type specimens were irradiated in the middle sections of the capsules. In the "low-temperature" capsule, 1/3-size Charpy specimens were irradiated at an average temperature of 288°C to ~4.7 dpa. In the "high-temperature" capsule, 1/3 size Charpy specimens were irradiated at an average temperature of 509°C to ~4.8 dpa. See details in [2].

Capsule JP26 was irradiated in a target position up to 8 dpa. This capsule had three temperature zones, 300, 400, and 500°C. Small three-point bend bar specimens were irradiated in each temperature zone of this capsule. The specimens were 1.65-mm thick, 3.3-mm wide, and 18 mm long. Capsule JP27 was irradiated in a target position up to 22 dpa. This capsule had two temperature zones, 300 and 400°C. In this capsule newly designed multi-notch specimens were used for fracture toughness evaluation. Basically, it was the same 1.65-mm thick and 3.3-mm wide specimen as in capsule JP26, only instead of stacking two single-notch specimens one on top of the other, it was machined as one piece with three notches along the length of the specimen. That design helps utilize space in irradiation capsule compared to "regular" single-notch bend bars. The raw fracture toughness data from capsule JP27 are given in [3].

Specimens were tested in general accordance with the ASTM E1921 standard. Test temperatures were coordinated between JAEA, UCSB and ORNL based on available tensile data and direct hardness measurements on bend bars prior to the fracture toughness tests. The main goal of this study was to measure the reference fracture toughness transition temperature, T_0 .

Thus the test temperatures were selected such that tests would be performed in the transition region where specimens would break by cleavage. Despite these efforts several specimens did not cleave. This highlights once again the very narrow temperature window that is available to generate meaningful results from these very small specimens. Moreover, in this report all data were analyzed using the ASTM E1921 procedure. ASTM standard E1921 utilizes the statistical-based size adjustment that takes into account crack length (thickness of specimen) as an adjustment parameter. No constraint-based adjustment has been performed in this report. However, it was shown recently [4] that a high degree of hardening may significantly reduce the usefulness of such small specimens for fracture toughness evaluation of highly irradiated steels.

One of the goals of fracture toughness evaluation of specimens in RB11J and RB12J was to compare data derived from relatively large DC(T) and smaller bend bar specimens. Unfortunately, post-irradiation evaluation of data from the capsules revealed that the RB capsule specimens were irradiated at different temperatures and to slightly different doses. Nevertheless, shifts of T_0 values derived from different specimen types provide a good description of the effect of irradiation temperature on embrittlement of F82H at 4-5 dpa, as shown in figure 1.

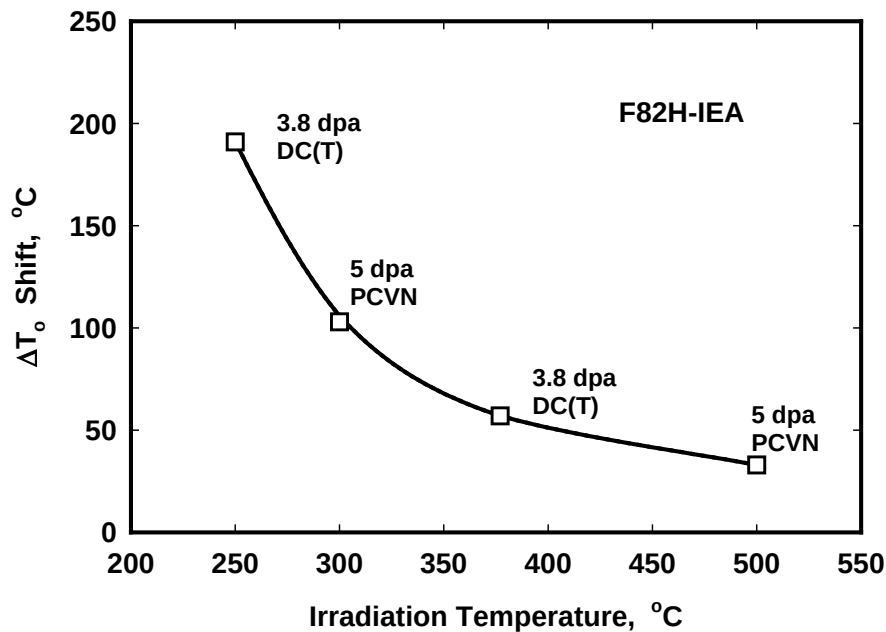


Figure 1. Fracture toughness transition temperature shifts from DC(T) and bend bars irradiated at different temperatures in capsules RB11J and RB12J.

As it was mentioned above, tensile specimens were also tested after irradiation in the same capsules so that hardening and embrittlement of F82H can be compared. Figure 2 illustrates the relationship between the shift of transition temperature and the increase of yield stress of F82H and some other RAFM steels. In addition to RAFM steels, the well-established database from low-alloyed reactor pressure vessel steels is also presented on this figure. The current data confirm previously observed trends for advanced RAFM steels to exhibit smaller amount of embrittlement (measured by shift of transition temperature) per unit of hardening (measured by yield stress increase) compared to low-alloyed RPV steels.

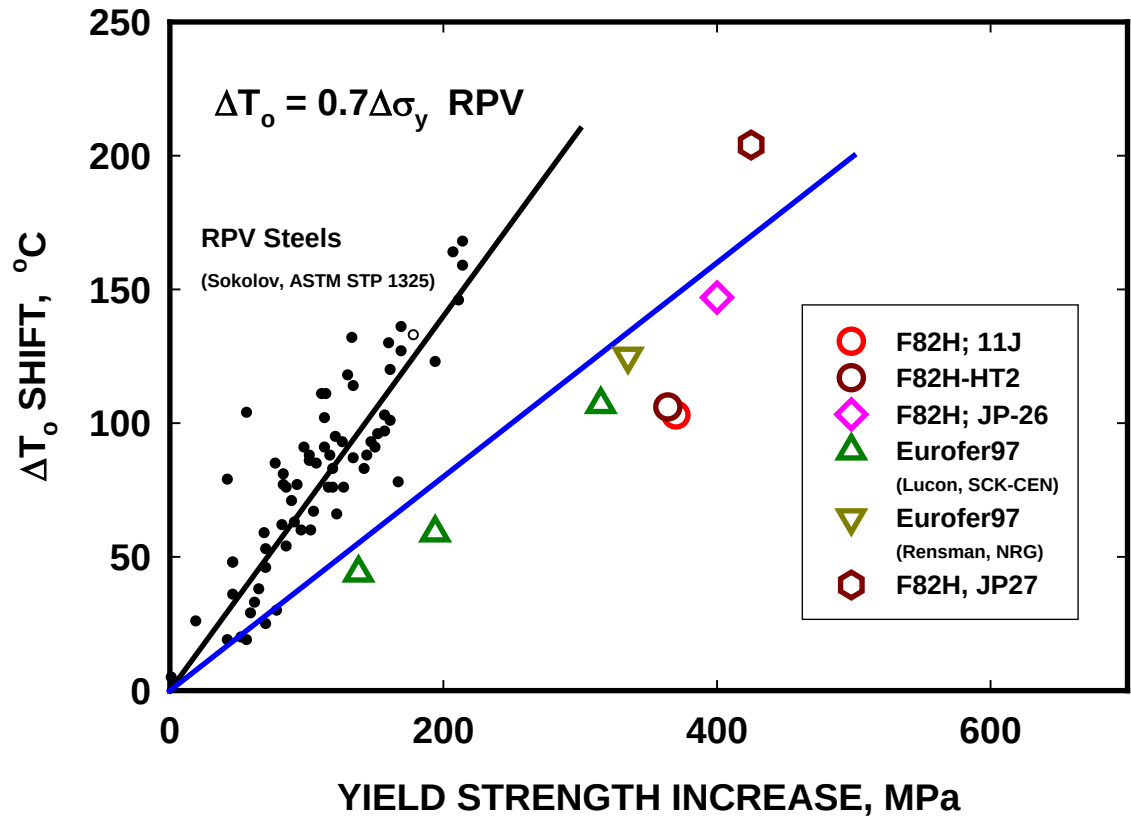


Figure 2. Comparison of shifts of fracture toughness transition temperature and yield strength increase for F82H and other RAFM and RPV steels.

Figure 3 summarizes the latest trend in shift of fracture toughness transition temperature of F82H steel at different irradiation temperatures for neutron doses up to ~20 dpa.

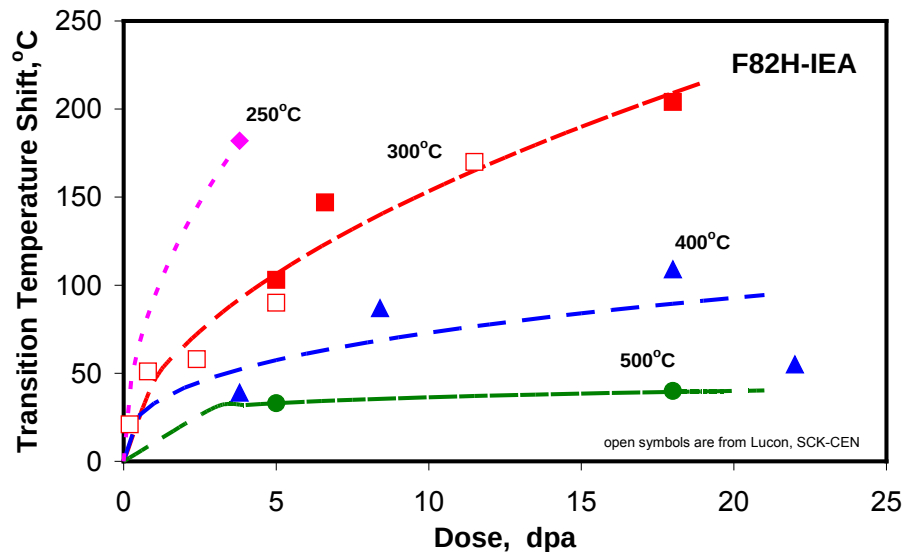


Figure 3 . Fracture toughness transition temperature shift v s dose at different irradiation temperatures.

It appears that at 500°C F82H exhibited a very small shift of transition temperature that is insensitive to dose. At 400°C, the shift of transition temperature tend to saturate at ~100°C after ~ 10 dpa. However, data at 300°C do not show saturation in the shift of transition temperature, at least up to ~20 dpa. This somewhat contradicts the trend of increase of yield strength of F82H that appears to saturate at ~ 10-15 dpa. Future experiments with higher irradiation doses will clarify the trends.

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Creep Behavior of MA957 and 14YWT (SM10 heat) - D.T. Hoelzer¹, J.P. Shingledecker², R.L. Klueh³, E.T. Manneschildt¹ and M.A. Sokolov¹ (¹Oak Ridge National Laboratory; ²Electric Power Research Institute and ³ORNL, Retired)

OBJECTIVE

The objective of this work is to expand the analysis of the creep data obtained from creep tests of MA957 that was reported previously and to show results from the first set of creep tests on the advanced ODS ferritic alloy 14YWT-SM10. The 14YWT-SM10 alloy was a 1.2 kg heat produced at ORNL in July, 2007.

SUMMARY

This study reports the data obtained from creep tests for MA957 that were started in 2003 and the results obtained from the initial creep tests for 14YWT-SM10. The creep tests of the as-received MA957 showed typical three-stage creep behavior at 875°C and above for stress of 70 and 100 MPa. However, the specimens failed in less than 1700 h. Abnormal creep behavior consisting of essentially no primary or tertiary creep was exhibited at 800°C and 100 MPa. However, this specimen failed after 38,555 h with a total strain just prior to failure of only 0.361% and a very low minimum creep rate of $\sim 1.2 \times 10^{-11} \text{ s}^{-1}$ ($d\epsilon/dt$).

Creep results for 14YWT-SM10 at 800°C and stresses of 100 to 300 MPa are the first such data for this material. They show abnormal creep behavior at 200 to 300 MPa, with essentially no primary or tertiary creep. This was attributed to the high stress levels, more than 50% of the yield strength. The creep test at 100 MPa has now accumulated close to 20,000 h without failure.

PROGRESS AND STATUS

Background

A set of thermal creep tests were conducted on as-received MA957 starting in August 2003 shortly after discovering a high number density of Ti-, Y-, and O-enriched nanoclusters that were similar to those that had been discovered in 12YWT by APT in 1999 [1-3]. Some of the results obtained from creep tests conducted on six samples of MA957 at temperatures between 800°C and 925°C and constant loads of 70 or 100 MPa were reported previously [4]. However, did not include much analysis of the data and focused on the stability of the NC and microstructure of the failed MA957 specimen that was tested at 800°C and 100 MPa. In addition, creep tests have now been initiated on the 14YWT-SM10 advanced ODS ferritic alloy produced at ORNL to obtain creep properties and to study creep deformation mechanisms at elevated temperatures and stresses. The initial creep tests were conducted at 800°C with stresses of 100, 200, 250 and 300 MPa.

Advanced oxide dispersion strengthened (ODS) ferritic alloys, also referred to as nanostructured ferritic alloys, contain a high concentration of Ti-, Y-, and O-enriched nanoclusters (NC). The dispersion of NC was first discovered in the 12YWT ferritic alloy that was developed in Japan during the late 1990's and subsequently in MA957 during the FY02-05 I-NERI project between ORNL, plus UCSB subcontract, and CEA, Saclay, in France [1,2,5]. Interestingly, MA957 was patented by INCO in 1978 [6]. Unfortunately, 12YWT was produced only once in a relatively small heat and INCO discontinued production of MA957 shortly after it was introduced commercially in the 1980's. However, these developments plus the scientific interest that arose from the early studies of NC in 12YWT and MA957 prompted the development of 14YWT starting in early 2001 and continuing to the present date.

At ORNL, the focus for developing the 14YWT ferritic alloy was to produce the high concentration of NC and to reduce the grain size to a few hundred nanometers. The much smaller grain size achieved in producing 14YWT is the most significant microstructural feature that distinguishes it from 12YWT and MA957. A total of 14 small heats (<1.2 kg) of 14YWT have been produced using Ar gas atomized powders procured from Crucible Research (now ATI Powder Metals) and Special Metals in 2001. In

2007, the 14YWT-SM10 heat, which was a 1.2 kg extrusion, was produced with ball milled powders from Special Metals. The larger size of this heat permitted numerous types and quantities of specimens to be prepared in order to obtain tensile, fracture toughness and thermal creep properties and to study high temperature deformation mechanisms. A number of TEM, DCT and tensile specimens were also prepared from 14YWT-SM10 for the Phenix Matrix II neutron irradiation experiment conducted by DOE (LANL) and CEA, Saclay in the GNEP program.

One of the most important properties associated with high-temperature alloys being developed for applications in advanced nuclear reactors, including both fission and fusion reactor systems, is creep performance. Shortly after NC were discovered in the as-received MA957, a total of 6 creep tests were initiated in August of 2003 to compare the creep properties of MA957 with those of 12YWT, which had been obtained during the SEED and subsequent LDRD projects from 1999 to 2002 at ORNL. Creep testing was initiated on 14YWT-SM10 in 2008 since this became a milestone in the INERI project between ORNL and CEA, Saclay that was started in 2007. All of the creep tests on MA957 and 14YWT were conducted in air at temperatures ranging from 800°C to 925°C with stresses of either 70 or 100 MPa. The main objective of this report is to expand the analysis of the creep data obtained from the creep tests on MA957 that was reported previously [4] and to show results from the first set of creep tests on 14YWT-SM10.

Experimental Procedure

The sample of MA957 that used in the creep tests was provided to ORNL by CEA, Saclay in August, 2002. The sample was a thick walled tube that was 10 cm long with an external diameter of 6.5 cm and wall thickness of ~0.9 cm. The fabrication history for producing the tube is not known. A total of 7 creep specimens were machined from the tube wall section with the gage parallel to the length of the tube. The specimens were 3.0 in. long and had cylindrical gages, which were 0.8 in. long and 0.199 in. diameter. A total of 6 time-to-failure constant load creep tests were started in August 2003.

The processing and fabrication history of the 14YWT-SM10 plate used in the creep tests consisted of: (1) annealing the vacuum degassed can containing the ball milled powder for 1 h at 850°C and subsequently extruding the can through a rectangular shaped die that had an opening of 1.5 in wide x 0.75 in high; (2) annealing 5 plates cut from the extruded bar for 1 h at 1000°C in vacuum; (3) hot rolling the 5 plates to 40% reduction in thickness at 850°C; (4) machining the creep specimens from 2 of the plates and (5) annealing the creep specimens for 1 h at 1000°C in vacuum. Two types of creep specimens were prepared from the plates. Two 3.0 in long cylindrical specimens were prepared with threaded grips, extensometer grooves and gage that was 0.8 in long and 0.198 in diameter. One of these specimens was used in the initial creep test that was started in April, 2008 using a constant load equal to 100 MPa at 800°C. Three 1.65 in long cylindrical specimens were prepared with threaded grips, extensometer grooves and gage that was 0.4 in long and 0.113 in diameter. These specimens were tested with an MTS unit in constant stress control using stresses of 300, 250 and 200 MPa at 800°C.

The specimen codes and the temperatures and stresses used in the creep tests on MA957 and 14YWT-SM10 are shown in Table 1. All of the creep tests were conducted in air.

Results and Discussion

The results of the creep tests performed on the MA957 and 14YWT specimens are shown in Table 2. The results for MA957 were shown previously, but were included in this report for comparison with the new results for 14YWT. The results for MA957 showed that failure of the specimens occurred in shorter times in creep tests conducted at 875°C and higher compared to much longer times to failure below this temperature. To emphasize this trend, the specimen being tested at 825°C and 70 MPa is still in progress and has now been exposed to these conditions for more than 60,000 h, or close to 7 years. The

results for 14YWT showed that the time to failure decreased significantly with increasing stress at 800°C. At the lowest stress, i.e. 100 MPa load, the test is still in progress after more than 19,000 h. However, increasing the stress to 200 MPa (constant stress control test) caused failure of the specimen in 102 h and the 300 MPa stress caused specimen failure after ~10 minutes. Although these are very short times to cause specimen failure, it should be mentioned that these stress levels are very high relative to the yield strength of 14YWT-SM10 at 800°C. Tensile tests have been conducted on 14YWT-SM10 and have shown that the yield (0.2% offset) and ultimate tensile strengths are $\sigma_{0.2} = 395$ MPa and $\sigma_{UTS} = 429$ MPa, respectively, at 800°C. Thus, the creep tests conducted with stresses of 200, 250 and 300 MPa were more than 50% of the yield strength. The most extreme creep test used 300 MPa, which was 76% of the yield strength, which partially accounts for the rather short time of ~10 minutes to failure.

Table 1. The conditions used in the creep tests of MA957 and 14YWT.

Alloy	Specimen Code	Type of Creep Test	Stress (MPa)	Temperature (°C)
MA957	ODS-01	Load	100	900
MA957	ODS-02	Load	70	925
MA957	ODS-03	Load	70	875
MA957	ODS-04	Load	100	800
MA957	ODS-05	Load	Not Tested	
MA957	ODS-06	Load	70	825
MA957	ODS-07	Load	100	875
14YWT	NFA00	Load	100	800
14YWT	NFA01	Load	Not Tested	
14YWT	NFA02	Constant Stress	250	800
14YWT	NFA03	Constant Stress	200	800
14YWT	NFA04	Constant Stress	300	800

Table 2. The time and strain to failure obtained from the creep tests of MA957 and 14YWT-SM10.

Alloy	Specimen Code	Time (h)	Strain at Failure (%)	Status
MA957	ODS-01	37	1.8	Ruptured
MA957	ODS-02	165	4.2	Ruptured
MA957	ODS-03	1640	3.4	Ruptured
MA957	ODS-04	38,555	6.5	Ruptured
MA957	ODS-06	60792*	N/A	In Test
MA957	ODS-07	42	6.6	Ruptured
MA957	NFA00	19776*	N/A	In Test
14YWT	NFA02	4.8	0.343	Ruptured
14YWT	NFA03	93.3	0.157	Ruptured
14YWT	NFA04	0.18	0.405	Ruptured

* Total time from start of test to July 27, 2010.

The Larson-Miller Parameters (LMP) calculated using the creep results obtained for MA957 and 14YWT are shown in Figure 1. This plot also shows the LMP for 12YWT and an advanced 9Cr-WMoVNb tempered martensitic steel (TMS) [7]. The 2 data points for MA957 at 650°C were obtained from the

INCO patent [1]. The test temperature and the time-to-failure for all of the 12YWT data and a few of the MA957 data in Figure 2 to compare the creep test conditions. The linear line fit through the data demonstrates that the overall creep properties of 12YWT are slightly better than that of MA957, but both of these MA ferritic alloys show significant improvements over the 9Cr-WMoVNb TMS. The LMP data for 12YWT and MA957 are 4 to 6 orders of magnitude higher than that for the 9Cr-WMoVNb TMS at all stresses. The LMP allows a general comparison of the creep performance of these alloys since it does not provide information about the creep strain history, total strain at failure, or temperature of the creep test. This information is obtained from the creep curves.

Creep curves showing the dependence of strain with time for the MA957 specimens are shown in Figure 2. The creep curves are grouped by variations in temperature for each load, which was 70 MPa (Fig. 2a) and 100 MPa (Fig. 2b). The results showed very rapid transitions occurring in the creep strain from the initial primary creep regime to the secondary and tertiary creep regimes for tests that were conducted with high stresses and temperatures, i.e. 70 MPa at 925 °C and 100 MPa at 875 and 900 °C. These tests showed secondary, or steady state, creep over short durations that then ended with rapid transition to tertiary creep and subsequent failure. At lower stresses and temperatures, the tests exhibited much more extensive secondary creep regimes for the specimens. For example, the specimen that was tested at 800°C and 100 MPa showed essentially no change in strain following the first 50 h of testing, which resulted in failure of the specimens tested at higher temperatures that are shown in Figure 2b.

Expanded creep curves of the specimen tested at 800°C and 100 MPa are shown in Figure 3. The plot shown in Figure 3a shows the creep strain as a function of time with the data processed to 100 points due to the very large number of data points for this test. Interestingly, the results do not show evidence of primary creep and only a small tertiary creep regime. The small tertiary creep can only be observed when the data covers the last 1000 h prior to failure of the specimen as shown in Figure 3b. Tertiary creep occurs for ~300 h before the specimen experiences an increasing strain rate that leads to sudden failure. The results show that the data followed nearly steady state creep rate from the beginning of the test to ~38,165 h and that the vast majority of strain, i.e. ~6.14%, occurred in the last 0.1 h of the test. Thus, the extensometer creep strain prior to rupture of the specimen was ~0.361%, which corresponded to a displacement of ~0.003 in. for essentially the entire test duration of 38,555 h. The catastrophic failure mechanism is not clearly understood, but is an ongoing topic of research activities.

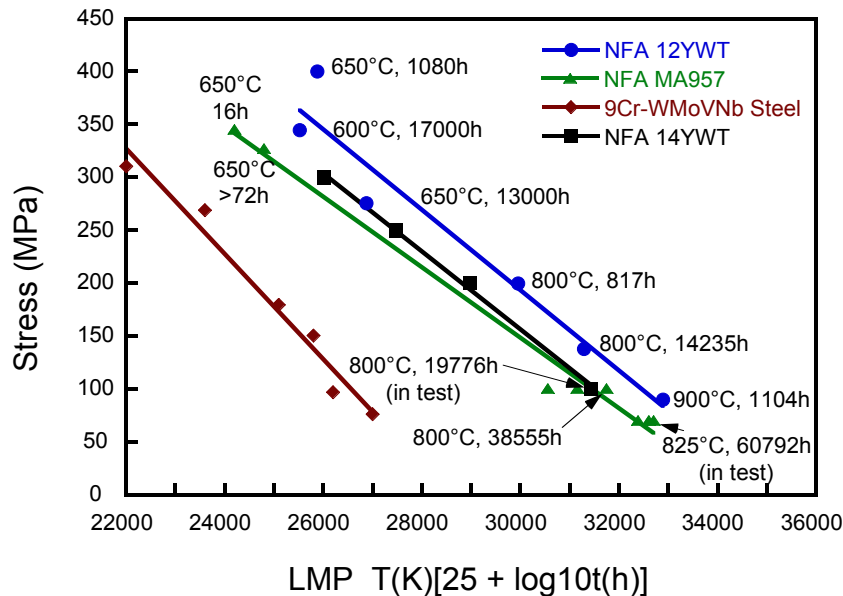


Figure 1. The Larson Miller Parameter plots of the new data for MA957 and 14YWT and those of MA957, 12YWT and 9Cr-WMoVNb TMS from previous studies [3,6,7].

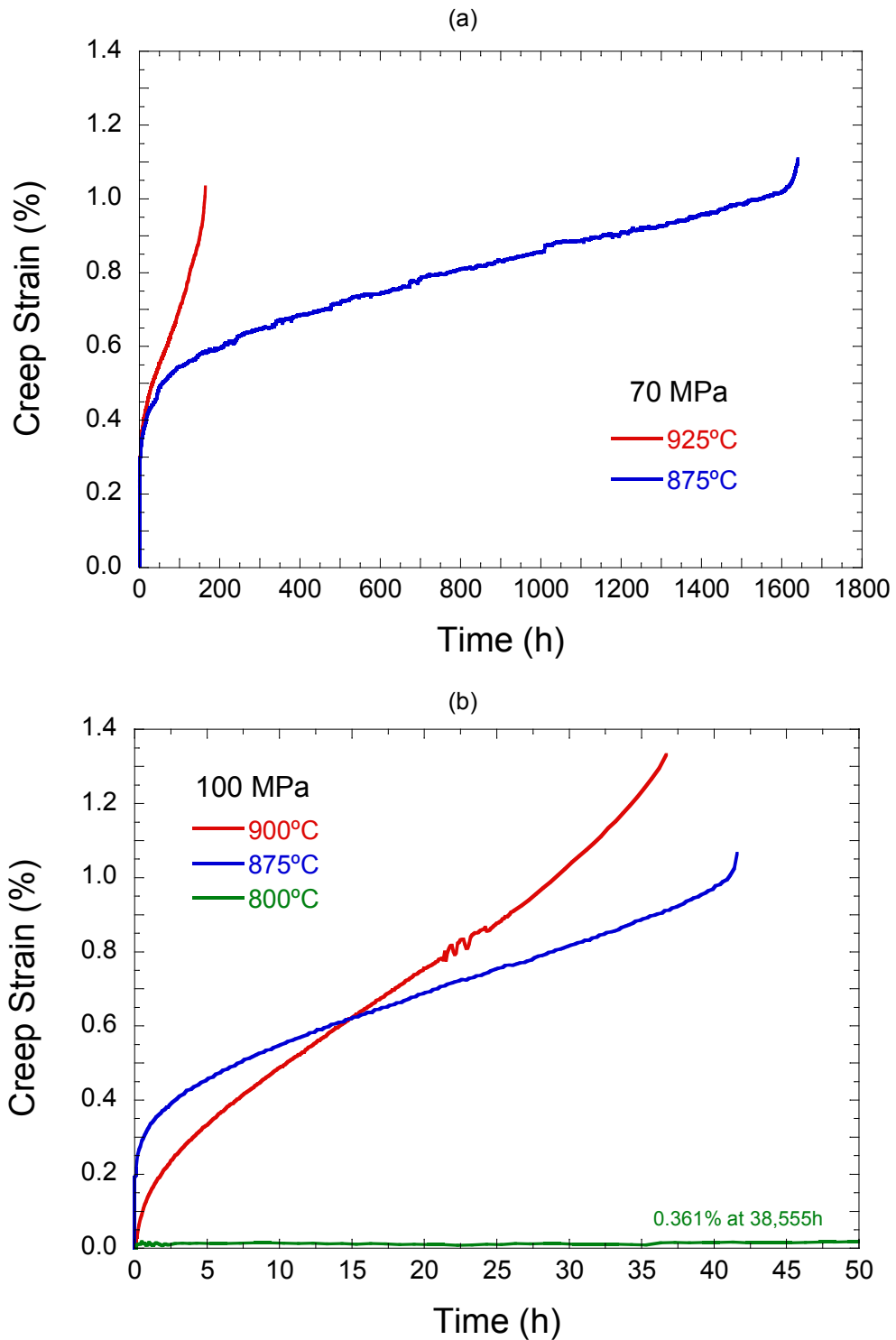


Figure 2. Creep curves of MA957 from tests conducted at elevated temperatures and with constant loads of: (a) 70 MPa and (b) 100 MPa.

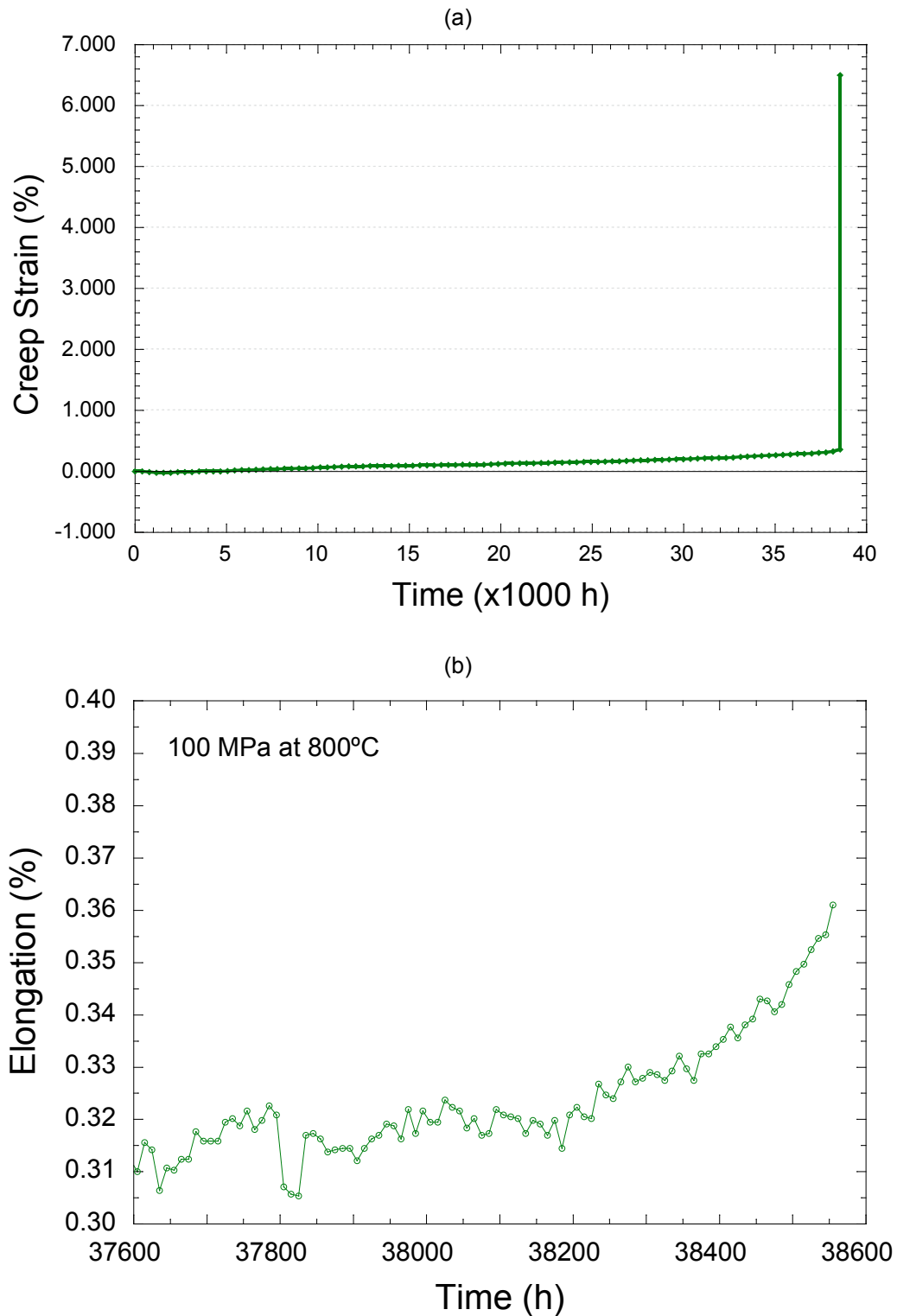


Figure 3. Creep curves of the MA957 specimen that failed after 38,555 h in the test the test that was conducted at 800°C and 100 MPa in air. (a) Shows the creep curve covering the total length of the test and (b) shows the creep curve for the last 955 h prior to failure. The large number of data points has been reduced for the plots.

The creep curves showing the dependence of strain with time for specimens of 14YWT are presented in Figure 4. The results showed the strain increased rapidly during primary creep and transited to secondary creep in a short amount of time in the tests using 200, 250 and 300 MPa at 800°C. The creep curve for the test at 200 MPa and 800°C does not show the variation of strain with time during the first ~60 hours because of a problem that was encountered with Labview not storing the acquired data after the buffer became overloaded. However, screen images were saved and the results showed the same trend. All of the tests indicated that secondary creep occurred over short durations that then ended with subsequent failure with essentially no evidence of tertiary creep. In addition, all 3 tests resulted in failure of the specimens at low (<1%) levels of strain. As mentioned previously, the stresses used in these tests at 800 °C were more than 50% of the yield strength for the 14YWT (SM10) heat and this contributed to the short time to failure experienced by the specimens. However, failure at low strains is unexpected. These characteristics of failure showing little to no tertiary creep and low strains are of major concern and will be the focus of further studies.

The minimum creep rates measured in secondary creep regime for tests on specimens of MA957 and 14YWT are shown in Table 3. With constant loads of 70 and 100 MPa, the creep results for MA957 indicated that the minimum creep rate (MCR) decreased as the test temperature was lowered. The lowest MCR value that was measured was for the test at 800°C and 100 MPa, which was $d\epsilon/dt = 1.2 \times 10^{-11} \text{ s}^{-1}$. For 14YWT, the MCR increased with stress at 800°C. These trends are expected for typical creep behavior. For 14YWT, the results indicated that the minimum creep rate increased with increasing stress at 800°C. The lowest MCR recorded for 14YWT was in the 200 MPa test, which was $3.2 \times 10^{-10} \text{ s}^{-1}$ and close to an order of magnitude higher than the lowest MCR recorded for MA957 in the test using a load of 100 MPa at 800°C.

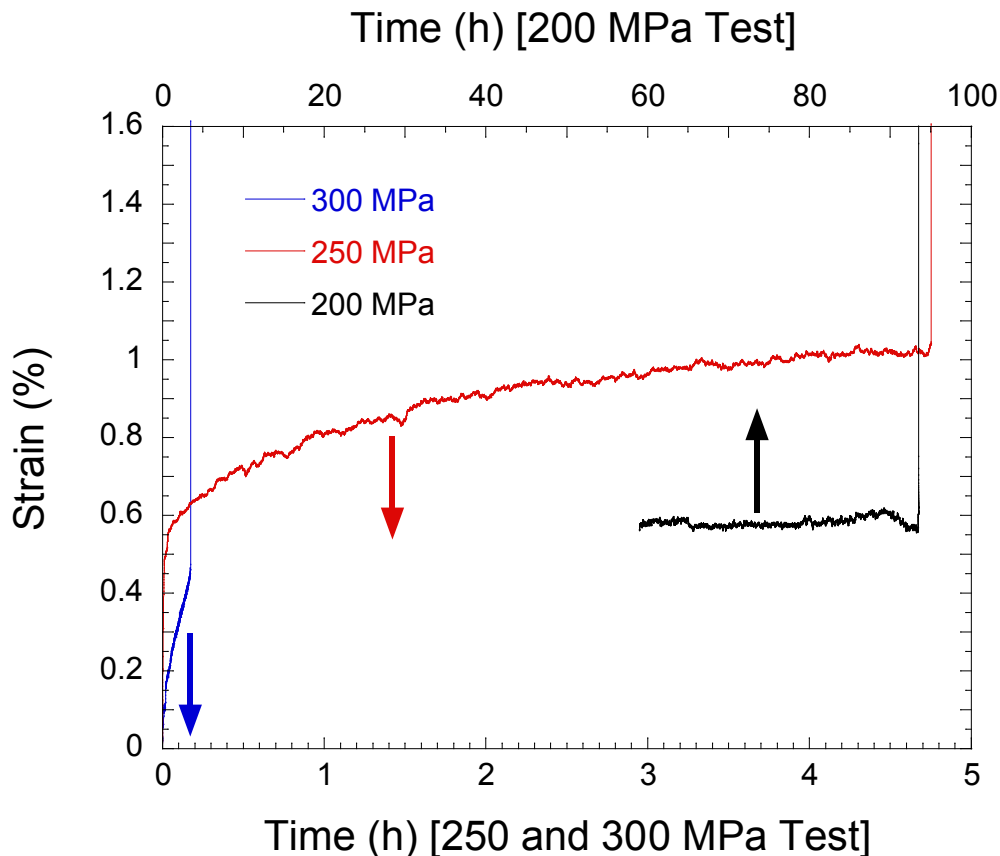


Figure 4. Creep curves of 14YWT from tests conducted at 800°C with constant stresses of: 200, 250 and 300 MPa.

Table 3. The minimum creep rates measured from the creep results for MA957 and 14YWT.

Alloy	Specimen Code	MCR (s ⁻¹)
MA957	ODS-01	7.4×10^{-8}
MA957	ODS-02	8.8×10^{-9}
MA957	ODS-03	7.7×10^{-10}
MA957	ODS-04	1.2×10^{-11}
MA957	ODS-06	N/A
MA957	ODS-07	3.7×10^{-8}
14YWT	NFA00	N/A
14YWT	NFA02	2.0×10^{-7}
14YWT	NFA03	8.4×10^{-10}
14YWT	NFA04	6.4×10^{-6}

The dependences of stress with minimum creep rate obtained from creep tests for MA957 and 14YWT are shown in Figure 5. Data obtained from previous creep tests for 12YWT [2] and from a study by Wilshire and Lieu [8] for MA957 are also shown in this plot. The results show that the dependences of the minimum creep rate on stress at 800°C for 14YWT can be described using the power law relationship for creep, which is of the form:

$$\dot{\epsilon}_m = A\sigma^n \exp(-Q_c/RT)$$

where values of A, stress exponent (n) and activation energy for creep (Q_c) typically vary with stress and temperature indicating different mechanisms are dominant. Thus, the linear fit to the values of MCR as a function of stress at 800°C indicated that the stress exponent for 14YWT was ~24. This high value of stress exponent is consistent with high values of the stress exponent (n ≅ 35) obtained for MA957 from creep tests at lower temperatures by Wilshire and Lieu [8]. These high values of stress exponent are commonly observed with dispersion strengthened alloys and suggest that the creep mechanism follows a threshold stress concept.

The data obtained for 12YWT cannot be plotted to obtain information about the stress exponent or activation energy for creep since these creep tests were not conducted using similar temperatures or stresses. Nevertheless, the limited results indicated that the creep performance of 12YWT was better than that obtained for MA957 by Wilshire and Lieu. For example, the MCR for 12YWT is similar to MA957 at 700°C, but was tested with a stress that was ~70 MPa higher. However, there could be a number of reasons to explain this comparison such as differences in mechanical properties of MA957 related to different processing and fabrication histories between the remnants of material that were originally produced by INCO [6]. The specimens of MA957 tested at ORNL were from a sample that was provided by CEA, Saclay during a previous INERI project. This version of MA957 seemed to have very good creep performance as noted with the exceptionally low value of creep strain and minimum creep rate at 800°C and 100 MPa.

Future Work

The creep testing of 14YWT will continue in the near future since a new heat, 14YWT-SM11, was recently produced. Specimens are being prepared. The research plan will be to perform creep tests at different temperatures using stresses that will allow the activation energy for creep to be obtained that will help elucidate creep mechanisms.

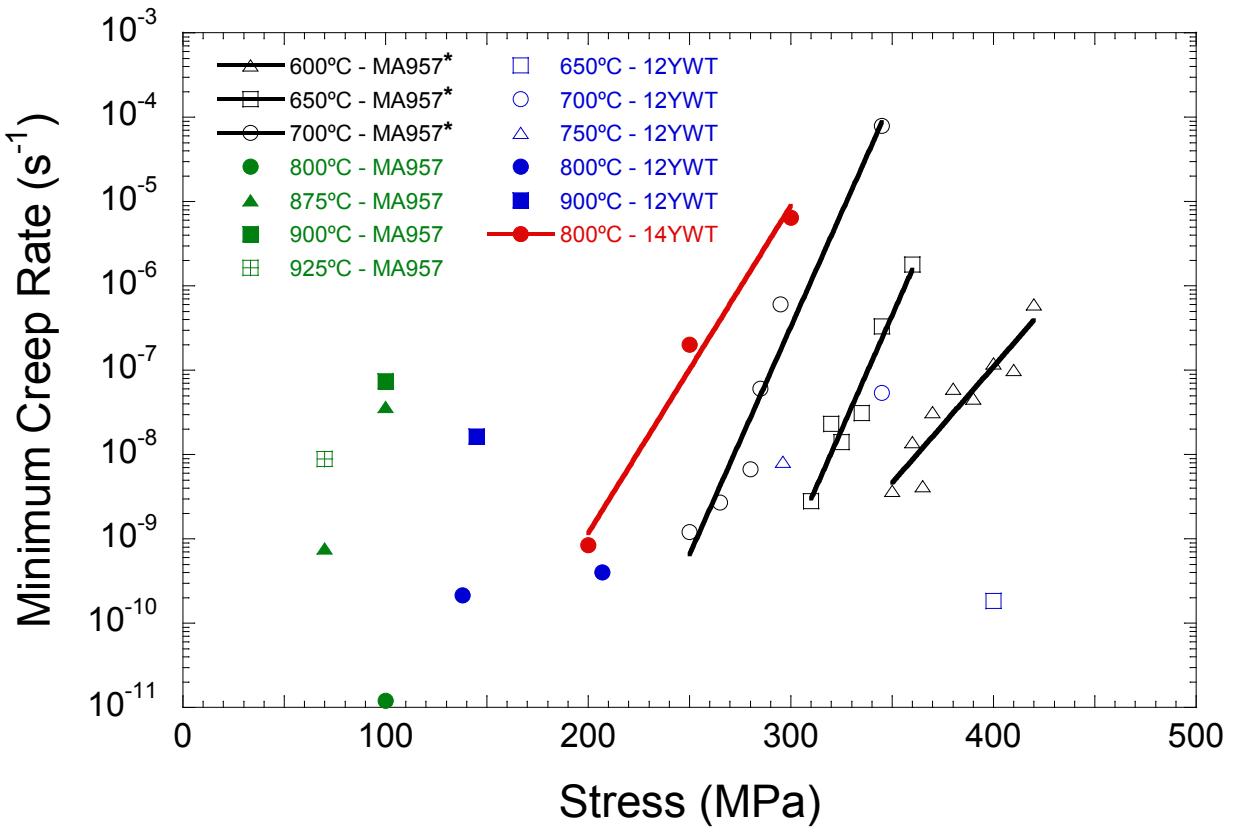


Figure 5. Shows the stress dependence of the minimum creep rates obtained from creep tests at high temperatures for MA957 and 14YWT. Also shown is data that was obtained from previous creep tests for 12YWT [3]. The * denotes data that was obtained from creep tests for MA957 from reference [8].

Conclusions

The results of the creep tests conducted on specimens prepared from the as-received MA957 showed:

- Typical creep behavior consisting of three regimes denoted by primary, secondary and tertiary creep was observed at temperatures of 875°C and above for test loads of 70 and 100 MPa. However, the specimens failed in short amounts of time (<1700 h) in these creep tests.
- Abnormal creep behavior consisting of essentially no primary and tertiary creep was exhibited by the specimen that was tested at 800°C and 100 MPa. However, this specimen failed after 38,555 h with a total strain just prior to failure of only 0.361% and a very low minimum creep rate of $\sim 1.2 \times 10^{-11} \text{ s}^{-1}$ ($d\epsilon/dt$).

The creep results for 14YWT-SM10 at 800°C and stresses of 100, 200, 250 and 300 MPa are the first such data for this material and showed:

- The creep tests conducted with constant stresses of 200, 250 and 300 MPa exhibited abnormal creep behavior showing essentially no primary and tertiary creep. The specimens in these tests showed low values of time-to-failure and sudden failure of the specimen at low strains. These characteristics of creep behavior were attributed to the high stress levels, which were more than 50% the yield strength of this heat.
- The creep test conducted at 100 MPa has now accumulated a total time of close to 20,000 h without failure.
- The stress exponent for creep at 800°C and stresses greater than 200 MPa was determined to be ~ 24 , which is consistent with the threshold stress concept.

Acknowledgements

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On the Oxide Nanofeatures and Precipitates in the Nano-Structured Ferritic Alloy MA957: A Multiple Technique Study of Heat to Heat Variations and the Effects of Friction Stir Welding and Long Term Thermal Aging - N.J. Cunningham, A. Etienne, Y. Wu, E.M. Haney and G.R. Odette (University of California-Santa Barbara, CA).

SUMMARY

We report on work supported by the DOE Offices of Fusion Energy Sciences and Nuclear Energy on nano-structured ferritic alloys (NFAs) that contain an ultrahigh density of nm-scale Y-Ti-O nanofeatures (NFs). Our objective is to explore the characteristics (number density, size distribution, volume fraction and structure) of the NFs. Small angle neutron scattering (SANS), transmission electron microscopy (TEM), and atom probe tomography (APT) were used to characterize the NFs in MA957 in both as-extruded round bar (US heat) and thick walled tube (French heat) conditions, as well as the US MA957 following long term thermal aging (LTTA) and friction stirred welds (FSW). MA957 was found to contain $\approx 1-10 \times 10^{23}$ NFs with an average diameter of ≈ 2.5 nm. The smaller NFs are cubic pyrochlore $Y_2Ti_2O_7$ oxides. The NFs coarsen slowly at 1000°C and are moderately degraded by severe deformation during friction stir welding.

INTRODUCTION AND BACKGROUND

Nano-structured ferritic alloys (NFA) have high tensile and creep strength permitting service up to more than 800°C , manifest remarkable resistance to radiation damage and can manage high concentrations of helium [1,2]. Note reference 1 contains a review of the literature up to about 2008 and will be used as the citation for a number of results in the literature described in this report. A summary of more recent work on NFA is described in [2]. NFAs typically contain 14(12-16) wt.%Cr, along with Mo or W and Y and Ti (14YWT). They are called NFAs because they contain an ultrahigh density of 1-5 nm Y-Ti-O features (NFs), which are largely responsible for their outstanding properties. The NFs provide dispersion strengthening, help stabilize dislocation and fine grain structures, reduce excess concentrations of displacement defects by enhancing vacancy-self-interstitial recombination and trap helium in fine, and relatively harmless (or, indeed, potentially beneficial) bubbles [1-4]. International Nickel Company (INCO) developed MA957 as the first commercial vendor 14Cr ODS alloy in the late 1970s for use in liquid-metal fast breeder reactors [5]. Note, however, we distinguish the 14CrYWT NFAs from ODS alloys, like higher Cr and Al INCO MA956 and Plansee PM2000, since the latter contain coarser (> 5 nm) oxide phases and are generally not as strong. Experimental ODS/NFA heats, for a range of compositions and processing routes, were studied in Japan by S. Ukai and co-workers in the 1990s, leading to the high performance Kobe J12YWT NFA. Early TEM and XRD studies indicated the presence of very fine scale oxide features in alloys such as MA957 and J12YWT [1] and 1-3 nm Y-Ti-O were first observed in APT by Kim et al. in 2000 [6].

NFA processing typically involves mechanical alloying (MA) rapidly solidified metallic powders with Y_2O_3 oxide powders by ball milling. The Y and O dissolve in the Fe-Cr-Ti matrix and subsequently precipitate with Ti during consolidation by hot extrusion or hot isostatic pressing (HIPing). NFAs are then usually further processed and fabricated into various product forms by a variety of post-consolidation thermal mechanical treatments (TMT). Ideally, the TMT result in fine grain sizes and high dislocation densities that, along with the NF, contribute to high NFA strength and, potentially, better fracture toughness.

Optimizing NFAs requires understanding of the detailed composition and structure of the NFs, as well as how alloying elements and processing variables affect their character. While it is clear that a suite of characterization tools are needed to develop such understanding, various techniques are not yet fully consistent with one another. In addition to understanding the basic NF character, other questions that are addressed in this work are NFA stability during extended service at high temperatures and finding joining methods that do not severely degrade the NFs.

MATERIALS AND METHODS

Three heats of MA957, originally manufactured by INCO, were studied [7]. The first two heats are as-extruded 1150°C , 25mm round bar that were acquired from Pacific Northwest National Laboratory are referred to as US-MA957 (DBB0114 and DBB0122). Both of these heats have been used for various research topics described in

this report and it has been assumed they are effectively similar. The third heat is a 9 mm thick, 65 mm outer diameter tube fabricated by center drilling an extruded bar followed by hot extrusion (HBB-0127). This heat was acquired from CEA Saclay in France via Oak Ridge National Laboratory and is referred to as French-MA957. The processing descriptions are nominal in both cases and the specific thermal mechanical treatment conditions are unknown. The measured compositions (at%) of the US MA957 from a previous study on the US heat [7] and current APT measurements on the French heat are shown in Table 1.

Table 1. Compositions of the MA957 Heats

at%	Fe	Cr	Ti	Mo	Y	O	Ni	Al	Mn	Si	C	Cu	S	P
DBB0114*	82.97	14.32	1.123	0.170	0.128	0.786	0.089	0.183	0.065	0.059	0.073	0.009	0.011	0.007
DBB0122*	82.19	14.97	1.206	0.177	0.125	0.781	0.093	0.142	0.067	0.049	0.171	0.009	0.012	0.009
HB-0127**	83.36	14.65	0.925	0.176	0.114	0.396	0.112	0.042	0.061	0.060	0.005	-	-	-

* Ref [7]; ** APT measurement

Long term thermal aging (LTTA) has been carried out on the US-MA957 between 800°C and 1000°C in 50°C increments for times up to more than 19kh. MA957 coupons were tightly wrapped in high Cr alloy foil, to minimize loss of this element [9], and encapsulated in quartz tubing containing dry He. Aging, which is ongoing, was interrupted periodically for microhardness measurements and nano-microstructural characterization studies. The outer region of the coupons was removed to avoid the effect of Cr depletion and other near surface effects.

The friction stir welding (FSW) was carried out by Edison Welding Institute where two 100 × 17 × 2 mm US-MA957 sectioned plates were butt-welded in the long dimension direction at a tool spindle speed of 130-160 rpm and travel speed of 150-200 mm/min [9,10]. Hardness traverses were previously carried out across the weld and coupons were removed from the middle of the FSW zone for nano-microstructural characterization [9]. In the current study the micro-nanostructure of the FSW examined by a variety of characterization methods. The characterization was also repeated on FSW after an 1150°C anneal for 3 hours, followed by air-cooling, using the same encapsulation procedure as for the LTTA samples. These annealing treatments were intended to explore the possibility of re-precipitating solutes dissolved by severe deformation during FSW.

The micro-nanostructures of the MA957 heats were characterized by SANS, APT and TEM. Nominally, APT has near atomic resolution for measuring the composition of the NFs, as well as their number densities and size distributions. However, APT samples only a very small volume of material ($\approx 10^{-3} \mu\text{m}^3$), which is a particular drawback for NFAs with somewhat inhomogeneous distributions of the NFs. Further, effects such as trajectory aberrations of the field emitted ions, caused by different evaporation fields for the matrix and the precipitates, can confound accurate measurements of the composition as well as the sizes and shapes of the NFs. SANS determines average size, number density, and volume fraction of NFs in bulk material, but cannot directly measure their compositions, or easily distinguish the presence of different types of NFs. However, the ratio of magnetic scattering to nuclear scattering (M/N) does contain information about the composition of the non-magnetic NFs. The combination of a number of TEM techniques can provide, perhaps, the most comprehensive characterization of the NFs, as well as the balance of NFA microstructures; however, TEM suffers several practical challenges like feature size and signal resolution limits. Thus all of these tools, as well as others not discussed in this report, are needed to develop a robust understanding of the NFs in NFAs. Here, we apply APT, SANS and selected TEM methods to the various heats and conditions of MA957. Note, the results of additional TEM studies will be reported separately.

SANS

The SANS measurements were performed at the NIST Center for Neutron Research in Bethesda, MD on the NG7 SANS instrument [11] at a neutron wavelength of $\lambda = 0.5 \text{ nm}$ with the two-dimensional ^3He detector located 1.54 m from the sample and offset by 40.65 cm to increase the q-range up to more than 3 nm^{-1} . The differential scattering cross section $d\Sigma(q)/d\Omega$ of the scattering features were derived from two-dimensional scattering measurements on $10 \times 10 \times 2 \text{ mm}^3$ MA957 coupons in a 1.7 T horizontal magnetic field. The magnetic field permits measurement of both nuclear (n) and magnetic (m) scattering, where the later depends on the angle from the horizontal magnetic field direction, θ , as.

$$d\Sigma(q)/d\Omega(\theta)_{\text{tot}} = d\Sigma(q)/d\Omega_n + \cos^2(\theta)d\Sigma(q)/d\Omega_m \quad (1)$$

The field was applied in the extrusion direction to improve the magnetization of the Fe matrix, assumed to be saturated [12,13]. Approximately 5 million detector counts were acquired for each run. The measured intensity was converted to an absolute differential scattering cross section, $d\Sigma(q)/d\Omega$, by subtracting background and empty container scattering and using the sample mass and measured transmission to normalize and calibrate the scattering intensity data to a water standard. The NF scattering was determined by subtracting the $d\Sigma(q)/d\Omega$ for a control that did not contain NFs. The control is a Fe14Cr0.9Ti0.3Mo alloy that was milled and HIP consolidated at 1150°C. Eq. 1, was used to derive $d\Sigma(q)/d\Omega_n$ and $d\Sigma(q)/d\Omega_m$ from the $d\Sigma(q)/d\Omega$ data averaged over the entire detector range of q and θ and to evaluate magnetic to nuclear scattering ratio, $d\Sigma(q)/d\Omega_m/d\Sigma(q)/d\Omega_n = M/N(q)$. The M/N were also evaluated by fitting $M/N(q)$ averaged over a wide q -range as a function of $\cos^2(\theta)$. Plots of the log of the averaged $d\Sigma(q)/d\Omega$ data as a function of q^2 for three $\theta = 0 \pm 30^\circ$, $45 \pm 15^\circ$, and $80 \pm 10^\circ$ were also used to present and examine the data.

The $d\Sigma(q)/d\Omega$ for features with a size r , volume V and number density N , is given by

$$d\Sigma(q)/d\Omega = NV^2(\Delta\rho)^2\{3[\sin(qr) - qr\cos(qr)]/(qr)^3\}^2 \quad (2)$$

The $\{ \}^2$ term is the form factor for well-separated spheres. The $\Delta\rho$ is the scattering length density difference between the matrix and NF, $\Delta\rho = \rho(\text{mat}) - \rho(\text{nf})$. The ρ values are the known magnetic or nuclear scattering length for a specified isotope divided by the atomic volume. Since the composition and atom volume in the NFs, hence the nuclear scattering contrast, $\Delta\rho_n$, are not known, $d\Sigma(q)/d\Omega_n$ cannot be used to analyze the SANS data. However, the Y-Ti-O NFs are unlikely to be magnetic, and this assumption has been verified by measuring the temperature dependence $d\Sigma(q)/d\Omega_m$ [12,13]. Assuming the particles act as magnetic holes in a saturated Fe-Cr ferromagnetic matrix allows the $\Delta\rho_m = \rho(\text{matrix})_m$ which is known; note, this requires properly accounting for the alloy composition [12, 13]. The distribution and average size of the NFs, N and their corresponding total volume fraction, f , were derived by least squares fitting computed scattering curves (Eq. 2) to the measured $d\Sigma(q)/d\Omega_m$ data, assuming a log-normal NF size distribution. In some cases the M/N varied significantly with q and the data assuming a single scattering feature over the entire q range did not provide a good fit to the data. In these cases the $d\Sigma(q)/d\Omega_m$ data was fit to two features with different r and M/N . Typically the second feature was very small with $r \leq 0.5$ nm with a low $M/N < 1$. It is not clear if these small features are real, or if they are artifacts of the approximate control subtraction procedure. In any case, the first larger feature is assumed to represent scattering from the actual NFs and precipitates. Further details on the data analysis is described elsewhere [12-14].

The M/N ratio also contains information on the NF composition due to their effect on the nuclear but not magnetic scattering. The composition cannot be uniquely determined from the M/N ratio, but rather the measured M/N can be compared to calculated M/N from NFs with assumed compositions such as the equilibrium bulk oxide phases $\text{Y}_2\text{Ti}_2\text{O}_7$ and Y_2TiO_5 . The measured M/N , however, is to some extent affected by the approximation associated with subtracting a control that may not fully represent the scattering not associated with the NFs. Further, the assumption that the matrix is magnetically saturated may be invalid in some cases.

APT

APT was performed using an Imago Local-Electrode Atom Probe (LEAP) 3000X HR. Samples are prepared by either electropolishing or using an FEI Helios 600 focused ion beam (FIB). Electropolished samples were made from $\sim 0.5 \times 0.5 \times 20$ mm bars using the two stage process described by Miller [15]. FIB sample preparation used the trench method outlined by Thompson [16]. Each sharpened tip is cleaned to remove Ga damage first using a 5KeV and then a final 2 KeV beam at 28 pA. The LEAP samples were examined in voltage or laser mode for a variety of run conditions. Temperatures ranged from 33K to 60K and laser pulse energies varied from 0.05 nJ to 0.45 nJ with a green ($\lambda = 532$ nm) laser. Laser and voltage pulses were held at 200kHz repetition rate, the evaporation rate was typically between 0.5% and 1%, and in the voltage mode the pulse fraction was either 20 or 25%.

The Imago Interactive Visualization and Analysis Software (IVAS) package was used for reconstruction and analysis of the LEAP data. To improve accuracy of the reconstruction, SEM images of the needle profile (52° stage tilt) were taken at the start and, when possible, at the end of the run. The actual length of the field evaporated region was determined by superimposing ovals representing the pre- and post-run tip radii onto the SEM image and comparing the measured length with the length of the IVAS reconstructed data. If the lengths did not match, the default evaporation field ($Fe = 33 \text{ V/nm}$) was adjusted until the IVAS reconstruction length agreed with the measured value from the SEM.

Analysis of APT data requires identifying all pertinent ion mass to charge ratios (m/c) that form a wide spectral distribution composed of specific isotopes and charge states, including ionic species, like TiO^{+2} , are also frequently field evaporated. The identity of an atom or ionic species is determined from the background-subtracted spectrum with m/c increments as signed to a particular peak in a process called ranging. The m/c spectrum is influenced by a large number of variables, such as voltage versus laser mode, specimen temperature, laser energy and even variations in the specimens themselves. Identifying the m/c peaks can be challenging because complex iron alloys have many overlapping and interfering peaks in their m/c spectrum. However, elements like Fe, Cr, and Ti have a number of isotopes, resulting in multiple peaks with some that are more isolated. The multiple peaks were exploited to better estimate the total number of ions based on the natural isotope abundance ratios using a method called de-convolution. This method allows a more accurate ion count, but ion position in the reconstruction cannot be determined separately for each ion species in a single peak. Large post-peak tails from Fe^{+2} isotopes with mass numbers from 54 to 60 are also a problem because they overlap the peaks for Y^{+3} and sometimes TiO^{+2} . The number of ions in these smaller peaks was characterized using the side-band method of systematic background subtraction of the major element tails [17]. After background subtraction the peaks are generally isolated although their corresponding ion count still has an associated uncertainty.

The NFs were identified using both isoconcentration surfaces and the maximum separation distance methods [18,19]. The total number of precipitates was counted by adding the number of complete precipitates to one-half of the precipitates on the edge of the data set [15], and was used to determine the number density as

$$N_d = \frac{N_p \zeta}{\Omega N} \quad (3)$$

Here N_p , ζ , Ω , and N are the number of precipitates, the detector efficiency (37%), the atomic volume (based on bcc iron with a lattice parameter of 0.288 nm), and the total number of ranged ions, respectively. The size and composition of the NFs was determined using the maximum separation method for the solute ions of interest, namely Y, Ti and O, including their ionic forms like TiO^{xx} and YO^{xx} . The radius of gyration (I_g) is one method for determining the size of precipitates and is equal to the distance from the precipitate center to a radial distance containing the entire mass of the precipitate as shown in Eq. 4 [15,20]. Here, n_i is the number of atoms at r_i , which is the atom's distance from the center of mass, and n is the total number of atoms in the cluster. This so-called radius of gyration is related to the actual physical radius of the cluster r , as $r = 1.29 I_g$ [15,20].

$$I_g = \sum n_i r_i^2 / n \quad (4)$$

Consistent with other studies [21, 22], the clusters were found to nominally contain significant quantities of Fe and Cr. This is believed to be an APT artifact associated with trajectory aberrations caused by different evaporation fields between the matrix and the clusters [21, 22]. If, as is the case for the NFs, the species in the cluster have lower evaporation fields, they are emitted preferentially and earlier than the matrix ions. This causes a dimple shaped local topology change in the needle tip, that images as a dark region in field ion microscopy micrographs. In this case, the cluster species and adjoining matrix ion trajectories overlap (are mixed with) one-another. An increase atom density in the cluster signals this condition. In contrast to the actual sequence of ion emissions, the reconstruction algorithm assumes the atoms are uniformly emitted from the tip of the needle one layer at a time in the z -direction. The consequences of this approximation are further discussed below with a specific example.

However, as a practical matter, the excess Fe should be removed in establishing the cluster compositions. If other information suggests that the cluster is unlikely to contain any significant quantity of Fe, then a practical expedient

is to simply remove it in estimating the cluster composition, using only the solute content. High concentrations of matrix solutes, like Cr, are also artificially enriched in the clusters. Examples of other APT artifacts, include the possibility of pre-emission of some species that are then not detected, surface diffusion, perhaps stimulated by the high electric fields and the presence of low index poles, fine scale structures like precipitate-matrix interfaces, surface ledges and ledge kinks, uneven temperature distributions during the laser pulse and several others. Indeed, given the local variations in the binding energies of various atoms in a cluster, the overall emission process inherently involves a wide range of evaporation potentials. In the present case, a variety of these aberrations appear to be operative. The Y is concentrated in the center of the clusters while the Ti and especially the O atoms are nominally more diffuse. A corrected composition can be found by completely removing the Fe and other matrix elements (e.g., Cr) based on the ratios of the solute to Fe in the matrix [21,22,23]. It is not necessary to carry out deconvolution and deconvolution on the m/c spectrum of clusters removed from the matrix, since the overlapping peaks and post peak tails of the major elements in the cluster m/c spectrum are greatly reduced.

TEM

The nanoscale features were observed in both thin TEM foils and on extraction replicas. Precipitates were extracted from the NFAs by etching the surface, applying a 10-20 nm carbon coating, and then electrochemically removing a deposited carbon film with a solution of 1% tetramethylammonium chloride-10% acetyl acetone-methanol. Thin TEM foils were prepared in an FEI-Helios-FIB using the in situ lift-out technique. The final thickness of the thin foil is between 30 and 70 nm. A final, low energy Ga beam (2kV and 5.5pA) cleaning step was used to remove the high-energy ion damage to achieve high quality samples. Scanning transmission electron microscopy (STEM) high angle annular dark field imaging (HAADF) studies were performed using an FEI TITAN at 300 kV. Conventional bright field scattering contrast (diffraction contrast) TEM imaging and high-resolution transmission electron microscopy (HRTEM) imaging (phase contrast) studies were performed on either an FEI TITAN at 300 kV or an FEI T20 TEM/EDX at 200 kV. EDX spectra were recorded in STEM mode with the stage tilted to $\alpha=10^\circ$, at a spot size of 3 or 4, and condenser aperture of 70 μm , which is the optimal experimental condition for taking EDX data from such small features. The analysis of the HRTEM images was carried out by fast Fourier transformation (FFT). The lattice spacing and inter-planar angles were measured by using Image J and Adobe Photoshop 6.0.

RESULTS AND DISCUSSION

Characterizing the NFs and precipitates in MA957

SANS

SANS measurements were performed on the US MA957 during four separate NIST campaigns and two campaigns in the case of the French heat. Figure 1a shows example absolute $q = 45 \pm 15$ averaged $d\Sigma(q)/d\Omega$ curves. The 45 ± 15 curve has the largest q range and includes contributions from the nuclear plus $\approx 50\%$ of the magnetic scattering. Both heats show an almost identical bulge in scattering compared to the control. Figure 1b shows an example NF $d\Sigma(q,q)/d\Omega$ curves, derived by subtraction of the control from the NFA scattering, plotted as a function of q^2 . The solid lines are two-feature least square fits to the q averaged data at $0 \pm 30^\circ$, $45 \pm 15^\circ$ and $80 \pm 10^\circ$.

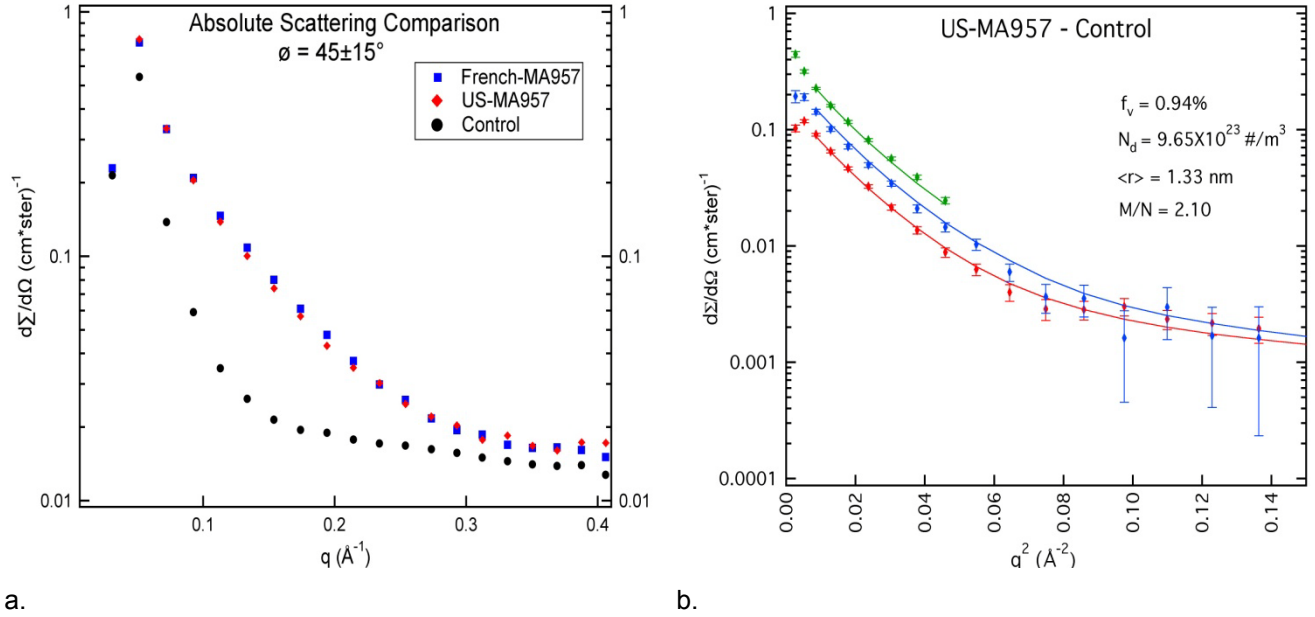


Figure 1. a) Comparison of US-MA957, French-MA957, and control scattering 45° curves; b) example fits to scattering data for NFs in the US-MA957.

The average r , N , f , and M/N for the US and French MA957, and the corresponding one standard deviation errors, are shown in Table 2. The precipitate size is essentially identical in both heats, while the N and f are nominally slightly smaller in the French-MA957. There is a larger difference in the M/N ratio, ranging from 1.1 (French heat) to 1.9 (US heat). As noted previously, there are a number of reasons that explain the range of measured M/N . First, the measured M/N depend on the magnetization of the matrix that may not have been fully saturated in all cases, leading to lower M/N . Further, the method for isolating the NF scattering by subtracting the scattering from a nominal control is approximate and may lead to some differences in the measured M/N . Of course, the variations in the M/N may also reflect real differences in the NFs and precipitates in the two heats of MA957. The M/N can be calculated for assumed NF compositions and structures of $\text{Y}_2\text{Ti}_2\text{O}_7$ and Y_2TiO_5 ; the M/N are both ≈ 1.4 in both cases. This suggests that the NFs in MA957 are not stoichiometric bulk oxides. Higher Ti and lower atom densities lead to smaller M/N , while lower Ti and higher atom densities increase M/N . Any Cr and Fe that is artificially included in small NF due to SANS resolution limits, or as actual constituents of the Y-Ti-O or other fine scale scattering features, also increase M/N . Further, it has been shown that differences in alloy compositions and processing conditions have a significant effect on the M/N [13], so heat-to-heat variations are not unexpected. Given the uncertainties in measuring and interpreting M/N , the SANS data are broadly consistent with somewhat non-stoichiometric oxide compositions and atom densities.

Table 2. SANS N , $\langle r \rangle$ and f for the US and French MA957

Alloy	N ($\text{\#}/\text{m}^3$)	r	f_v	M/N
US-MA957	$9.40 \pm 0.93 \times 10^{23}$	1.33 ± 0.01	0.93 ± 0.08	1.92 ± 0.14
French-MA957	$7.56 \pm 1.00 \times 10^{23}$	1.32 ± 0.03	0.72 ± 0.04	1.13 ± 0.12

APT

APT measurements were carried out on one French and nine US MA957 samples. Small Y-Ti-O enriched NFs were observed in all cases and larger precipitates were found in some of the reconstructions. Figure 2a shows a region containing a relatively uniform distribution of small NFs. Figures 2b and c show front and side views of a sample containing a mixture of small NFs and larger precipitates in the US MA957. The large precipitates appear

to be aligned, most likely on a grain boundary lying just outside the data set. The single French MA957 sample had a very high density of small, uniformly distributed NFs.

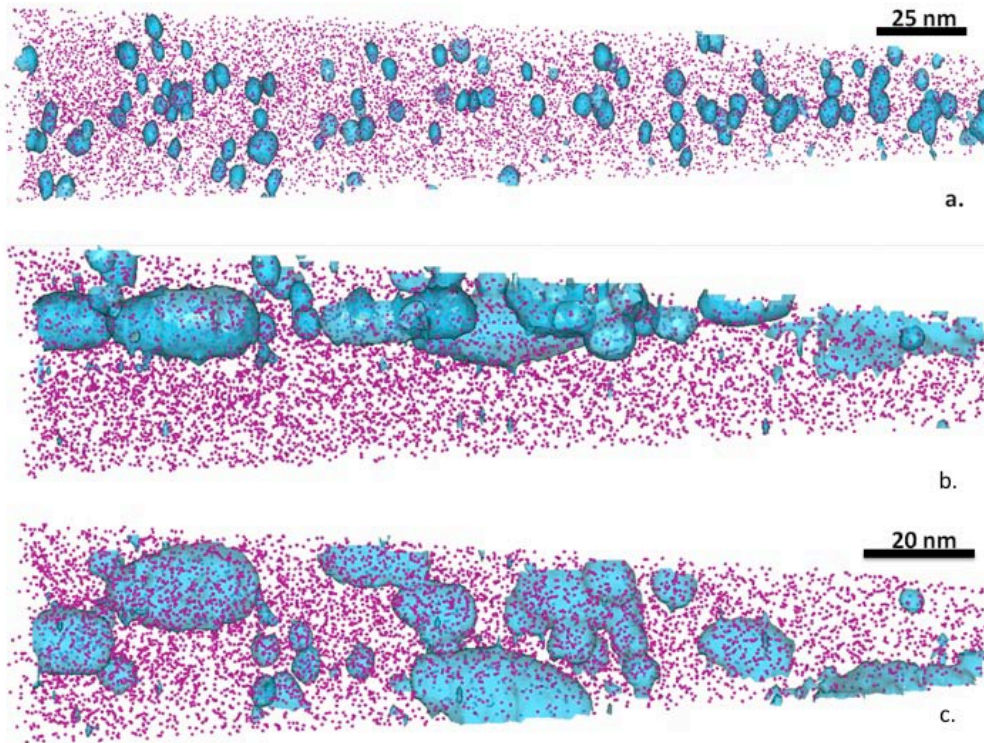


Figure 2. Isoconcentration surfaces showing: a) A US MA957 needle with a uniform distribution of small NFs; b) front and c) side views of a needle with large precipitates on the edge of the data set, possibly on a boundary.

APT run conditions such as temperature, laser or voltage mode, laser power, sample orientation, etc. can affect the m/c resolution. The APT compositions for the US MA957 in Table 3 are for a m/c spectrum with high resolution that was analyzed using the peak decomposition and de-convolution methods described above. The first two columns in Table 3 compare the previously measured bulk composition to that measured in the volume shown in Figure 2b and c. The agreement is generally good except for the Y. This difference is probably due to the fact that the small volume sampled contains a locally high volume fraction of the large precipitates. Table 3 also shows the matrix composition of the APT dataset shown in Figure 2 after removing the precipitates. The matrix analysis shows that the Y, O and Ti are highly depleted relative to their bulk values, consistent with the fact that these elements are associated with the NF and larger precipitates.

The NFs and precipitates were separated into large ($r > 2.5$ nm) and small ($r < 2.5$ nm) size categories for composition measurements. Note the larger precipitates often fall on the edge of the reconstruction volume, hence cannot be completely analyzed. The compositions of the small NFs and a larger precipitate in the US-MA957 shown in Figure 2a are shown in Table 4. Note, as previously discussed, the nominal Fe and Cr contents are high due to trajectory aberrations. Corrected compositions are also shown in Table 4. The average Y/Ti/O ratio of the small NFs in both US and French-MA957 are similar at $\approx 14/44/42$ and $13/48/40$, respectively. The average Y/Ti/O ratio for the larger precipitates is $\approx 18/34/48$ for the US-MA957. Note the Y/Ti and O/(Y+Ti) are much lower than for the equilibrium oxide phases in the Y-Ti-O system: Y_2TiO_5 (25/12.5/62.5) and $Y_2Ti_2O_7$ (18/18/64). However, these results are consistent with other atom probe data [1,2].

Table 3. Bulk chemistry and APT total and matrix compositions of US MA957

At%	Nominal	APT US- MA957	APT US MA957 Matrix
Fe	82.97	82.49	84.06
Cr	14.32	14.51	14.71
Ti	1.123	1.181	0.648
Mo	0.170	0.118	0.120
Y	0.128	0.318	0.006
O	0.786	0.929	0.075
Ni	0.089	0.113	0.116
Al	0.183	0.095	0.012
Mn	0.065	0.078	0.079
Si	0.059	0.070	0.032
C	0.073	0.006	0.006
Cu	0.009	-	0.014
B	-	0.003	0.002
Co	-	0.043	0.052
V	-	0.044	0.045
Nb	-	0.004	-

Table 4. Composition of small NFs in the MA 957 including a matrix corrected composition.

Element at%	Fe	Cr	Mo	Ti	Y	O	Al	Mn	Si	B	C	Co	V
Small NF	73.82	12.71	0.133	5.536	1.550	5.713	0.133	0.089	0.044	-	0.044	-	0.089
Corrected	-	-	0.215	38.86	12.09	46.77	0.957	0.150	-	-	0.312	-	0.377
Larger Precipitate	72.67	13.73	0.141	5.48	1.45	5.71	0.216	0.075	0.083	0.125	0.008	0.125	0.033
Corrected	-	6.70	0.248	32.59	9.53	47.63	1.36	0.043	0.149	0.814	-	0.590	-

Figure 3 illustrates another artifact that can occur in APT measurements, in this case for a large precipitate. The specific run conditions were: 30K, 200kHz pulse rate, 0.5% evaporation rate, and 0.3nJ laser pulse energy. The nominal precipitate length is more than 20 nm. The elongated shape of the feature and the distinct TiO tail on the bottom are APT artifacts. The precipitate ions have a lower evaporation field, thus are evaporated more rapidly and earlier than the matrix atoms, creating a dimple in the needle surface. The resulting local convex-concave radii resulting in the matrix-feature mixing effect and some spreading in the x-y direction as noted above. The elongation artifact arises from the IVAS algorithm that assumes all the ions are uniformly removed, layer-by-layer, over a hemispherical tip shape, when in fact the Y, Ti and O ions are actually emitted earlier in the sequence, and at a higher z-position. As a result the position of the Y, Ti and O ions are artificially extended in the z-direction in the reconstruction. The TiO tail represents another artifact, since it always appears on the bottom of the precipitates, which in fact do not have a top and bottom. This behavior has been previously observed and may be indicative of a core/shell structure [22], although the exact mechanism is not understood. One possible explanation is that the TiO ions in a shell region have a higher required evaporation field than the core of the precipitate. If the core has the lowest evaporation field these ions are removed (scooped out) first leaving a pocket still surrounded by the shell on the needle tip surface. After the core has been removed, the shell would continue to evaporate at a slower rate. However, the reconstruction algorithm would incorrectly assign the shell ions to a deeper z-position at the bottom of the precipitate. Other atom positioning artifacts of APT are surface

diffusion, perhaps stimulated by high electric fields, and preferential-delocalizing effects of the plane-pole crystallography of the needle tip.

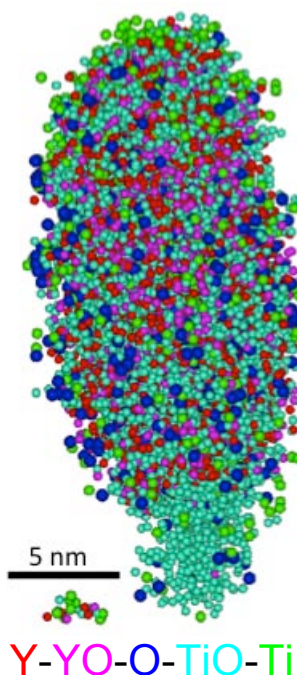


Figure 3. a) Large elongated precipitate in US-MA957.

The APT measurements give an average number density $N \approx 1.8 \times 10^{23}/\text{m}^3$ and average diameter $\langle d \rangle \approx 2.3$ for the US MA957, versus $N \approx 6.0 \times 10^{23}/\text{m}^3$ and $\langle d \rangle \approx 3.1$ for the French heat. Note significantly higher N have been previously found in other studies of US MA957, including some of our own results. The N and $\langle d \rangle$ of the NFs measured in SANS, APT and TEM are shown in Table 5, including data that will be reported separately [Y. Wu et. al. to be published]. The $\langle d \rangle$ are in good agreement for the various techniques in both heats of MA957. However the number densities vary over factors of ≈ 3.5 to 5.5 between the various techniques and factors of ≈ 1.25 to 3.3 for the two heats. These differences are likely to be partly due to the inhomogeneity in the NF distributions. The overall technique averages are similar for the two heats: US heat $\langle d \rangle = 2.5$ nm and $N = 5.6 \times 10^{23}/\text{m}^3$; French heat $\langle d \rangle = 2.7$ nm and $N = 5.3 \times 10^{23}/\text{m}^3$.

TEM

Further composition comparisons, including TEM results, will be reported elsewhere. However, in summary, the TEM results show:

Excluding TiO_x and other coarser carbon/nitride phases, HTREM-FFT measurements of plane spacing's and inter-planar angles show that the diffracting features in the size range from 8-20 nm are primarily consistent with variants of orthorhombic Y_2TiO_5 , and in a few cases $\text{Y}_2\text{Ti}_2\text{O}_7$, as well as unidentified phases. EDX shows Y/Ti ratios generally between 1 and 2, and the individual oxides are non-stoichiometric.

The HRTEM-FFT diffraction measurements of plane spacing's and inter-planar angles, as well as electron powder diffraction, suggest that the smaller < 8 nm NFs are most consistent with cubic $\text{Y}_2\text{Ti}_2\text{O}_7$ with near stoichiometric Y/Ti ratios ≈ 1 and with nominal $\text{O}/(\text{Ti} + \text{Y}) \approx 2.1$.

The compositions and oxide structures measured by TEM are not consistent with the APT composition values.

These results represent a significant advance in the understanding of smallest NFs. Additional research is being carried out to establish the small NF (e.g., $\text{Y}_2\text{Ti}_2\text{O}_7$) orientation relationships with the ferrite matrix. The fact that the NFs now appear to be near to equilibrium phases, rather than far from equilibrium solute clusters as previously believed based on APT data interpretations, is very important since it opens new opportunities for both experiment and modeling.

Table 5. Number density and average diameter of NFs in MA957

NF parameters	Technique	US-MA957	French-MA957
Average diameter ($\langle d \rangle$ nm)	TEM	2.5	2.6
	APT	2.3	3.1
	SANS	2.7	2.6
Number density ($\text{N} \cdot 10^{23} \text{ m}^{-3}$)	TEM	5.6	2.2
	APT	1.8	6.0
	SANS	9.4	7.6

Friction Stirred Weld Study

The US heat of MA957 joined by friction stir welding (FSW) was previously examined by TEM and SANS [9]. The severe deformation in the joint region of the FSW produced a uniform fine-scale ($\approx 0.7 \mu\text{m}$) equiaxed ferrite grain structure, with a high dislocation density. This contrasts with the baseline MA957 microstructure with grains elongated in the extrusion direction, with aspect ratios of $\approx 5/1$. The FSW process also appeared to slightly coarsen the NFs, decreasing N by an average factor of 0.5 ± 0.1 and increasing d by about a factor of $\approx 1.2 \pm 0.08$. Microhardness and tensile measurements showed a modest reduction of $\approx 7.5 \pm 1.5\%$ in the strength of the joint compared to the as-extruded MA957. In the present work the microstructures of the FSW are re-examined using more advanced TEM and newly applied APT techniques. The FSW was also studied in the $1150^\circ\text{C}/3\text{h}$ annealed state to determine if any significant degree of thermal recovery of the NFs is possible.

Figure 4 shows the FSW grain microstructure before and after annealing. Figure 4a shows the microstructure in the as-FSW condition consists of a uniform distribution of fine-scale equiaxed grains containing a high number density of dislocations. Figure 4b shows that the $1150^\circ\text{C}/3\text{h}$ anneal does not have any discernable effect on the MA957 FSW microstructure at this length scale.

The TEM at higher magnification in Figure 5 shows a high number density of NFs, in the as FSW. Figure 6 shows the NFs after annealing. The $N \approx 5.6 \times 10^{23}/\text{m}^3$ in the as-extruded condition versus $1.1 \times 10^{23}/\text{m}^3$ in both the FSW and FSW plus annealed conditions. The corresponding $\langle d \rangle$ are 2.5 and 2.9 nm, respectively. Note these are not one-to-one comparisons since the as-extruded data is based on the average of a number of studies, while the FSW cases are for more recent and limited measurements. However, TEM suggests that FSW significantly decreases N and slightly increases d . The faceted interfaces of the features, especially in Figure 6b, are particularly notable and consistent with oxide NFs down to the smallest sizes. The features are also aligned along grain boundaries and/or dislocations.

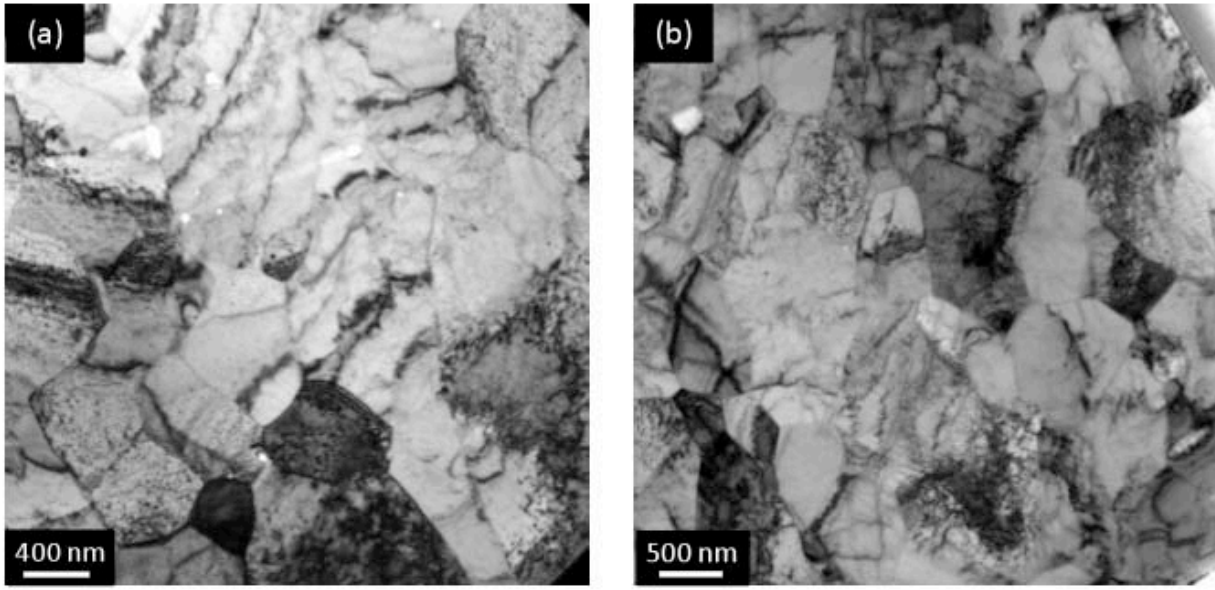


Figure 4. TEM images of the grain and dislocation microstructure in the MA957FSW (a) before and (b) after annealing 3h at 1150 °C.

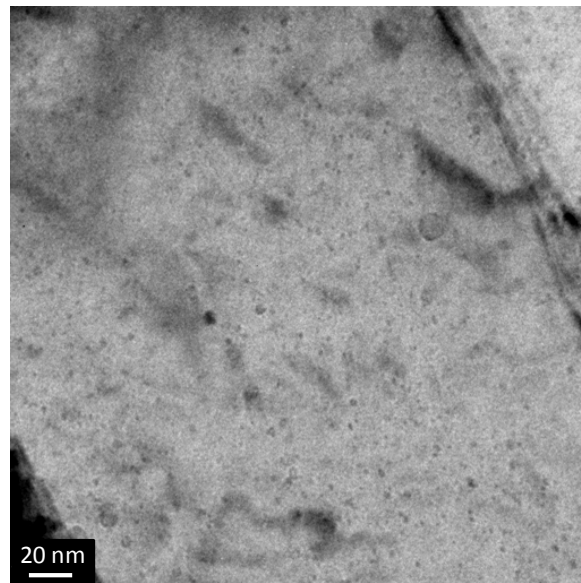


Figure 5. TEM images of NFs in the MA957 FSW.

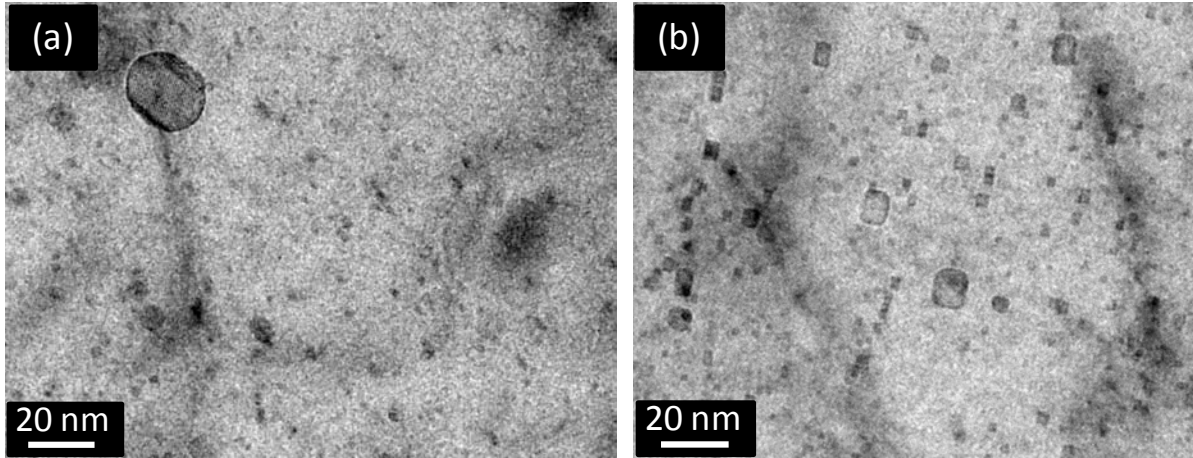


Figure 6. TEM images of the NFs in the FSW and annealed MA957.

The APT reconstruction in Figure 7 shows a fine distribution of NFs that appear to be far more aligned with grain boundaries and dislocations than in the as-extruded MA957. However, the compositions of the NFs are similar in both cases. Figure 7 also clearly shows that the distributions of O and TiO are much broader than for the Y and YO species. Such possible core shell structures have been reported in several studies of steels with small Y-Cr-O and Y-Ti-O features characterized by APT [22]. However, this also may be an APT artifact due to chemically dependent shifts in nominal versus actual atom positions which has been referred to as APT chromatic aberrations [22,23], as well as the trajectory aberrations and the artifacts due to evaporation field differences that result in a species dependent evaporation sequence, as discussed previously. In this case the YO and Y atoms are evaporated before other species.

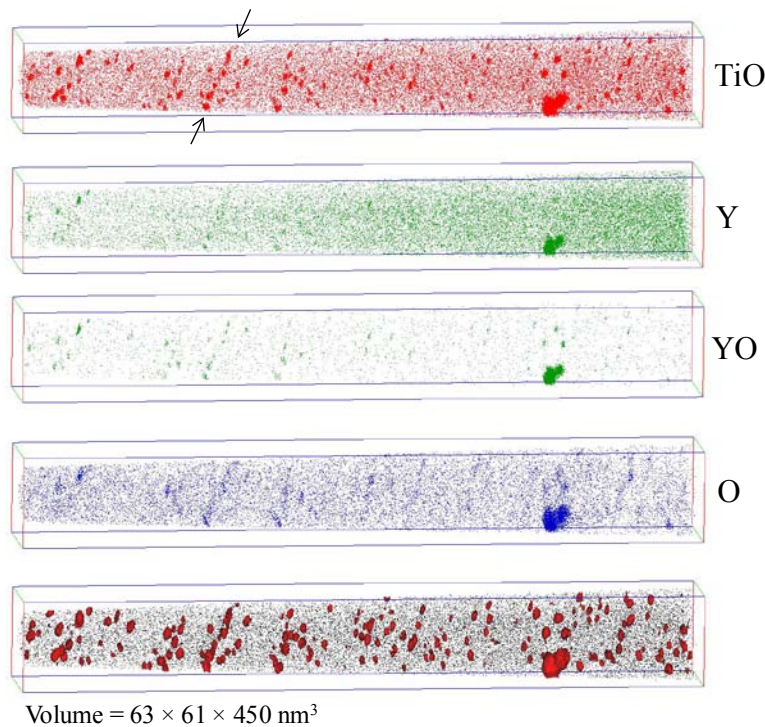


Figure 7. 3-D reconstruction of a MA957 FSW analyzed by APT. Separate TiO, YO, Y and O map atoms are shown in the top 3 reconstructions. The Ti atoms are shown in black and NF in red isoconcentration surfaces in the bottom reconstruction.

The radius and composition of the NFs in the FSW were determined using a maximum separation distance of 0.8-0.9 nm and erosion distance of 0.4-0.45 nm for the TiO, YO and Y ions. The d ranges from 1.3 to 3.6 nm, although a few larger than 5 nm were observed. The $\langle d \rangle \approx 2.2$ nm and the average $N \approx 1.7 \pm 0.2 \times 10^{23}/m^3$. These are only slightly smaller than the corresponding NF $\langle d \rangle$ and N in the as-extruded MA957, thus the APT data suggest that FSW has a minimal to modest effect on the NF. Table 6 summarizes the APT and TEM results along with previous SANS measurements [9]. Overall FSW has a minimal effect on $\langle d \rangle$ and results in decreases in N by factors ranging from 1.05 to 5.5, and averaging 2.7. Annealing has no discernable effect on the NFs. However, since there was only one APT measurement on this condition to date, the corresponding $\langle d \rangle$ and N remain to be determined.

Table 6. Comparisons of N and $\langle d \rangle$ of the NFs in FSW MA957

NF Parameter	Technique	US-MA957	FSW	FSW + anneal
$\langle d \rangle$ nm	TEM	2.5	2.9	3.0
	APT	2.3	2.2	TBD
	SANS	2.7	2.5	-
N $10^{23} m^{-3}$	TEM	5.6	1.1	1.1
	APT	1.8	1.7	TBD
	SANS	9.4	3.5	-

Small oxide particles are enriched in Ti, Y, O and Al, and their composition in the FSW sample is given in Table 7. Both measured and matrix-corrected [21] compositions are shown in Table 7. The Y/Ti/O ratios are $\approx 15/40/45$ and the Y/Ti ≈ 0.38 , that again do not correspond to known stoichiometric oxides. APT also found some larger features with $N \approx 3 \pm 2 \times 10^{21}/m^3$ and $\langle d \rangle \approx 6$ nm. These features are sometimes found to be associated with one another. The larger features are generally enriched in Ti, Y, O and Al. The Y/Ti/O ratio of the large features is 21/29/50 and the Y/Ti ratio is 0.7, which is closer to the composition of $Y_2Ti_2O_7$.

Table 7. Composition of small NFs in the MA957 FSW.

Element at. %	Fe	Cr	Mo	Ti	Y	O	Al	Mn	Si	B	C	Co	V	P
Nominal	67.8	13.8	0.20	6.5	2.2	6.7	0.28	0.10	0.13	0.11	0.04	0.10	0.06	0.03
Corrected	-	10.4	0.39	34.4	12.7	38.5	1.4	0.56	0.43	0.61	0.17	-	0.15	0.13

Long-term Thermal Aging (LTTA) Study

Long-term thermal aging (LTTA) studies are being carried out on US-MA957 from 800 to 1000°C in 50°C increments. We report here on SANS studies of the NFs after LTTA at 950 and 1000°C for times between 3kh and 19kh and TEM and APT characterization for the 1000°C, 19kh aging condition. The SANS results are shown in Figure 8. Significant coarsening is observed at 1000°C, as characterized by a decrease in N from 9.4 to $2.3 \times 10^{23}/m^3$ (Fig 8a) an increase in $\langle d \rangle$ from 2.7 to 3.9 nm (Fig. 8b) and a slight decrease in the NF volume fraction f (Fig. 8c) and microhardness (Fig. 8d). TEM measurements show decreases in N from 5.6 to $1.6 \times 10^{23}/m^3$ and increases in $\langle d \rangle$ from 2.5 to 2.3 nm

APT measurements also show that the NFs coarsen somewhat with decreases in N from 1.8 to $0.67 \times 10^{23}/m^3$ and increases in $\langle d \rangle$ from 2.3 to 2.6 nm. Finally TEM indicates such coarsening with decreases in N from 5.6 to $1.6 \times 10^{23}/m^3$ and increases in $\langle d \rangle$ from 2.5 to 3.0 nm. These results are summarized in Table 8. On average N decreases by a factor of $\approx 3.4 \pm 0.7$ and $\langle d \rangle$ increases by a factor of $\approx 1.33 \pm 0.15$. Figure 9 compares the size distribution of the as-extruded and LTTA MA957 measured by APT and TEM, again showing a slight amount of coarsening.

One significant effect of the LTТА was a large reduction in the total Ti content of the MA957 from nominal levels of ≈ 1.1 to 0.22 at.%. Most of the Ti was found to be associated with the precipitates while the balance was missing from the matrix. However, the composition of the NFs is only modestly affected, with a slight decrease in Ti level. The average Y/Ti/O ratio for the small precipitates was 15.7/37.0/47.3, which is still highly non-stoichiometric. This effect is under further investigation.

Table 8. Comparison of N and $\langle d \rangle$ of NFs in as-extruded and LTТА MA957

NF N or $\langle d \rangle$	Technique	US-MA957	LTТА
Average diameter ($\langle d \rangle$ nm)	TEM	2.5	3
	APT	2.3	2.6
	SANS	2.7	3.9
Number density ($N \cdot 10^{23} \text{ m}^{-3}$)	TEM	5.6	1.6
	APT	1.8	0.67
	SANS	9.4	2.3

CONCLUSIONS

The multi-technique analysis of the NFs and precipitate oxide phases in US-MA957 in various conditions and a French-MA957 heat yielded the following conclusions.

SANS, TEM and APT characterization of MA957 show N, $\langle r \rangle$ and F are in reasonable to good agreement for the various techniques, with $1\text{-}10 \times 10^{23}/\text{m}^3$, $\langle d \rangle \approx 2\text{-}3$ nm NFs, along with a lower density of various larger oxide precipitates.

The nominal APT measurements indicate that the NFs contain a large amount of Fe. This is believed to be an APT artifact, largely associated with trajectory field evaporated ion aberrations.

The compositions of the NF in APT measurements are deficient in Y and to a lesser extent O compared to stoichiometric $\text{Y}_2\text{Ti}_2\text{O}_7$ and Y_2TiO_5 phases.

The Y and O deficiencies may be due to either a core shell NF structures, or APT artifacts, or a combination of both.

TEM indicates that the larger (> 8 nm) NFs are primarily non-stoichiometric Y_2TiO_5 or oxide phases that cannot be identified with $\text{Y/Ti} \approx 1$ to 2.

TEM indicates that the smaller (< 8 nm) NFs are approximately stoichiometric $\text{Y}_2\text{Ti}_2\text{O}_7$ oxide phases with $\text{Y/Ti} \approx 1$.

The NF N decrease in FSW and FSW plus an annealing conditions compared to the as-extruded condition, accompanied by a slight increase in $\langle d \rangle$.

The overall effect of FSW on the strength of MA957 is modest.

The NFs slowly coarsen for long term thermal aging at 1000°C for more than 19kh.

The effects of thermal aging on the strength of MA957 are modest.

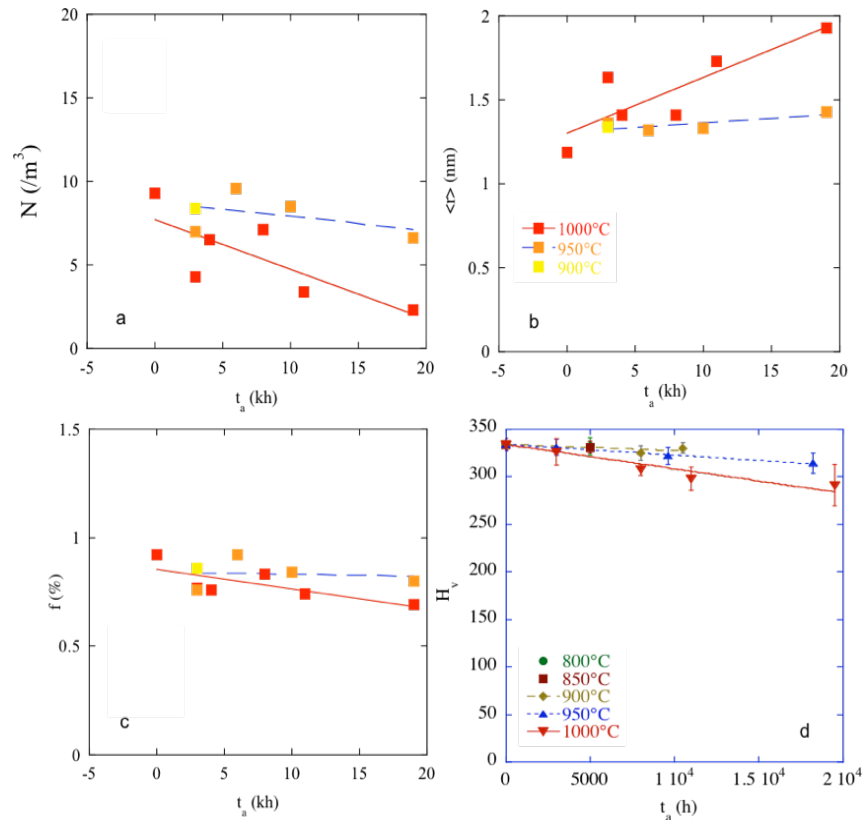


Figure 8. SANS measurements of a) N , b) $\langle r \rangle$ and c) f for LTТА at temperatures up to 1000°C and times in excess of 19 kh; d) corresponding microhardness changes.

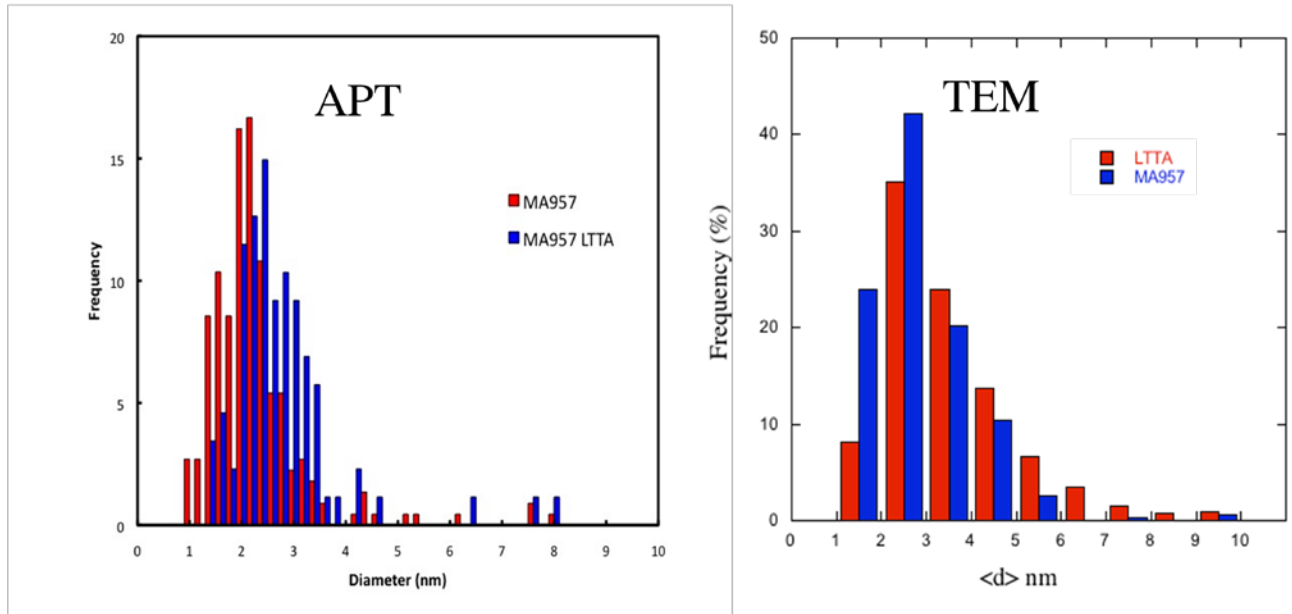


Figure 9. NF size distributions in as-extruded and LTТА MA957 measured by a) APT and b) TEM.

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TUNGSTEN-BASED MATERIALS FOR DIVERTOR APPLICATIONS - A. F. Rowcliffe (Oak Ridge National Laboratory)

OBJECTIVE

Summarize the current efforts of international fusion programs to utilize tungsten as a divertor material both for ITER and for future DEMO systems. Within this framework indicate how the scientific knowledge and expertise developed within fusion and non-fusion materials programs can be brought to bear to improve the performance of W-based materials designed for operation in the divertor environment.

SUMMARY

This paper summarizes the requirements for W-based materials for the ITER and DEMO divertor environments and the limitations of currently available commercial materials. On-going efforts to understand and to improve the behavior of W-based materials within the international fusion community are summarized together with non-fusion efforts to improve ductility and toughness via nano-scale microstructural development. Theoretical and experimental topics which could form the basis of new initiatives within the US fusion community include four steps:

- a.) Critical analyses of the existing data base,
- b.) Fundamental studies of flow and fracture in W and W alloys,
- c.) Theory and modeling of radiation damage in these materials, and
- d.) Applying alloying and nanoscale strategies developed for other metallic systems.

1. INTRODUCTION

The past 10-15 years has seen significant progress in the understanding of the fundamental mechanisms underlying radiation-induced changes in the microstructure and the mechanical behavior of both metallic and non-metallic systems. Data from experimental programs utilizing fission reactor and charged particle facilities, combined with sophisticated multi-scale modeling, have generated a scientific knowledge base embracing a broad range of topics including defect production and migration, radiation –induced segregation, nucleation and growth of bubbles and voids, phase stability, plastic deformation mechanisms, fracture mechanics behavior and phase stability [1-4]. This knowledge base was successfully utilized in assessing the impact of the ITER thermal and neutron environment on materials properties and to validate the selection of a broad range of structural and non-structural materials [2]. Beyond ITER, the development of advanced concepts for power reactors continues to be heavily dependent on this knowledge base on structural materials which continues to evolve through a network of national and collaborative programs in the US, EU, RF and Japan [1].

Although plasma-facing materials have received only limited attention from the US fusion materials program in recent years, it is apparent that many of the phenomena which strongly impact the behavior and lifetime of the structural materials of the first wall and blanket (FWB) are of equal relevance to the performance of the plasma –facing and heat sink materials of the divertor. The operating conditions of the latter however are even more complex due to the extremely high heat flux conditions coupled with surface phenomena related to erosion and blistering, injection of energetic

alphas and the absorption, migration and release of tritium. Although carbon has been the material of choice over the past 20 years of tokamak development, the transition to ITER foresees the utilization of Be as a first wall armor and the deployment of both carbon fiber composites (CFCs) and W in the divertor. Testing of blanket modules in ITER will see the continued application of Be layers on the FW. However the even more arduous operating conditions of subsequent machines leading to DEMO and subsequent power plants may require the full application of W to all plasma –facing surfaces [5,6].

The most attractive attributes of W are a very high melting point, good thermal conductivity, low sputtering yield and low activation properties in terms of long-term waste management. These advantages are unfortunately coupled with very low fracture toughness characterized by brittle transgranular and intergranular failure regimes which severely restrict the useful operating temperature window and also create a range of fabrication difficulties. Even for temperatures above the ductile-to-brittle transition temperature (DBTT), the fracture toughness of pure W falls within the range of the lower shelf fracture toughness for reduced activation ferritic –martensitic steels (RAFM). In spite of this, the favored pathway to the development of replaceable divertor components for machines beyond ITER involves a combination of inventive design solutions to accommodate the brittle behavior of W coupled with advanced cooling concepts using high pressure helium. The requirements of high power densities and high operating temperatures for thermal efficiency will dictate a set of operating conditions for a DEMO divertor which will severely challenge the performance of the currently available commercial tungsten products and probably result in unacceptably short component lifetimes [7]. The intent of this document is to summarize the current efforts of international fusion programs to utilize tungsten as a divertor material both for ITER and for future DEMO systems, and then to indicate how the scientific knowledge and expertise developed within both fusion and non-fusion materials programs can be brought to bear on the challenging issues of improving the performance of W-based materials for divertor applications.

2. THE DIVERTOR ENVIRONMENT

The surface of the divertor and the underlying heat sink structure present a complex materials–engineering challenge which must be met if a fusion-based energy source is to be successfully developed. Impurity control and ash removal requires that the outer plasma layers are directed out of their poloidal symmetry to interact with the surfaces of the divertor, the interaction being mediated by the properties of the scrape-off layer (SOL). Progress in developing sustainable structures for this environment requires a close interaction between advances in understanding and controlling the properties of the SOL, ingenuity in structural design and both evolutionary and revolutionary advances in materials. At the recent ReNeW Workshop[8], the full scope, complexity and significance of this area of fusion science and engineering were fully explored within Theme 3, "Taming the Plasma-Materials Interface". The final report of the Workshop presents a set of research activities or thrusts designed to advance the scientific and technological frontiers of the fusion program over the next two decades. The issues related to the plasma-materials interface are embodied in thrusts 9 through 12 and present a cogent overview of the multidisciplinary field of Plasma-Materials Interactions and a sobering assessment of the limitations of currently available W-based materials and their potential for fulfilling the overall long-range goal of developing a viable divertor system for DEMO.

Approximately two decades of research and engineering development within the ITER partnership have culminated in viable concepts for the various segments of the ITER divertor, and the thermal performance of these concepts has been successfully validated by the cyclic heat flux testing of prototype modules. The evolution of this effort is summarized in a series of papers spanning the past

decade or so [9-17]. The development of in-vessel components for ITER was based on the philosophy of utilizing existing commercially-available materials with minor compositional adjustments where needed to meet radioactivation requirements. An extensive materials property database was assembled under the auspices of the ITER Materials Handbook with contributions from each of the ITER Home Teams and culminated in the publication of the Materials Assessment Report (MAR) [15]. Section 2.2 of the MAR contains the most comprehensive set of information and properties data that is currently available for pure W and a limited number of W alloys, and covers processing, component fabrication, physical and mechanical properties, thermal fatigue, thermal shock resistance, and radiation effects data.

A summary of the design of the various sections of the ITER divertor, high heat flux (HHF) testing of mock-ups and procurement issues was presented recently by Lorenzetto et al. [16]. The reference ITER design (Fig.1), utilizes water-cooled CFC monoblock for the strike-point region of the vertical target, (steady state heat loads $\sim 10 \text{ MW/m}^2$, slow transients $\sim 20 \text{ MW/m}^2$), the choice of material being primarily dictated by the capacity of CFCs to withstand high levels of thermal shock without any surface layer melting. The monoblock is bonded to a water-cooled Cu-Cr-Zr alloy heat sink via active metal casting. However, since tritium retention and re-distribution is a serious issue with CFCs [17], tungsten is specified for the upper section of the vertical target ($\sim 5 \text{ MW/m}^2$ heat load) in the form of 10 mm thick tiles with a cast Cu inter-layer brazed or HIPped on to the Cu-Cr-Zr heat sink. Prototypes of the CFC sections have survived thermal loads up to 23 MW/m^2 for up to 1000 cycles and the tungsten sections have survived up to 1000 cycles at 10 MW/m^2 ; both of these conditions are well in excess of the ITER machine requirements. Details of the design and testing of prototypes of the CFC and W prototype components have been published recently [18-20]. Synergistic effects related to radiation damage in W from the fluxes of 14 MeV neutrons and 3.7 MeV alphas are not thought to be critical in ITER since the W does not have a structural function and component replacement is planned after 300 cycles.

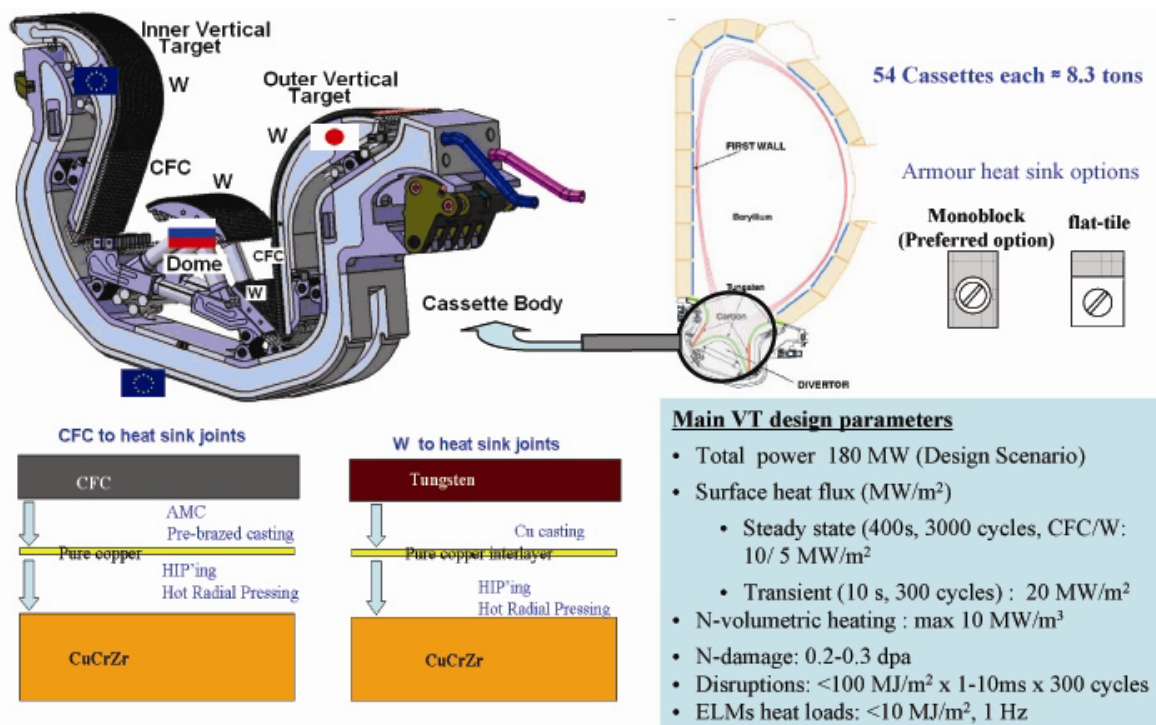


Figure 1. Layout of the ITER divertor and summary of heat loads on the vertical target. From Lorenzetto et al. [16].

Because of the seriousness of the T retention issue in the CFC sections of the ITER divertor, the possibility of converting to an all-W divertor before the start of D-T operations is being debated. Near term and long term research plans on plasma-wall interactions in ITER were presented recently as part of the overall ITER Research Plan (IRP) [17]. Operational experience with a combination of Be, C and W first wall materials are being obtained at JET under the ITER-like wall project [21]. ASDEX-Upgrade has been converted to an all-W wall and recent results indicate reliable operation under ITER-relevant high power/high density discharges with tolerable W concentration levels in the plasma of $< 5 \times 10^{-5}$ and strongly reduced levels of D retention [22].

Since ITER is an experimental machine designed to study the behavior and control of burning plasmas, there is continuing concern regarding the impact of seemingly unavoidable high transient heat loads from ELMs ($1\text{--}4 \text{ MJ/m}^2$ for $0.3\text{--}0.6 \text{ ms}$) and of vertical displacement events (up to 60 MJ/m^2 for 0.5 s) on the integrity of W divertor components. Recent results of surface loadings up to 1.3 MJ/m^2 in the JUDITH-1 e-beam facility have identified various regimes of severe cracking and surface modification as a function of surface temperature and absorbed heat load [23]. The extent of the cracking regime was shown to be dependent on both the specimen orientation in relation to the forging directions and to the final annealing treatment. The implications of off-normal events on the integrity and lifetime of the plasma facing materials have been discussed recently [24,25] and it appears that damage due to surface melting, brittle crack propagation and the erosion of broken particles to form W dust will determine the lifetime of W- armored components in ITER during D-T operation. It is clear that only a very limited number of plasma disruptions could be tolerated without inflicting major damage to the components of the divertor. [25].

Both the steady state operating conditions and possible disruption conditions in machines beyond ITER are even more severe. The operational requirements for a DEMO greatly exceed those of ITER with the plasma materials interface required to remove a four times higher power density and to operate for periods of approximately five times higher duty factor, with surface operating temperatures at $\sim 700^\circ\text{C}$ compared to $\sim 200^\circ\text{C}$ in ITER. The continuous reconstitution of the plasma-facing material surface layers by erosion, re-deposition and intermittent melting will necessitate the periodic removal and replacement of divertor components to avoid unacceptable levels of plasma contamination. As a result, goal neutron fluences will probably be considerably lower than for the first wall/blanket but still sufficient ($\sim 20 \text{ dpa/y}$) to produce significant property changes to bulk properties, raising the likelihood of synergisms between the bulk and surface related phenomena. For example injection of alphas and tritium at the surface could lead to accelerated degradation of the mechanical integrity and dimensional stability of the bulk material depending on the relative effectiveness of transport and trapping mechanisms for helium and tritium [26-28]. In addition to the overarching issues of thermomechanical loading and surface re-structuring during off-normal events, there is a range of potential bulk and surface damage mechanisms related to the radiation environment which need to be explored and quantified including:

- a) radiation hardening-induced shifts in the DBTT,
- b) recrystallization during very high temperature excursions and the potential for subsequent brittle intergranular failure regimes,
- c) void swelling and the impact of high temperature excursions on subsequent swelling behavior,
- d) grain boundary bubble nucleation and growth and the effects of temperature excursions,
- e) the fate of injected high energy alpha particles,
- f) absorption, transport, trapping and release of T, and
- g) nano-scale surface fuzz formation.

Since the DEMO operating conditions are so arduous, it is clear that the experience gained from operating a W divertor in ITER will not provide the full knowledge base needed to allow a transition to a robust design for DEMO. A radically different approach is required, based on high pressure helium cooling coupled with revolutionary improvements in materials performance. The huge gaps in our knowledge of the science of plasma-surface interaction and the serious deficiencies in the performance of existing materials which will have to be overcome in order to reach the goal of a power-producing DEMO have been highlighted by Whyte [7]. Some of the critical differences between the divertor parameters of ITER and DEMO are summarized in Table 1. The magnitude of the gaps between near-term and long term divertor concepts are comprehensively addressed, with emphasis on the materials and physics issues, by Raffray et al. [29]. Because of the complexity of the scientific and technological issues involved in the development of a robust divertor system, it has been argued that an intermediate fusion device specifically designed to qualify divertor concepts in a fusion environment will be an essential requirement before moving forward with a DEMO reactor [30, 31].

Table 1. Summary of critical divertor parameters; (from Whyte [7])

Issue / Parameter	Present Tokamaks	ITER	DEMO	Consequences
Quiescent energy exhaust <i>GJ / day</i>	~ 10	3,000	60,000	- active cooling - max. tile thickness ~ 10 mm
Transient energy exhaust from plasma instabilities $\Delta T \sim MJ / A_{wall}(m^2) / (1 ms)^{1/2}$	~ 2	15	60	- require high $T_{melt/ablate}$ - limit? ~ 60 for C and W - surface distortion
Yearly neutron damage in plasma-facing materials <i>displacements per atom</i>	~ 0	~ 0.5	20	- evolving material properties: thermal conductivity & swelling
Max. gross material removal rate with 1% erosion yield <i>(mm / operational-year)</i>	< 1	300	3000	- must redeposit locally - limits lifetime - produces films
Tritium consumption <i>(g / day)</i>	< 0.02	20	1000	- Tritium retention in material and recovery

Design work on a number of helium cooled W divertor concepts has been in progress within the EU and US for several years; details of the designs under development and the related fabrication and joining technologies may be found in references [32-37]. The most advanced design concept from the point of view of progress in the manufacture, qualification and high heat flux testing of individual modules is the European HEMJ design, the main features of which are illustrated in Fig. 2. The design principle is to utilize a small W tile ~5 mm thick as a thermal shield and sacrificial layer; these tiles are brazed to a thimble ~15 mm diameter and ~1 mm thick fabricated from W-1%La₂O₃, which forms a cooling finger for helium at 10 MPa and ~ 600/700°C inlet/outlet temperatures. The cooling fingers are

attached to a support structure fabricated from ODS Eurofer steel and the mismatch in thermal expansion between the W and the steel is accommodated by a cast Cu interlock. A summary of the current status of this effort, including design details, materials fabrication, thermal performance analyses and the results of high heat flux testing of individual finger modules, was presented at the IHMF Meeting in 2008 by Norajitra et al. [38].

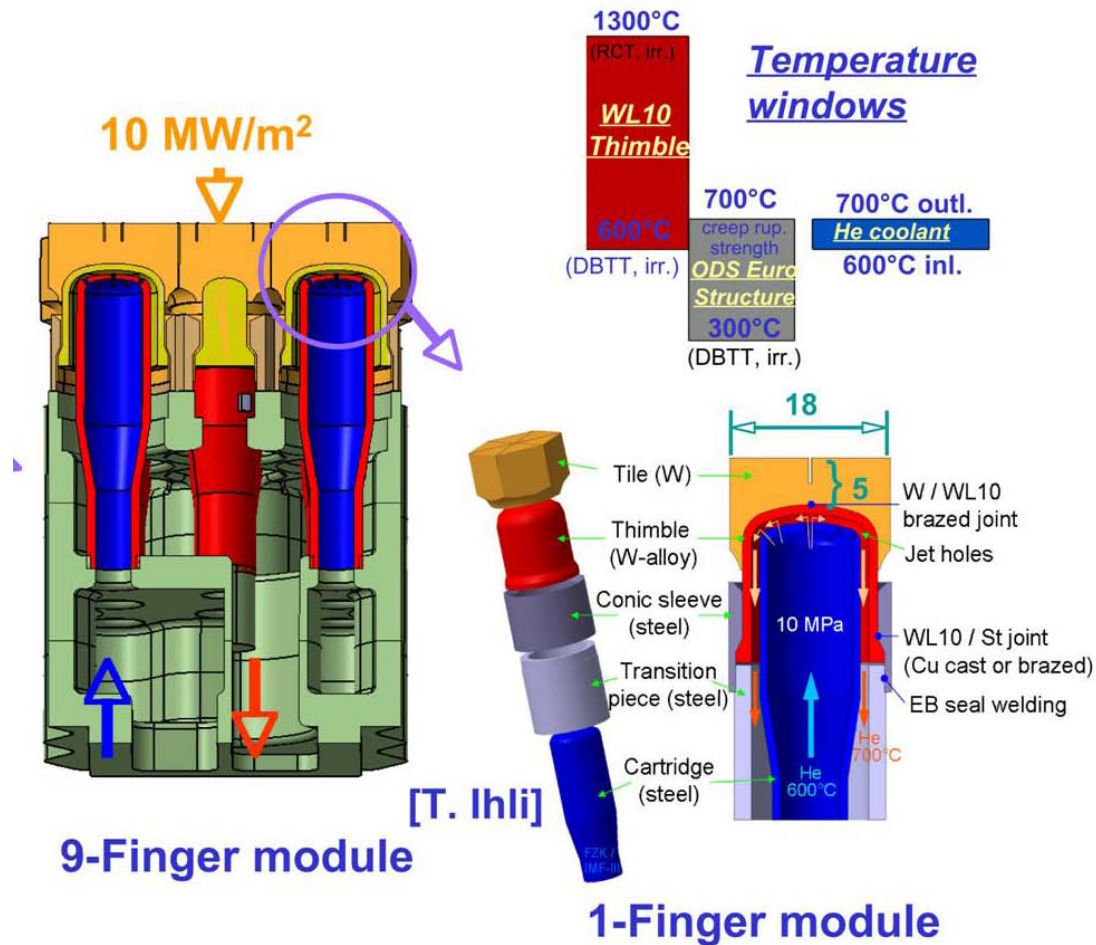


Figure 2. Schematic of the EU helium cooled divertor HEMJ design and the estimated materials operating temperature windows. From Norajitra et al. [35].

Preliminary results of high heat flux testing of prototypes of this and related designs were published recently [39], providing a graphic illustration of the problems associated with using the currently available W materials for this extremely demanding environment. Following high heat flux testing at $\sim 10 \text{ MW/m}^2$ for 70-100 cycles in an electron beam facility, all of the modules suffered serious structural damage (Fig. 3). Subsequent examination revealed:

- a dense network of cracks perpendicular to the surface extending ~ 200 microns,
- coverage of the exposed tile surface with a layer of brazing alloy,
- cracking of all brazes,
- propagation of cracks parallel to the elongated grain structure of the W-La₂O₃ and completely through the thimble wall, and
- development of a gap between the thimble and the sacrificial tile.

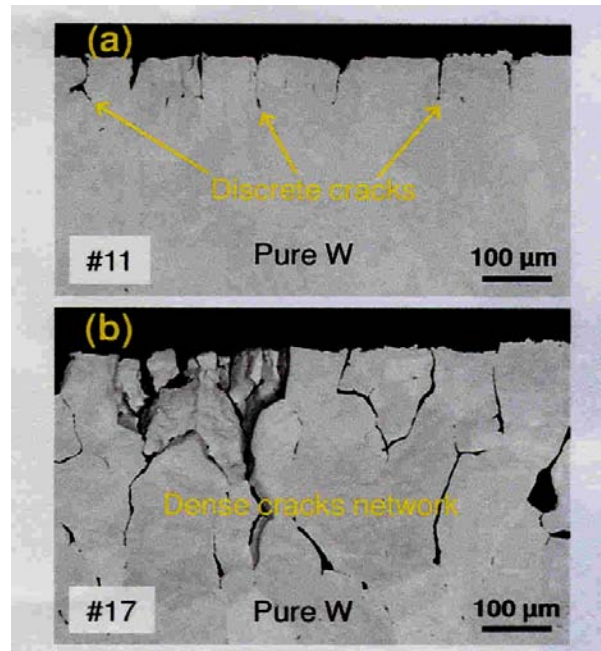


Figure 3. W tile for the HEMJ module, a) surface cracks induced by EDM during manufacture and b) cracking induced during HHF testing for 89 cycles at 10 MW/m^2 . From G.Ritz et al. [39]

This experience clearly demonstrates the complexity of the materials issues and design challenges that need to be overcome even without considering the additional deterioration in materials properties induced by neutron irradiation. The application of electro-chemical machining and electro-chemical deposition technologies to mitigate some of the fabrication issues associated with surface cracking and achieving high-integrity brazes was described recently by Krauss et al. [40]

It is generally recognized that to meet the performance requirements of divertor components beyond ITER, innovation in component design and cooling technologies will have to be coupled with dramatic advances in the science and technology of high heat flux materials. Addressing the extreme brittleness of existing commercial rod and plate W materials is probably the most pressing need. Any improvements in the ductility / fracture toughness properties and resistance to recrystallization would have immediate benefits in terms of the ability to survive thermally-induced mechanical stresses without severe brittle failure and also in easing fabrication difficulties. These endeavors must be accompanied by developing an increased understanding of the effects of radiation hardening on flow and fracture in W since any gains in terms of ductility and toughness could be negated by radiation hardening –induced shifts in the DBTT. Any compositional or multi-scale microstructural changes designed to improve fracture resistance will inevitably affect the response to radiation damage.

The additionally important problems related to surface erosion and restructuring during severe thermal and particle fluxes induced by during disruptions, fall primarily into the realm of plasma control and component design rather than the development of new materials. However, the potential for utilizing micro-engineered tungsten, in the form of nano-porous plasma spray or an open cell foam, for armor material in an inertial fusion energy system are being explored [41,42]. More recently, the deployment of W refractory foam materials to enhance heat removal in a flat plate divertor concept has been discussed [43].

3. DEFORMATION AND FRACTURE OF TUNGSTEN

Tungsten in various forms has a wide range of non-nuclear applications, including welding rods, heating elements, lighting filaments, and projectiles. There is a well established fabrication technology based on powder metallurgy and high temperature processing to produce a variety of wire, rod and plate forms. Product consistency in terms of impurity level and grain structure and strength properties is assured via the appropriate industrial standards [44]. The basic physical, mechanical and corrosion properties, details of various processing technologies, alloying behavior (including oxide and carbide dispersion strengthening) are compiled and reviewed in the book by Lassner and Schubert [45]. Theoretical and experimental studies of the fundamental mechanisms of deformation and the influence of microstructural parameters and impurity levels on the DBTT in W and other BCC metals have been extensively pursued for the past 25 years or so and a critical review of this voluminous topic is far beyond the scope of this document. However a thorough appreciation of the materials science of brittle materials, and tungsten in particular, must obviously form the underlying basis of any practical initiatives to moderate the inherent brittleness of W either through alloying or microstructural control. A selection of some of the most relevant contributions to the field of the brittle behavior of BCC materials and of W in particular is provided in references [46-68].

One of the recurring concerns that arise in all high temperature applications of W is the extremely brittle behavior of recrystallized W. There are only limited data on the physical parameters controlling recrystallization, (dislocation density, subgrain structure, texture, time and temperature etc.) and a systematic study has never been attempted. The Group VIA metals in general exhibit intergranular brittle behavior when they are in a recrystallized condition and this phenomenon is generally considered to be related to the behavior of interstitial impurities and their segregation to grain boundaries during the high temperature excursion and subsequent cooling. Molybdenum provides a well known example; Kumar and Eyre [69], considered that the brittle behavior of recrystallized Mo was associated with the segregation of oxygen to grain boundaries and that the effects could be mitigated by the addition of carbon. Earlier Auger fractography studies on W implicated the segregation of P to grain boundaries with the concentration of P increasing with the grain size [70]. More recently, the effects of impurities on the intrinsic fracture resistance of grain boundaries in W have been investigated using a molecular dynamics simulation, Grujicic and Zhao [71] and Grasco [72]. These calculations show that B, C and N strongly increase the cohesive strength of grain boundaries whereas O, Al and Si do not significantly affect the ideal work of decohesion or crack blunting processes. However, both P and S are shown to significantly lower the work of grain boundary decohesion and impede crack tip blunting processes. The fundamentals of grain boundary segregation and the impact of segregation on grain boundary cohesion and fracture were reviewed by Hofmann and Lejcek [73].

4. RADIATION EFFECTS

The data base on radiation effects in W is very limited since given the brittle behavior, there has been very little interest in W-based materials in the nuclear field except as a potential target material for spallation neutron sources [74]. In fact even the basic dose and irradiation temperature dependence of radiation hardening have yet to be determined. Most of the available radiation effects data were collected and summarized in the ITER Materials Assessment Report [15], and subsequently there has been very little added to that database. It is known that neutron irradiation at temperatures below $\sim 500^{\circ}\text{C}$ to low doses (1.0-1.5 dpa) produces large increases in yield stress and a complete loss of total

elongation. Using data from bend bars and tensile specimens, severe embrittlement has been observed in W and several alloys irradiated to doses below ~ 1 dpa at temperatures below $\sim 400^\circ\text{C}$ (Fig. 4).

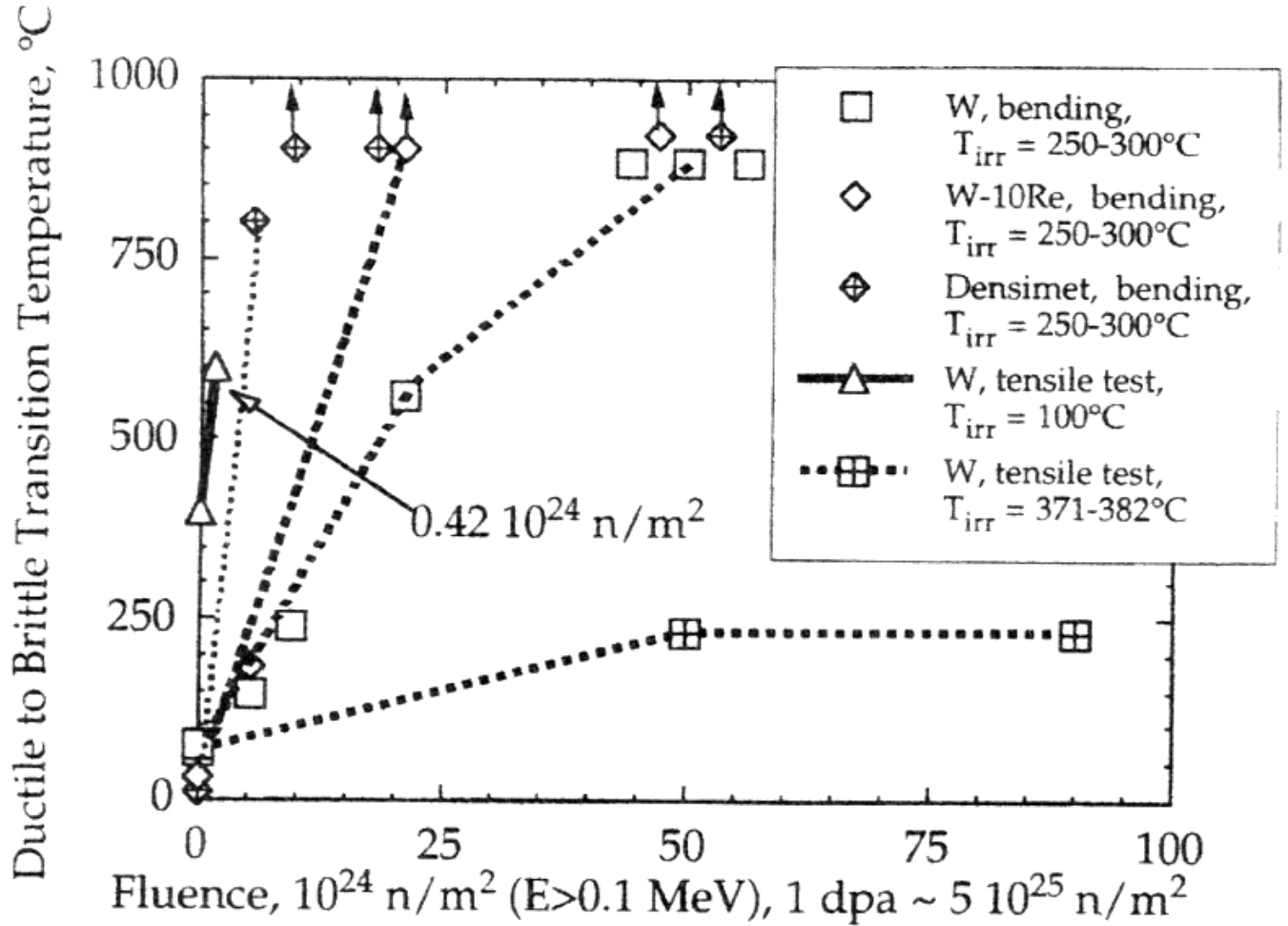


Figure 4. Neutron dose dependence of the DBTT assessed from tensile and bend tests for W, Densimet, and W-10%Re. From the ITER Materials Assessment Report [15].

The minimum irradiation temperature which will avoid serious radiation embrittlement for doses appropriate for DEMO or even for ITER are not known. However, based on available measurements and extrapolating from the data for Mo and TZM, this temperature is probably in the region 800-900°C. The available neutron irradiation data on several W alloys indicate a peak swelling temperature of ~ 800°C for doses up to ~ 9 dpa (Fig. 5) and the formation of void lattices in the range 550-750°C. The behavior of point defects in nanostructured metals during irradiation was discussed by Wurster and Pippan [74] together with a summary of recent experimental data for W-based materials. Additional information on radiation effects may be found in Refs. [75-80]

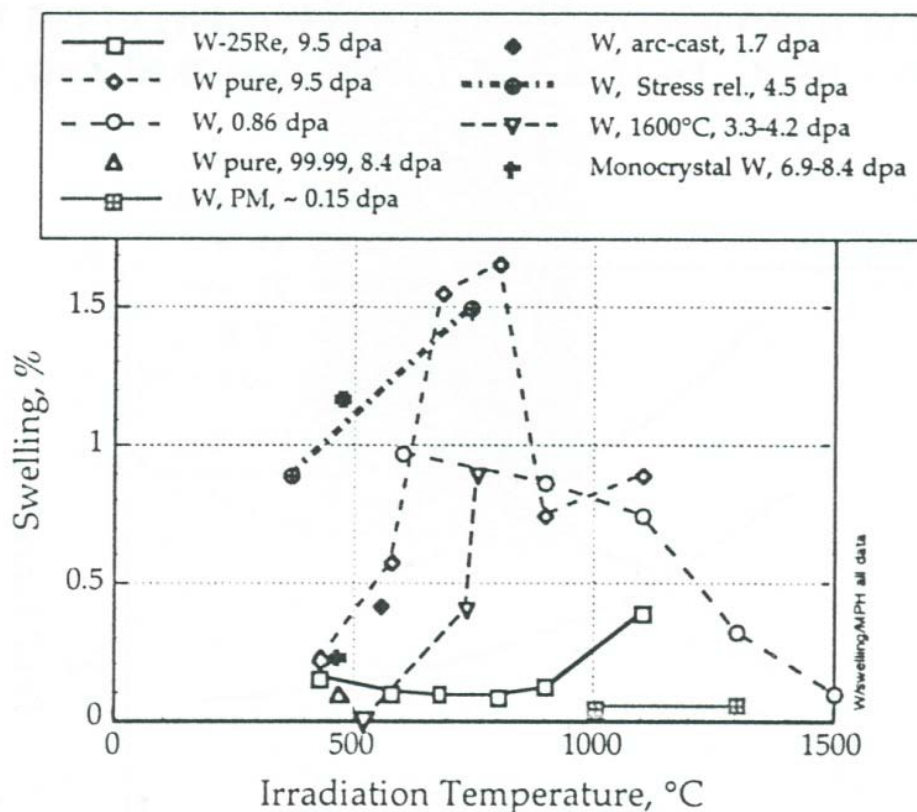


Figure 5. Summary of swelling data for W and W alloys suggesting a peak temperature at ~ 800°C for 5-10 dpa. From the ITER Materials Assessment Report [15].

5. IMPROVING DUCTILITY AND TOUGHNESS: ALLOYS AND MULTI-PHASE MATERIALS

A summary of earlier empirical efforts to improve the ductility of W through alloying and by incorporating oxide or carbide particles may be found in Lassner and Schubert [45]. Currently, several fusion and non-fusion materials programs in Japan and the EU are pursuing several possible routes to developing W-based materials with improved ductility. These are primarily empirical in nature with a focus on W-Re alloys, W-1%La₂O₃, and W-1%TiC. An overview of these efforts was presented by Rieth and Dafferner in 2005 [81].

W-Re alloys

The commercial W-23%Re alloy is now regarded as unsuitable for fusion applications for several reasons:

- a) limited data indicate that radiation hardening-induced shifts in DBTT are similar to W,
- b) neutron activation issues and enhanced decay afterheat,
- c) reduced conductivity compared to W, and
- d) the formation of radiation –induced or radiation-enhanced intermetallic phases [82-84].

Alloys containing 0.1-5.0 wt.% Re may have more potential. Based on fracture toughness data, it has been shown that the addition of ~5 wt.% Re reduces the DBTT of W by ~ 300°C; recrystallization and grain growth are also inhibited [85]. The addition of 0.1-1.0% Re has been observed to reduce the DBTT for W single crystals [86]. The results of atomistic modeling of the ductilizing effects of alloying with Re were presented recently by Gludovatz et al. [68] indicating that alloying with Re results in a transition to an asymmetric dislocation core and a significant reduction in the Peierls stress. The possibility that other alloying elements such as Ti, Ta and V could produce similar effects is under investigation.

W-1% La₂O₃

Originally developed as an improved material for welding electrodes, W-1% La₂O₃ is also being considered for high temperature turbines in hydrogen energy systems [87,88]. However there is no materials science basis for expecting improved fracture toughness or improved radiation behavior in the commercially available alloy compared to pure W. The commercially available material contains a coarse distribution of La₂O₃ particles 5-20μ long aligned in the hot-working direction [89], see (Fig 6).

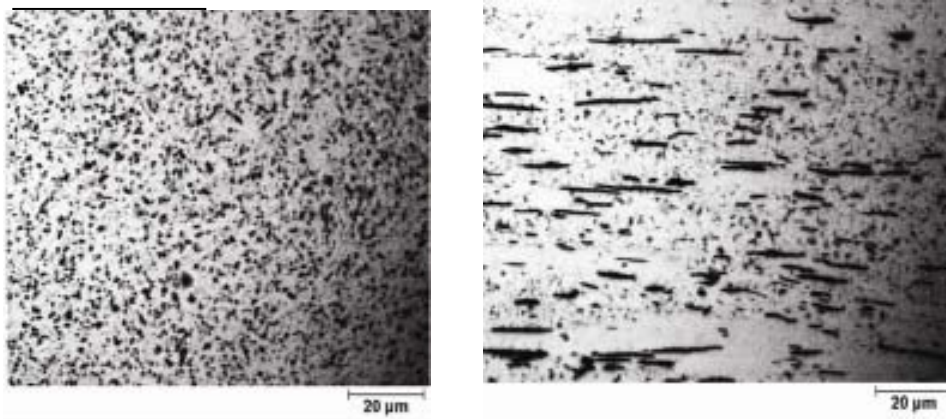


Figure 6. Transverse and longitudinal sections of commercial W- La₂O₃; coarse non-uniform dispersion with La₂O₃ particles strongly elongated in the hot-working direction. From Rieth and Hoffman [89].

A mechanism for the development of the elongated particle morphology during processing has been discussed by Z. Chen et al. [90]. High heat flux testing results indicate enhanced surface erosion related to vaporization of elongated La₂O₃ particles resulting in blistering [91,92]. This material was dropped from consideration for the ITER divertor [15], but it is still regarded as a potential material for the

thimble structure for a He-cooled divertor for DEMO [35, 36] since the La_2O_3 particles appear to inhibit recrystallization to some extent. Efforts to improve the performance of welding electrodes by varying processing parameters indicate that it may be possible to refine the particle size distribution into the nano-size range [93]. It has not been determined whether or not these radically different microstructures would also translate into improved mechanical behavior.

W-TiC

Researchers in Japan are pursuing various empirical approaches to producing TiC dispersions in W via mechanical alloying followed by HIPing at 1350°C or high temperature forging [94-98]. Kurishita et al. [95] reported that the W grain size became increasingly refined as the TiC content was increased from 0.3-1.5%; average grain sizes in the 50-100 nm range were achieved when processing was carried out in purified Ar. Grain size refinement was attributed to grain boundary pinning by TiC particles. Evidence was presented for the precipitation of TiC during processing although there is very little information on the size and number density of the dispersoid [95]. In subsequent work, the concentrations of Ti, C and Ta were varied in a successful effort to suppress the formation of the W_2C phase during processing. It was found that a W-0.3Ti-0.006C alloy exhibited appreciable ductility in room temperature tensile and three point bend tests with un-notched specimens. However, the ductility appears to be related to the very high aspect ratio grain structure and delamination during fracture [96]. Recently it was reported that W-TiC materials exhibit superplastic behavior at temperatures above ~1500°C for TiC contents > 0.25% [97]. The possible advantages of W-TiC materials in terms of improved radiation performance have also been discussed recently [98]. In related studies it has been shown that nano crystalline TiC is formed during prolonged ball milling of micron –sized powders of Ti and graphite [99,100], possibly indicating a means of improving the homogeneity of TiC dispersions.

W- W_{wire} composites.

Composite tungsten materials containing high volume fractions of various metal oxides and carbides have been investigated extensively [45]; however the thermal conductivity of tungsten is substantially reduced by the introduction of 20-40 vol.% of dispersoid. For fusion applications the incorporation of W wires into a W matrix is a more viable approach in which a fiber/matrix interface is engineered to dissipate the crack energy via interfacial de-bonding and friction. Preliminary results of a proof-of principle study were presented recently by You et al. [101].

6. IMPROVING TOUGHNESS THROUGH GRAIN SIZE ENGINEERING

Advances in processing techniques and computational materials research have made it possible to achieve grain sizes in the ultra-fine grain regime, (UFG, $d \sim 100\text{-}500\text{ nm}$) and the nanocrystalline regime, (NC, $d < 100\text{ nm}$) for a wide range of metallic materials. The drive and interest in nanocrystalline materials comes from the development of higher strength and /or ductility with increasing strain rate and the possibility of superplastic deformation at lower temperatures. Most of this work has focused on fcc materials and the refinement of the grain size of bcc materials into the UFG/NC regimes is more difficult. A number of reviews of this rapidly growing field are available [102-108]. While there is reason to believe that microstructures in the NC regime would result in some advantages in terms of resistance to radiation damage compared to coarse-grained W, the possible advantages in term of fracture toughness and the high temperature microstructural stability of bulk UFG/NC materials remains to be demonstrated [109]. In this regard, Yang and Yang [110] have discussed the competing mechanisms of grain boundary dominated plastic deformation and grain boundary decohesion which possibly control the DBT in nanostructured metallic systems.

The principles of synthesizing nanostructured materials via mechanical milling and high temperature consolidation have been reviewed for example by Koch [102]. This approach, often referred to as bottom-up processing, has advantages when dealing with brittle materials but requires special precautions with regard to contamination and to the development of defects during the consolidation stages. The alternative top-down approach employs a forged or HIPed powder metallurgical product as a starting point and accesses the UFG and NC regimes via the imposition of very high levels of strain, i.e. severe plastic deformation (SPD) processing. (This distinction is somewhat artificial since mechanical milling also involves the imposition of severe levels of plastic deformation). The various techniques employed in the top-down mode of processing have been reviewed for example by Valiev et al [103]; a comprehensive set of papers dealing with SPD of a broad range of metals and alloys has been presented in a Materials Science Forum [111]. Both approaches are currently being utilized in attempts to induce some level of ductile behavior and to lower the DBTT in tungsten. Refinement of the grain size of W and W-10% Re has been demonstrated by Oda et al. [112] via mechanical milling combined with consolidation utilizing spark plasma sintering. The development of nano-sized grains within the deformed powders was tracked via TEM and Fig. 7 illustrates the equiaxed nature of the ultra-fine grains produced by this approach. Evidence was also presented for the suppression of grain growth of nano-grains in the W-Re alloy related to segregation of Re to the grain boundaries. It has been shown recently by Wang et al. [113] that nanocrystalline tungsten powders produced by ultra-high energy milling have greatly enhanced sintering properties; 97% densification was achieved by pressureless sintering in hydrogen at temperatures as low as 1100°C.

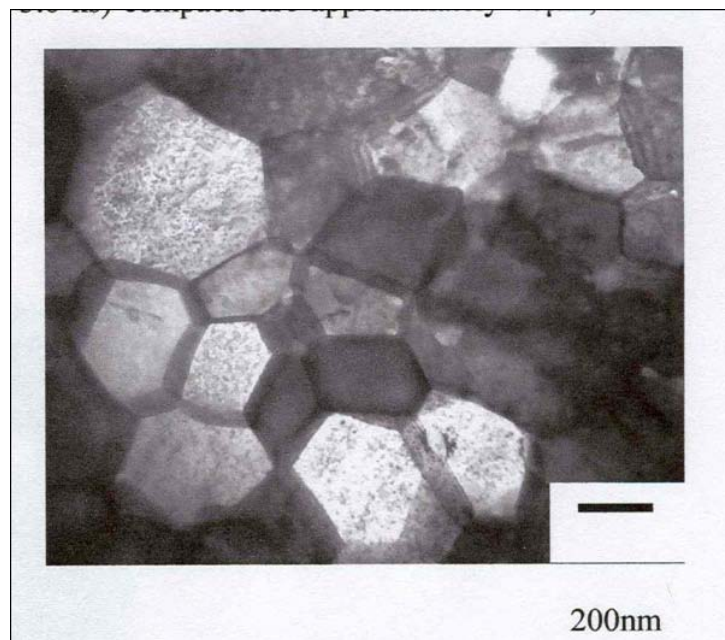


Figure 7. TEM microstructure of nanocrystalline tungsten produced via mechanical milling and spark plasma sintering at 1200°C. From Oda et al. [112].

There is an on-going effort to modify the deformation behavior of W by producing UFG and NC materials with the goal of improving the penetrating power of W-based projectiles [114-116]. Because of difficulties in avoiding rapid grain growth and achieving full density during the consolidation stage during bottom-up processing of pure tungsten, in this area more attention has been focused on top-down processing utilizing Equal Channel Angular Extrusion (ECAP) and high pressure torsion (HPT) [115]. Microstructures of tungsten in the UFG/NC regime produced by ECAP and HPT processing are shown in Fig.8. Under compressive loading conditions at room temperature, it was demonstrated that failure in the UFG materials occurred primarily by localized shearing rather than by brittle fracture [116].

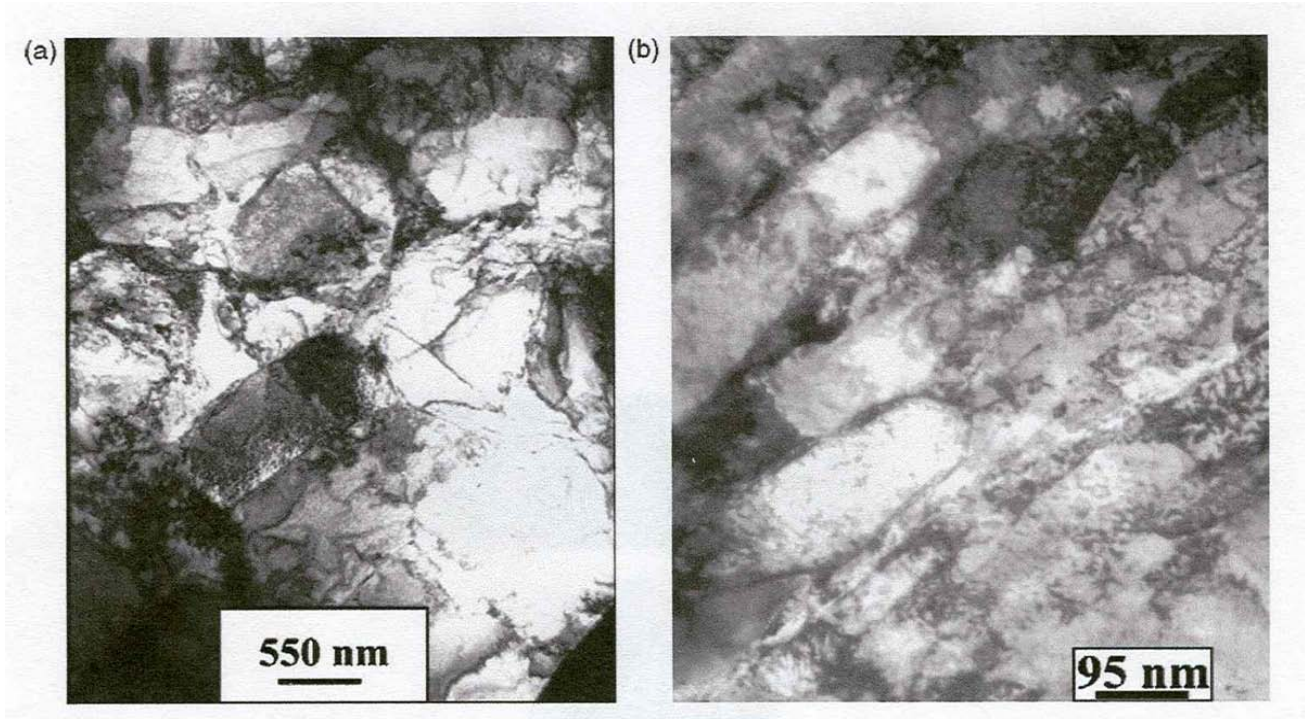


Figure 8. TEM micrograph of pure tungsten (a) processed by Equal Channel Angular Extrusion, four passes at 1000°C followed by lower temperature rolling, average grain size ~500nm and (b) processed by HPT to give an average grain size ~120 nm. Both structures characterized by high dislocation densities and low levels of texture. From Kecskes et al. [115].

Pure W, W-La₂O₃ and K-doped W have also been produced via SPD processing with grain sizes in the ~ 300 nm regime [117]; fracture toughness testing demonstrated a significant increase in RT toughness with increasing levels of deformation and simultaneous reductions in grain size, (Fig.9). Qualitative improvements in the fracture behavior of UFG equiaxed tungsten produced via ECAP were reported by Zhang et al. [118]. Data on the high temperature stability of UFG and NC tungsten is practically non-existent although Zhou et al. [119] recently reported an increased resistance to recrystallization in UFG tungsten fabricated by resistance sintering under ultra-high pressure.

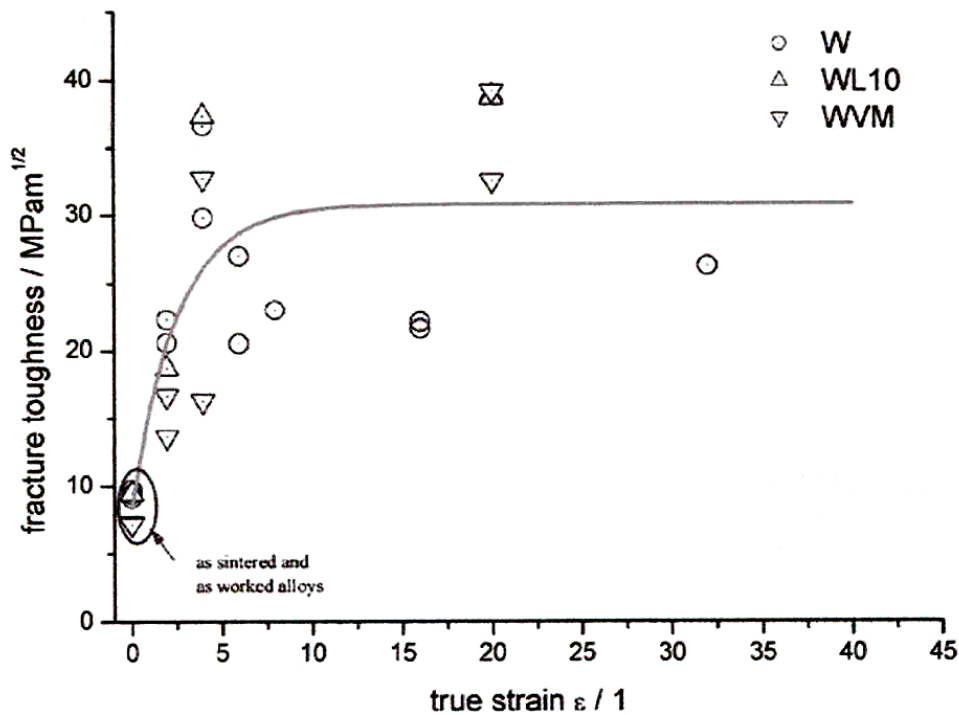


Figure 9. Fracture toughness (DCT specimens) of pure W, W-La₂O₃ and K-doped W as a function of plastic strain applied via high pressure torsion processing; grain sizes ~300 nm. From Faleschini et al. [117].

7. DESIGN OF IMPROVED TUNGSTEN-BASED MATERIALS

Achieving the widest possible operating temperature window for tungsten-based divertor materials presents a major challenge involving not only solutions to the high strength /low ductility paradigm in BCC materials but also the development of strategies to mitigate damaging mechanisms related to plasma –surface interactions, radiation effects and high temperature excursions during off-normal events. A long-term multidisciplinary effort will be needed characterized by close interactions between the materials and PMI communities together with industrial partnerships in order to access a variety of processing technologies.

On-going efforts to improve the ductility of W-based materials based on W-La₂O₃, W-TiC and grain size engineering, as summarized above, are unlikely to succeed in producing materials that meet the full range of desirable characteristics in terms of fabricability, improved ductility over a wide temperature range, radiation damage resistance and microstructural resistance to high temperature excursions. Clearly, the development of materials with improved properties in all of these areas simultaneously will require a science-based approach to developing a set of compositional and microstructural design principles, the establishment of microstructure-property relationships, and the appropriate processing-microstructure relationships. To support these efforts, it will also be necessary to develop processing technologies which will deliver the required control of impurity levels coupled with predictable, consistent, and uniform microstructures. In order to develop science-based strategies for improving the properties of W-based materials, the fundamental knowledge –base will need to be strengthened in many areas including deformation and fracture, chemical and mechanical alloying,

formation and stability of carbide and oxide dispersions and solute clusters, high temperature microstructural stability and radiation damage. As noted above, a significant amount of new information is currently being generated in both fusion and non-fusion materials programs in the EU, China, Japan and the US. There is a broad range of theoretical and experimental topics which could be used as a basis for new initiatives within the US Fusion community; these are summarized below in four main categories.

7.1 Critical analysis of the existing data base

The existing literature data needs to be evaluated and analyzed in order to clarify the current state of knowledge in the following areas:

- a) The current experimental data base on the fracture behavior of tungsten based materials.
- b) The conditions which control transitions from transgranular to intergranular fracture the factors causing de-lamination; the effect of interstitial impurities, grain size and texture; the influence of processing methods and parameters on microstructure and fracture behavior; and the methodology of fracture testing.
- c) The relative effectiveness of various approaches to achieving dispersions of oxide and carbide particles and varying particle size distribution thermodynamics of alloy systems, alloying behavior with potential dispersoid-forming elements; mechanisms of mechanical alloying in tungsten
- d) Improving ductility and toughness via reduction of grain size into the UFG and NC regimes; examination of the data for FCC and BCC materials to elucidate the potential advantages of grain size engineering as a viable approach to improving the fracture properties of tungsten.
- e) Data on the recovery and recrystallization behavior of refractory metals and controlling mechanisms; role of initial grain size and texture, dislocation density, time and temperature.

7.2 Fundamental studies of flow and fracture in tungsten

Theory and modeling work coupled with fundamental experiments is needed in the following areas, some of which are the subject of on-going studies in the EU and in Japan;

- a) Definition of principles for microstructural design for higher toughness in low, medium and high temperature regimes; influence of grain size and texture, particle dispersions, dislocation substructures and grain boundary structure.
- b) Atomistics of brittle fracture, both transgranular and intergranular; crack tip plasticity in tungsten, dislocation generation and mobility; influence of interstitial and substitutional solutes.
- c) Deformation and fracture mechanisms in BCC materials with grain sizes in the UFG and NC regimes; thermal stability of nano-engineered grain structures.

7.3 Theory and modeling radiation damage in tungsten

Nanoscale microstructures designed for improved ductility and toughness may alter the basic radiation damage response of tungsten-based materials and could possibly result in increased recombination rates of point defects and enhanced trapping of helium. Additional needed studies could include:

- a) Development of principles for the design of damage resistant microstructures; effects of grain size reduction into the NC regime; dislocation substructures; oxide and carbide nano- scale precipitates as traps; development of solute nanoclusters and their thermal stability.

- b) Primary damage, defect production and cluster formation in W migration and trapping of helium and tritium, interaction of dislocations with defects, radiation hardening mechanisms, effect of grain size from micron to nano-scale regimes.
- c) Radiation-induced segregation and phase stability in dilute W alloys; potential sources of non-hardening embrittlement.
- d) Carefully controlled low dose neutron irradiation experiments to map out the dose-temperature characteristics of radiation hardening, deformation and fracture behavior in polycrystalline and single crystal W

7.4 Alloying and nanoscale strategies developed in other metallic systems

Several new strategies for modifying the strength and ductility of metallic systems and for modifying radiation response have evolved in recent years. The potential application of these approaches to tungsten-based systems needs to be examined in terms of how these new ideas could be utilized in the design of new alloys and microstructures to meet alloy development goals.

- a) First principles density functional theory calculations have been used to predict Poisson ratio in Cr alloys and to identify potential ductilizing additives and the design of new materials using quantum mechanical calculations [120].
- b) Design principles for nano-clustered alloys and related fabrication technologies have been successfully developed for the NC ferritic steels [121,122]; these alloying principles could possibly be extended to W-based systems in order to develop nanoscale precipitates and solute clusters.
- c) The potential for optimizing strength and ductility in a wide range of materials by engineering coherent internal boundaries at the nanoscale has been reviewed recently [123]. Although primarily focused on FCCs, this methodology could possibly provide a new approach to the development of W-based materials with nanoscale sub-structures
- d) Evidence has been presented for a reduction in the Peierls stress in W by alloying with Re; it is proposed that this could be the primary source of the observed ductilizing effect of Re; other solutes may have similar effects and so contribute to enhanced crack-tip ductility, Gludavatz et al. [68]
- e) Nanocrystalline microstructures via bottom-up and top-down technologies have been developed for a wide range of metallic systems including tungsten [114-119]. Modeling efforts are needed in the areas of the mechanical behavior, thermal stability and irradiation behavior of UFG and NC tungsten-based systems.

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FIRST-PRINCIPLES INVESTIGATION OF THE INFLUENCE OF ALLOYING ELEMENTS ON THE ELASTIC AND MECHANICAL PROPERTIES OF TUNGSTEN— G. D. Samolyuk, Y. N. Osetskiy, and R. E. Stoller (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this research is to support possible approaches to the design of ductile tungsten alloys through the use of relevant *ab initio* electronic structure calculations.

SUMMARY

The equilibrium lattice parameter, elastic constants and phonon dispersions were calculated for set of binary $W_{1-x}Re_x$ alloys with different Re concentrations within the local density approximation of density functional theory (DFT). Reasonable agreement between results obtained using conventional super-cell and virtual crystal approximation (VCA) approaches has been demonstrated. Increasing the Re concentration leads to reduction of the c' elastic constant which becomes negative at a Re concentration of 85%. This change of sign means that the bcc structure is no longer stable at high Re concentrations. In contrast to the c' dependence, Poisson's ratio increases with increasing Re concentration. The value of this latter parameter is used as a screening parameter to identify improvement in the alloy ductility.

PROGRESS AND STATUS

Introduction

The alloys of W with Re have been studied extensively both using experiment [1, 2] and theory [3, 4]. Alloying with Re has the effect of ductility improvement of the tungsten. In the present research we are going to investigate the concentration dependence of elastic constants and phonons from first-principles electronic structure calculation. This result will be used in future search for the other alloying elements causing similar changes in tungsten alloy elastic properties.

Formalism

We calculate the electronic structure within the local density approximation of density functional theory using the quantum espresso package [5]. The calculation has been done using plane-wave basis set and ultrasoft pseudo-potential. The Brillouin zone (BZ) summations were carried out over a $24 \times 24 \times 24$ BZ grid for the system with one unit cell and $16 \times 16 \times 16$ grid for the supercell, representing $2 \times 2 \times 2$ unit cells, with Gaussian broadening 0.02 Ry. The plane wave energy cut off at 42 Ry allows reaching accuracy 0.2 mRy/atom. As a realization of VCA for the pseudo potential method we used the scheme proposed in Ref. [6]. The phonon frequencies were calculated using the density-functional linear response method [7, 8].

The elastic constants were calculated from the total energies obtained for the set of unit cell deformations [9] with strain tensor

$$\hat{\varepsilon} = \begin{bmatrix} e_1 & e_6/2 & e_5/2 \\ e_6/2 & e_2 & e_4/2 \\ e_5/2 & e_4/2 & e_3 \end{bmatrix} \quad (1)$$

Under this strain the change of the energy equals

$$\Delta E = -P(V)\Delta V + V \sum_{i=1}^6 \sum_{j=1}^6 c_{ij} e_i e_j / 2 \quad (2)$$

Thus for the orthorhombic strain

$$e_1 = -e_2 = x, e_3 = x^2/(1-x^2), e_4 = e_5 = e_6 = 0 \quad (3a)$$

the energy change equals

$$\Delta E = V(c_{11} - c_{12})x^2 \quad (3b)$$

and for monoclinic strain

$$e_6 = x, e_3 = x^2 / (4 - x^2), e_1 = e_2 = e_4 = e_5 = 0 \quad (4a)$$

it equals

$$\Delta E = V c_{44} x^2 / 2 \quad (4b)$$

where c_{ij} are elastic constants.

The Poisson's ratio equals

$$\nu = \frac{c_{12}}{c_{11} + c_{12}} \quad (5)$$

Results

The results for the density of states calculated for 2x2x2 super cell containing 16 atoms in total, 16 W for pure metal and 15 W and 1 Re for the modeling of W alloy with 6.25 Re atoms alloying, and calculated in VCA approximation are presented on Figures 1a and 1b respectively.

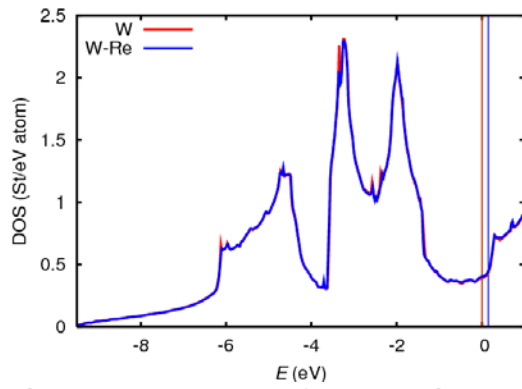


Figure 1a $W_{1-x}Re_x$ DOS for $x=0$ and $x=0.0625$ calculated in VCA

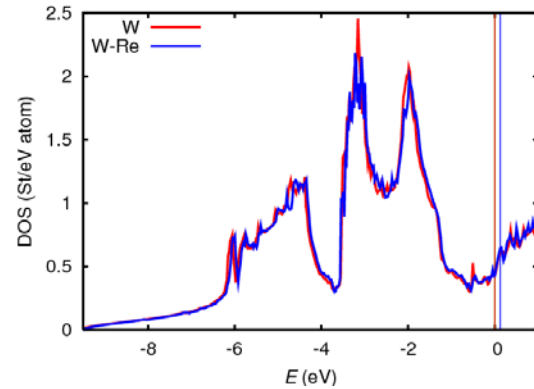


Figure 1b $W_{1-x}Re_x$ DOS for $x=0$ and $x=0.0625$ calculated for super cell 2x2x2

The zero energy in these figures corresponds to occupation of valence states by 6 electrons per atom and Fermi energies are shown by the vertical line red for pure metal and blue for the W-Re alloy. Thus for the pure tungsten the Fermi energy is placed at 0 eV. The similarity of the DOS calculated by two methods supports the conclusion of applicability of the VCA approximation for W-Re alloys at low Re concentration. As can be seen from both figures the only effect of Re alloying on the electronic DOS is the shift of the Fermi energy corresponding to occupation of each virtual atom by an additional 0.0625 electrons. It means that the so called rigid band approximation can be applied. Thus, all diluted tungsten based alloys with the same number of electrons per atom (e/a) have the same elastic constants. The concentration of different alloying elements which keep the same (e/a) value can be calculated through the simple expression

$$x = \frac{(e/a)}{Z - Z_w} \quad (6)$$

where Z is number of valence electrons of the alloying atom and Z_w - of tungsten.

The calculated elastic properties reproduce experimental results with 10% accuracy, as can be seen from the comparison of calculated phonon dispersions with experiment, shown in Figure 1.

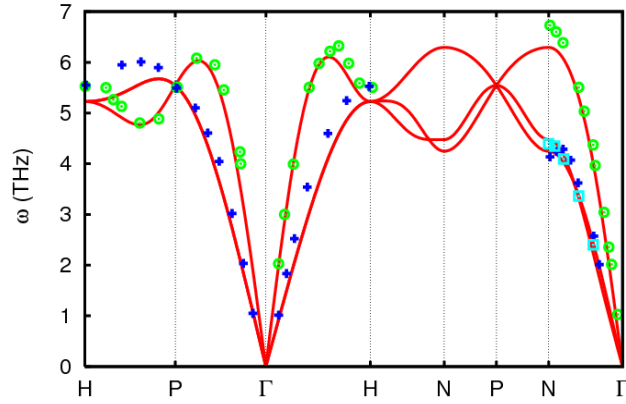


Figure 2 Calculate and experimental [10] phonons in pure W.

In order to check the accuracy of the VCA approximation we calculated the elastic modulus of a $W_{1-x}Re_x$ alloy for the concentration $x= 0.0625$ by both super cell and VCA methods. The results are presented in Table 1 and figures 2-5.

Table 1. Experimental (first row) and calculated lattice parameter (a), bulk modulus (B), elastic constants (C_{ij}) in GPa and Poisson's ratio ν .

		a (a.u.)	B	$C_{11}-C_{12}$	C_{44}	C_{11}	C_{12}	ν
exp	W	5.98	314	328	163	533	205	0.278
1x1x1	W	6.03	307.1	320.7	141.1	520.9	200.2	0.278
	$W_{1-x}Re_x$, $x=0.03$	6.024	306.1	311.9	142	514.0	202.1	0.278
	$W_{1-x}Re_x$, $x=0.05$	6.022	305.5	306.2	142.9	509.6	203.5	0.285
	$W_{1-x}Re_x$, $x=1/16$	6.020	305.2	302.6	143.5	506.9	204.3	0.287
	$W_{1-x}Re_x$, $x=0.10$	6.015	303.8	292.0	144.6	498.5	206.5	0.293
	$W_{1-x}Re_x$, $x=0.30$	5.988	296.0	259.9	155.6	469.3	209.4	0.309
	Re	5.918	338.3	-60.5	162.9	298.0	358.5	0.546
2x2x2	W_{16}	6.019	305.9	308.9	138.6	511.8	202.9	0.284
	$W_{15}Re$	6.015	299.0	295.6	139.3	496.1	200.5	0.288

For the elastic constants the largest difference between calculated and experimental values was obtained for c_{44} and is about 13 % for the one unit cell calculations and slightly larger for 2x2x2 super cell calculations. The VCA and super cell results are in reasonable agreement, except for the c_{44} dependence on Re concentration. c_{44} increases in VCA calculation and decreases in super cell case with addition of 6.25 % of Re to W. However, the VCA result is in agreement with experiment, see Figure 3.

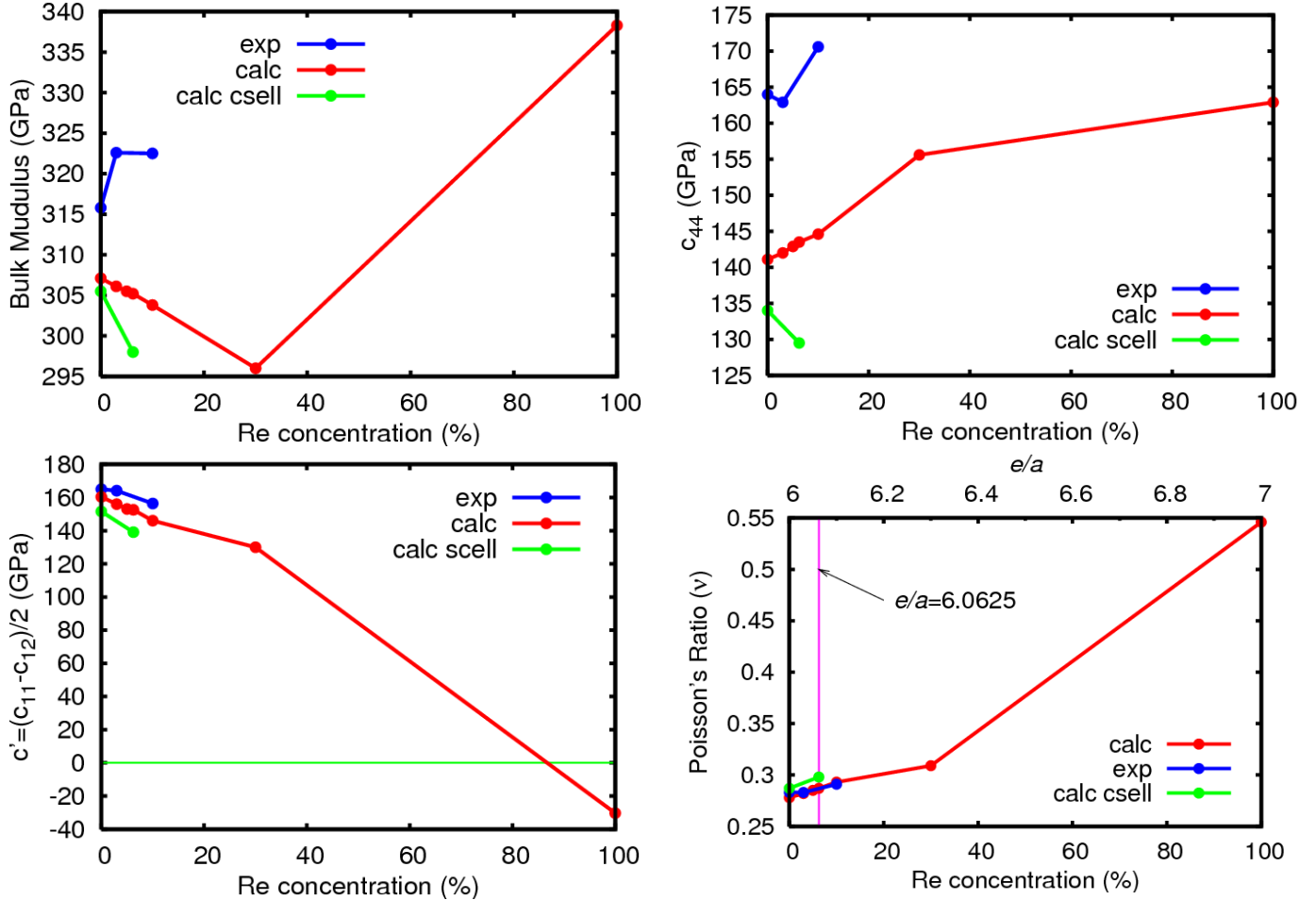


Figure 3 Elastic constant calculated by VCA (red) and super cell (green) methods and experiment [11] (blue) as a function of concentration.

Surprisingly, a large difference in behavior of bulk modulus between VCA result and experiment was obtained. It increases in experiment, see Figure 3, and decreases in our calculations for low Re concentrations. At Re concentrations larger than 30 % the calculated value of B starts to increase. However, the applicability of VCA should be checked at such larger alloy concentrations. Also, it should be mentioned that the experimentally observed phase of $W_{1-x}Re_x$ at this concentration is σ -phase not a bcc solid solution. Both c' and ν are in good agreement with experiment and super cell calculations. The c' modulus decreases with Re concentration until it turns negative at 85 % Re. This change of c' sign corresponds to dynamic loss of stability of the bcc structure. The c' elastic constant corresponds to long-wave transversal phonons branch in $[\xi\xi0]$ directions ($T_{[1-10]}[\xi\xi0]$). The softening of this phonon mode (see Fig. 4) provides a transition path from the bcc to dhcp structure (see discussion in [3]).

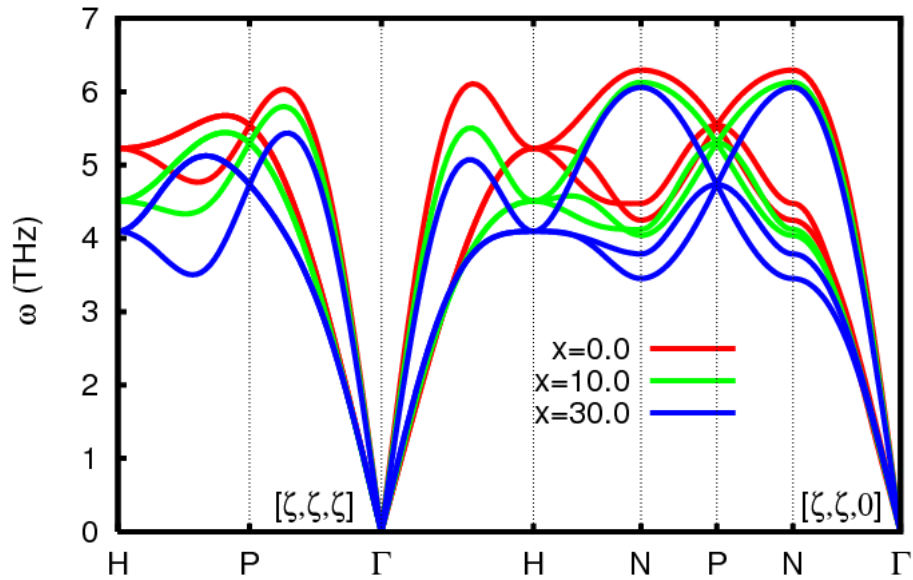


Figure 4 Calculated phonons dispersion in $W_{1-x}Re_x$ calculated in VCA for three Re concentrations.

Experimentally the Re rich W-R alloy is an ordered hcp structure. Such a decrease of bcc crystal could be used as an indicator of the Re ductilizing effect, see discussion in Ref. [2]. Another indicator of ductility improvement discussed in the literature [12] is Poisson's ratio. The author in that publication uses the thesis "the higher the Poisson ratio, the better ductility the crystal has". Within this assumption the authors looked for potential ductilizers in Cr. We found that the Poisson's ratio ν increases with increase of Re concentration and this result could probably support the point of view of the authors in [12]. According to expression (6) the same change in the elastic properties of tungsten alloy as 6.25 % of Re will result for the concentration of alternate elements shown in Table 2.

Table 2. Equivalent concentrations of alternative alloying elements to produce the same change in elastic properties of tungsten as produced by 6.25% rhenium

e/a=6.0625	Concentration (%) in W
Re	6.25
Os	3.125
Ir	2.08
Pt	1.563

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COMPATIBILITY OF MATERIALS EXPOSED TO ISOTHERMAL Pb-Li – B. A. Pint and K. A. Unocic (Oak Ridge National Laboratory, USA)

OBJECTIVE

One proposed U.S. test blanket module (TBM) for ITER uses ferritic-martensitic alloys with both eutectic Pb-Li and He coolants at ~475°C. In order for this blanket concept to operate at higher temperatures (~700°C) for a DEMO-type reactor, several Pb-Li compatibility issues need to be addressed. Two of the issues currently being investigated are the potential for dissimilar material interactions in Pb-Li and the effect of impurities in the Pb-Li on the amount of alloy dissolution.

SUMMARY

Initial isothermal capsule experiments were conducted to address two Pb-Li compatibility issues. First, the effect of Fe and Ni impurities in the Pb-Li on the amount of mass loss of representative austenitic (316SS) and ferritic (P92) steels was investigated at 700°C by adding controlled amounts of these elements to the Pb-Li in the capsule. Unexpectedly, the specimens tested with Fe and Ni additions showed higher mass losses. The second set of experiments investigated the potential dissimilar material interaction between Fe and SiC in Pb-Li. Using carbon steel capsules, the mass loss of Fe and SiC samples was measured after isothermal exposures at 500°, 600° and 700°C. For the SiC specimens, larger mass changes were measured than in prior studies at higher temperatures. These tests will be repeated with SiC capsules. For all of these recent experiments, variations in the composition of the Pb-Li source material has confounded the results.

PROGRESS AND STATUS

Introduction

A current focus of the U.S. fusion materials program is to address issues associated with the dual coolant Pb-Li (DCLL) blanket concept[1] for a test blanket module (TBM) for ITER and enhanced concepts for a DEMO-type fusion reactor. A DCLL blanket has both He and eutectic Pb-17 at.%Li coolants and uses reduced activation ferritic-martensitic (FM) steel as the structural material with a SiC/SiC composite flow channel insert (FCI). Thus, recent U.S. compatibility research has examined compatibility issues with Pb-Li.[2-6] Compared to Li,[7] a wider range of materials can be compatible with Pb-Li because of the low activity of Li.[8] In particular, SiC readily dissolves in Li, but not Pb-17Li.[2,4,9] However, like Pb, Pb-Li dissolves Fe, Cr and especially Ni from many conventional alloys above 500°C.[10,11] This is not a concern for a DCLL TBM operating at <500°C. However, a DCLL blanket for a commercial reactor would be more attractive with a higher maximum operating temperature, perhaps >600°C if oxide dispersion strengthened (ODS) ferritic steels[12] were used. Even at 550°C, a recent study of Eurofer 97 (Fe-Cr-W) showed a very high dissolution rate in flowing Pb-Li.[11] Therefore, preliminary Pb-Li compatibility capsule experiments are being conducted at 500°-700°C in order to investigate several concepts before flowing Pb-Li compatibility tests are conducted. Recent capsule experiments have investigated (1) the effectiveness of Al-rich coatings to inhibit dissolution, (2) the effect of Fe and Ni impurities on the amount of dissolution and (3) potential dissimilar material effects between Fe and SiC. Additional capsule experiments to address the second and third topics are presented here to follow up on results presented in the previous report.[6] The planned dissimilar capsule experiments with SiC capsules have been delayed due to problems machining the chemical vapor deposited (CVD) SiC.

Experimental Procedure

Static capsule tests were performed using Mo or carbon steel inner capsules and type 304 stainless steel

outer capsules to protect the inner capsule from oxidation. The specimens were ~1.5 mm thick and 4-5 cm² in surface area with a 600 grit surface finish and were held with 1 mm diameter Mo wire. (Mo can be considered to be essentially inert under these conditions.) The representative FM steel was P92 (Fe-9Cr-2W) and the austenitic steel was type 316 (Fe-19Cr-10Ni-2Mo). For the dissimilar metal experiments, unalloyed Fe specimens were used to simplify the experiment and the CVD SiC specimen was high-purity material from Rohm & Haas. The Mo and Fe capsules were loaded with 125g of commercial purity Pb-Li in an argon-filled glove box. Commercial Pb-Li was earlier obtained from UCLA and is designated Pb-Li (1). The Li content of this material typically measured <15 at.% after exposure. Because of the higher Li contents noted in the initial experiments with a new batch of commercial Pb-Li from Atlantic Metals, denoted Pb-Li (2), the experiments with carbon steel capsules used 100g of Pb-Li and 25g of high purity Pb. Additions of Fe or Ni powder (1000 ppma) were made during capsule loading. The capsules were welded shut in a glove box to prevent the uptake of impurities during exposure. After exposure, residual Pb-Li on the specimen surface was removed by soaking in a 1:1:1 mixture of acetic acid, hydrogen peroxide and ethanol for up to 72 h. Mass change was measured with a Mettler-Toledo balance with an accuracy of 0.01 mg/cm².

Results and Discussion

Figure 1 shows the mass change data from the study of Fe and Ni impurities on the mass loss of P92 and 316SS. All of the exposures were performed in Mo capsules for 1,000 h at 700°C. Because of the differences in the two commercial Pb-Li sources, the exposures without additions were repeated with the second Pb-Li source. However, the mass losses were not significantly different despite the large differences in the Li content between the two batches, Table 1. It was expected that the addition of Fe and Ni impurities to the Pb-Li would reduce the mass loss because the isothermal rate of dissolution of an element *i* is governed by:

$$J_i = k (C_i^S - C_i) \quad [1]$$

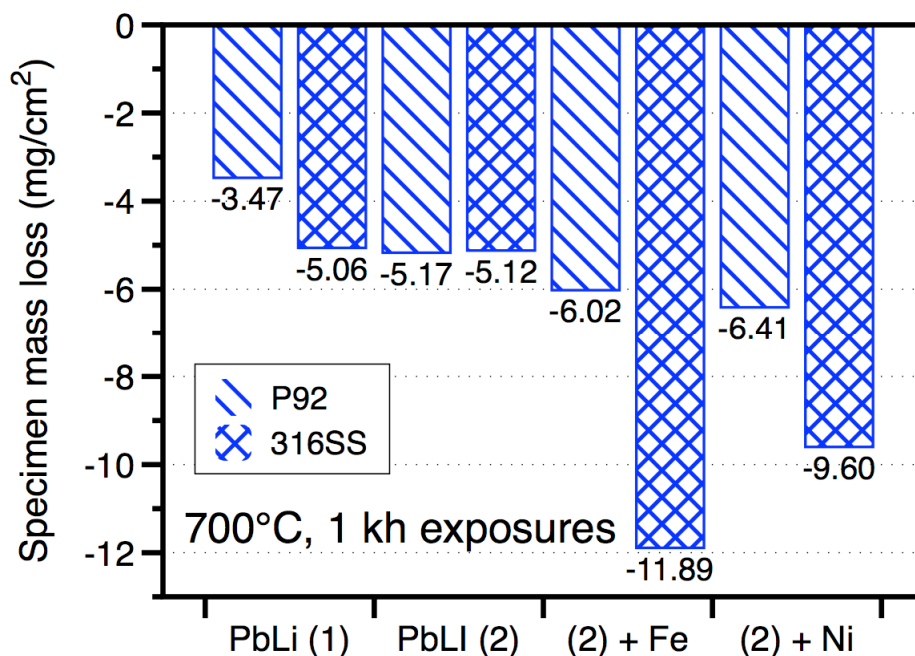


Figure 1. Mass loss results from P92 and 316SS exposed for 1,000 h at 700°C with two different Pb-Li sources and with either 1000 ppma Fe or Ni additions to Pb-Li (2).

Table 1. Chemical composition measured using inductively coupled plasma and combustion analysis of the Pb-Li after the 1,000 h capsule test.

	Pb-Li source	Add	Li at. %	O at. %	Fe ppma	Ni ppma	Cr ppma
316SS	Comm.1	No	13.7	0.21	19	52	7
	Comm 2	No	37.3	1.95	481	305	1436
		+Fe	23.5	4.52	422	283	304
		+Ni	21.0	1.37	520	874	210
P92	Comm 1	No	14.7	0.29	28	3	<3
	Comm 2	No	33.3	9.90	751	6	570
		+Fe	20.4	2.41	182	8	31
		+Ni	29.7	1.17	171	717	97

where J_i is the flux of species i into (positive) or from (negative) the liquid metal, C_i^S is the solubility of i in the Pb-Li and C_i is the instantaneous concentration of i in the liquid. In a capsule experiment, dissolution continues until the liquid metal is saturated, i.e. $C_i^S = C_i$. [13] Thus, by adding Ni to the capsule, this should have increased C_{Ni} , thereby decreasing the magnitude of J_{Ni} . The largest decreases were expected for the dissolution of P92 with the Fe addition and 316SS with Ni. However, the expected decrease was not observed, the amount of dissolution was higher with the additions. The variation in Li content in the capsules may have confounded the results, Table 1. Table 1 also includes the Fe, Ni and Cr contents in the Pb-Li in units of ppma. Higher Ni levels were evident after Ni was added to the capsule but the Fe addition was not as evident compared to the other experiments. The Fe powder may not have been incorporated into the Pb-Li as readily as the Ni powder which has a higher solubility in Pb. [10] Another possibility is that the dissolution of other elements compensated for the addition. For example, when Ni was added, the 316SS specimen lost more Fe and Cr. Or, when Fe was added, the P92 specimen lost more Cr. Cross-sections of all of the specimens are being prepared for chemical analysis. The Pb-Li chemical analysis suggested that the higher Li levels resulted in more Cr in the liquid, perhaps due to the formation of the Li-Cr-N compound. [14,15] Table 1 also includes the O content measured. It is not clear if this variation is due to the source material or variability in contamination during handling and measurement. A higher O content could have increased Cr dissolution by first forming Cr_2O_3 or a Cr-rich oxide, which then dissolved.

Based on the initial dissimilar materials experiments performed at 600°C, [6] a plan for a more complete data set was developed with carbon steel and SiC capsules at 500°-700°C. The SiC capsule experiments have been delayed due to problems machining the capsules. After addressing a problem with the CVD SiC feedstock, capsules are expected in the next quarter. Figure 2 shows the mass change data for the Fe and SiC specimens in a carbon steel capsule. Since iron carbides are more stable than SiC, it is possible that mass transfer could occur [16]. However, very small mass changes were observed at 500° and 600°C for both samples. The small mass losses for SiC are higher than those observed at 800°-1200°C. [2,4] The previous SiC specimen exposed in a steel capsule at 600°C showed a 0.04 mg/cm² mass loss but surface analysis of the specimen revealed only residual Li and C and no clear degradation. [6] The 700°C SiC specimen will be characterized to determine the source of the mass gain. The high mass loss for the Fe specimen at 700°C suggests increasing Fe dissolution between 600° and 700°C, as expected. The Fe in the Pb-Li after the experiment increased from 1380 ppma after the 600°C experiment to 17,150 ppma after 700°C. The addition of Pb to these capsules reduced the Li contents to 14-27% from the higher range seen in Table 1. However, the Pb addition did not address the apparent Li variability in the commercial source that will have to be addressed either by remelting or acquiring a

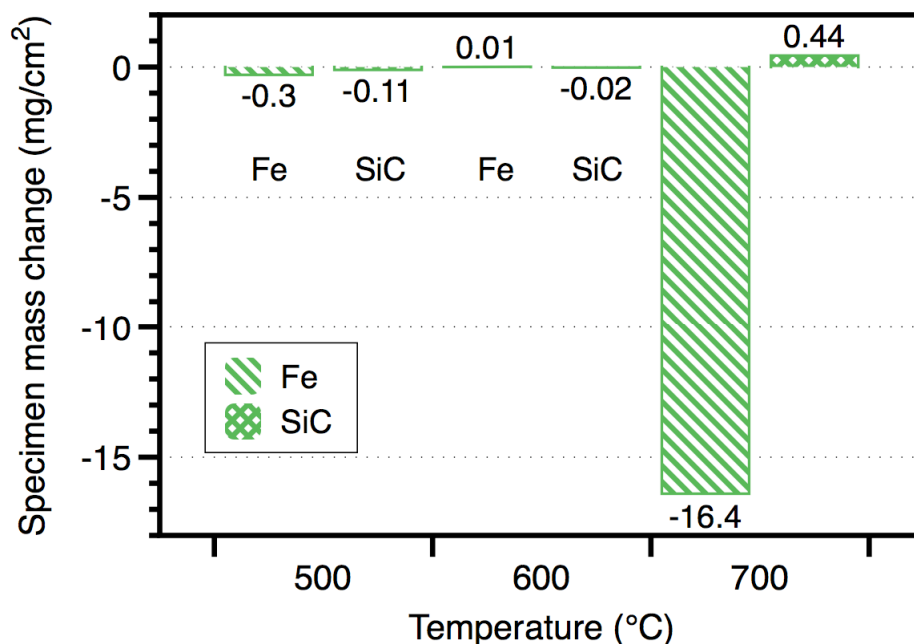


Figure 2. Specimen mass change from a series of capsule experiments with carbon steel capsules and Fe and SiC specimens exposed to Pb-Li for 1,000 h at each temperature.

different supply before additional capsule experiments are conducted.

Further characterization is needed on both groups of specimens. Also, the dissimilar materials results will have more context for evaluation when the results for the SiC capsules are available for comparison.

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FURTHER CHARACTERIZATION OF THE COMPATIBILITY OF Al_2O_3 WITH Pb-Li – B. A. Pint and K.A. Unocic (Oak Ridge National Laboratory, USA)

OBJECTIVE

One proposed U.S. test blanket module (TBM) for ITER uses ferritic-martensitic steels with both eutectic Pb-Li and He coolants at $\sim 475^\circ\text{C}$. In order for this blanket concept to operate at higher temperatures ($\sim 750^\circ\text{C}$) for a DEMO-type reactor, several Pb-Li compatibility issues need to be addressed. One issue is the viability of functional coatings such as alumina for corrosion resistance and/or as a tritium permeation barrier.

SUMMARY

In order to study the compatibility of $\alpha\text{-Al}_2\text{O}_3$ with Pb-17Li, FeCrAl substrates were pre-oxidized at 1000°C to thermally grow an external alumina scale. Prior work showed that a 1,000 h isothermal exposure of these specimens to Pb-Li at 700° or 800°C transformed the $\alpha\text{-Al}_2\text{O}_3$ to LiAlO_2 . In this experiment, the pre-oxidized specimen was isothermally exposed to Pb-Li for 1,000 h at 500°C . Characterization showed that some $\alpha\text{-Al}_2\text{O}_3$ remained but cross-section transmission electron microscopy (TEM) showed that the outer ($\sim 180\text{ nm}$) portion of the original $\alpha\text{-Al}_2\text{O}_3$ microstructure was disrupted. Further work is needed to determine if Li is present or if a reaction occurred in this outer layer of oxide.

PROGRESS AND STATUS

Introduction

A current focus of the U.S. fusion materials program is to address issues associated with the dual coolant Pb-Li (DCLL) blanket concept that has both He and eutectic Pb-Li coolants.[1] The interest in this concept has focused compatibility-related research on Pb-Li.[2-5] Many materials have poor compatibility with liquid Li,[6] but the activity of Li is much lower in Pb-17Li,[7] and this allows a wider range of materials to be considered. For example, SiC and $\alpha\text{-Al}_2\text{O}_3$ readily dissolve in Li, but not in Pb-17Li.[2-6,8] For a reduced activation, ferritic martensitic (FM) steel structural material, an Al-rich coating can inhibit dissolution in Pb-Li by forming an Al-rich oxide layer. This layer can also function as a permeation barrier.[4,5,9,10] While the DCLL maximum operating temperature for an ITER test blanket module (TBM) will be $<500^\circ\text{C}$, this blanket concept would be more attractive for a commercial reactor with a higher maximum operating temperature, perhaps $>700^\circ\text{C}$ if oxide dispersion strengthened (ODS) ferritic steels[11] were used. Compatibility is even more of a concern at these higher temperatures. In order to study the Pb-Li compatibility and potential for corrosion protection of $\alpha\text{-Al}_2\text{O}_3$ in Pb-Li, a model system was used with ODS FeCrAl substrates pre-oxidized at 1000°C to thermally grow an external alumina scale. Prior work showed that in 1,000 h isothermal Pb-Li exposures at 700° and 800°C , the $\alpha\text{-Al}_2\text{O}_3$ layer on ODS FeCrAl specimens fully transformed to LiAlO_2 . [3,4] As a follow up experiment, a similar pre-oxidized specimen was exposed at 500°C , closer to the current TBM conditions. The results from this experiment are presented in this report.

Experimental Procedure

Specimens of ODS FeCrAl (Plansee alloy PM2000, Fe-20at.%Cr-10.6Al-0.7O-0.4Ti-0.2Y) with dimensions of $\sim 15 \times 18 \times 1\text{-}1.5\text{ mm}$ were polished to a $0.3\text{ }\mu\text{m}$ finish. Pre-oxidation was conducted with a rapid insert to a pre-heated furnace at 1000°C in dry, flowing O_2 for 2 h. Isothermal exposures to Pb-Li were conducted for 1,000 h in a Mo capsule containing 125 g of Pb-Li with the specimen suspended by a Mo wire. 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 for ~1 h to allow the Pb-Li to melt. The capsule was then inverted to submerge the specimen in Pb-Li. After 1,000h at the test temperature, the system again was inverted to allow the liquid metal to drain away from the specimen. To remove residual Pb-Li on the specimen, it was soaked in a 1:1:1 mixture of acetic acid, hydrogen peroxide and ethanol for up to 72 h. The mass change was then measured. A summary of the experimental conditions is given in Table 1. The post-exposure Li content was measured using inductively coupled plasma analysis. After exposure, the specimen was characterized including light microscopy of polished cross-sections, scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), x-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) with EDS. Cross-sectional TEM specimens were prepared using focused ion beam milling. A C layer followed by a W layer was deposited on the specimen surface to protect the outer surface of the reaction product.

Results and Discussion

Table 1 summarizes the conditions of the three exposures conducted to date and the resulting specimen mass change. Unfortunately, the Li content in the experiments has not been consistent. This issue is being addressed for the final experiment in this series to be conducted at 600°C. The mass changes were all relatively low compared to Fe-base alloys without Al (e.g. Fe-9Cr or Fe-18Cr-10Ni). The higher mass loss after exposure at 500°C could be related to the higher Li content in this experiment, Table 1.

To characterize the surface oxide after exposure to Pb-Li at 500°C, the specimen was first examined using XRD and plan-view SEM. Figure 1 shows the XRD results. Peaks were present for α -Al₂O₃ but were far less distinct than before exposure to Pb-Li.[3] Figure 2a shows the surface morphology. Nodules rich in Ti were present on the surface and Fe and Cr peaks were present in the EDS spectra along with Al and O. If present, Li would not be detected by EDS. The specimen was then sectioned for further examination. Figure 2b shows the polished cross-section. At this magnification, the oxide appears very similar to that after pre-oxidation at 1000°C with no clear changes. However, because the oxide is <1 μ m in thickness, it is not possible to characterize the microstructure without a TEM section as was done for a specimen that received only the pre-oxidation.[3]

Figure 3 shows the TEM cross-section of the oxide after exposure to Pb-Li. Before exposure, the thermally-grown α -Al₂O₃ had a mainly columnar structure with an outer ~100nm layer of equiaxed oxide grains rich in Fe and Cr.[3] After Pb-Li exposure at 500°C, only the inner half of the remaining oxide appears to retain the original columnar structure. Voids (arrows) are present on some of the oxide grain boundaries. This is not uncommon in thermally-grown α -Al₂O₃ .[3,12] There is no indication of an outer equiaxed layer. The outer half of the oxide, ~180nm, does not appear to have a distinct grain structure. Maps using EDS showed the oxide consisted primarily of Al and O with some enrichment of Ti in the metal adjacent to the oxide. Maps at higher magnification are needed to determine if Y and Ti ions remain segregated to the oxide grain boundaries after exposure.[3,13,14] The specimen also will be examined using Auger electron spectroscopy to determine if Li is present in the oxide. It appears that some reaction

Table 1. Summary of Pb-Li experiments conducted on pre-oxidized ODS FeCrAl.

Temperature	Pb-Li source	Li (post-test) (at.%)	Mass Change (mg/cm ²)	Phases (XRD)
500°C	Atlantic (ORNL)	27.3	-0.11	Al ₂ O ₃
600°C	(currently being assembled)			
700°C	Atlantic (UCLA)	13.2	-0.06	LiAlO ₂
800°C	Mixed Pb and Li	17.3	+0.24	LiAlO ₂

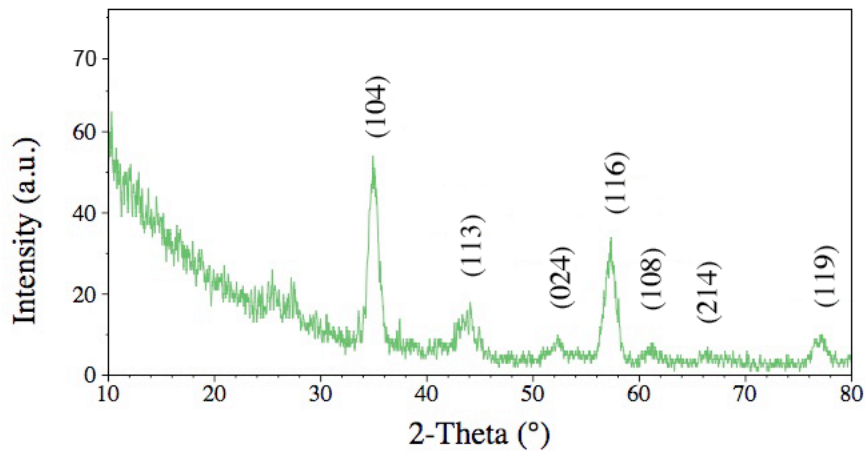


Figure 1. X-ray diffraction from ODS FeCrAl after pre-oxidation for 2h at 1000°C followed by 1 kh in Pb-Li at 500°C. The α -Al₂O₃ peaks are noted.

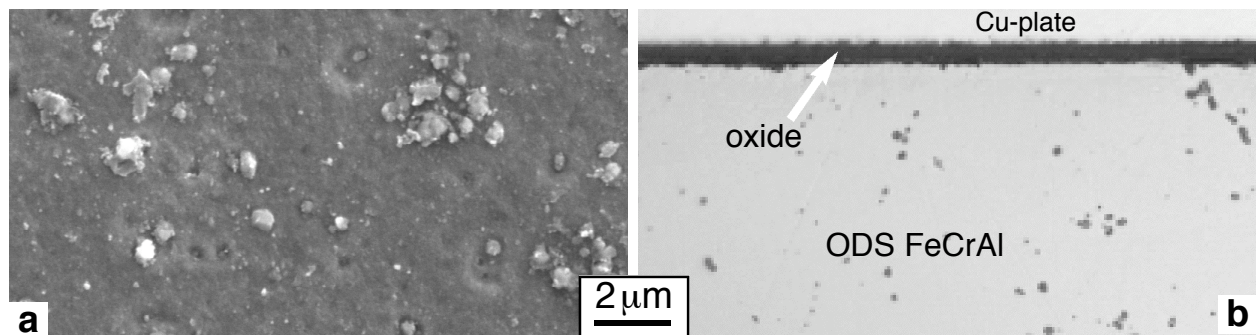


Figure 2. ODS FeCrAl after pre-oxidation followed by exposure to Pb-Li at 500°C for 1kh (a) SEM plan-view image and (b) light microscopy of polished cross-section with protective Cu plating layer.

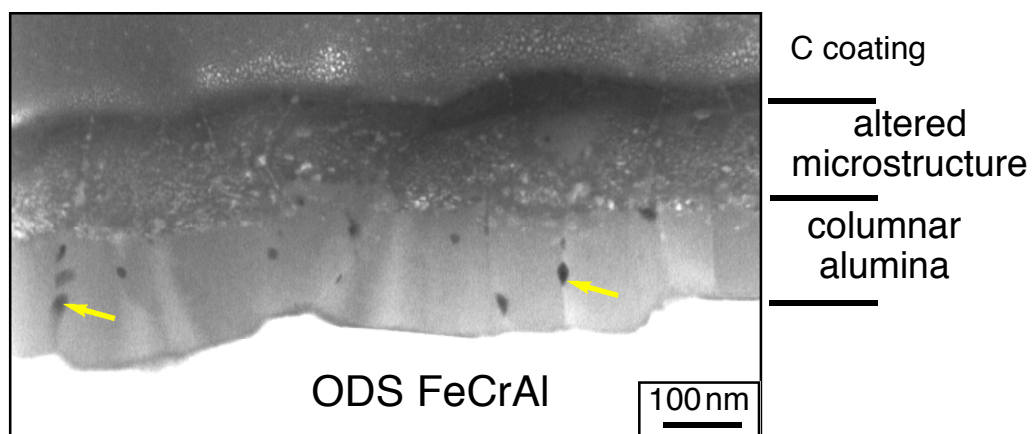


Figure 3. STEM high angle annular dark field image of the surface oxide on ODS FeCrAl after pre-oxidation and subsequent exposure to Pb-Li for 1 kh at 500°C. It appears that the microstructure of the outer portion of the α -Al₂O₃ layer adjacent to the Pb-Li has been disrupted possibly due to a reaction. Voids in the inner, columnar-grained layer are marked by arrows.

or disruption of the alumina microstructure occurred but, based on the XRD data, the oxide was not transformed to LiAlO_2 at 500°C.

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INHIBITED ALUMINIZATION OF AN ODS FeCr ALLOY – A. Vande Put and B. A. Pint (Oak Ridge National Laboratory, USA)

OBJECTIVE

One proposed U.S. test blanket module (TBM) for ITER uses reduced activation ferritic-martensitic (FM) steels with both eutectic Pb-Li and He coolants at ~475°C. In order for this blanket concept to operate at higher temperatures (~700°C) for a DEMO-type reactor, several Pb-Li compatibility issues need to be addressed. One strategy to reduce dissolution of conventional and dispersion-strengthened FM steels in Pb-Li above 500°C is to aluminize the surface. The performance of coatings is currently being evaluated.

SUMMARY

Prior work characterized the performance of Al-rich coatings made by chemical vapor deposition (CVD) on Grade 92 (Fe-9Cr-2W) and type 316 stainless steel in isothermal Pb-Li experiments. Specimens of oxide dispersion strengthened (ODS) ferritic steel (14YWT, Fe-14Cr) were exposed in the same CVD reactor using similar conditions. However, the measured mass gains were extremely low compared to other wrought and ODS materials. After aluminizing at 900°C with two Al activities and at 1100°C, characterization showed that 14YWT formed a dense, primarily AlN layer that prevented Al uptake. Since the N content of 14YWT is similar to other FM steels aluminized, this result suggests that the combined O and N contents and the unique microstructure with a fine (~140nm) grain size and Y-Ti oxide nano-clusters lead to this behavior. If 14YWT cannot be aluminized, another strategy for reducing dissolution in Pb-Li will need to be developed.

PROGRESS AND STATUS

Introduction

A current focus of the U.S. fusion materials program is to address issues associated with the dual coolant Pb-Li (DCLL) blanket concept[1] for a test blanket module (TBM) for ITER and enhanced concepts for a DEMO-type fusion reactor. A DCLL blanket has both He and eutectic Pb-Li coolants and uses reduced activation ferritic-martensitic (FM) steel as the structural material with a SiC/SiC composite flow channel insert (FCI). Thus, recent U.S. compatibility research has examined compatibility issues with Pb-Li.[2-8] Compared to Li,[9] a wider range of materials can be compatible with Pb-Li because of the low activity of Li.[10] In particular, SiC and α -Al₂O₃ readily dissolve in Li, but not in Pb-17Li.[3,4,9,11] However, because of higher Ni and Fe solubilities, Pb-Li readily dissolves many conventional alloys above 500°C. This is not a concern for a DCLL TBM operating at <500°C, however, a DCLL blanket for a commercial reactor would be more attractive with a higher maximum operating temperature, perhaps >600°C if ODS FM steels[12,13] were used. Even at 550°C, a recent study of Eurofer 97 (Fe-Cr-W) showed a very high dissolution rate in flowing Pb-Li.[14] Therefore, preliminary Pb-Li compatibility capsule experiments are being conducted at 500°-800°C in order to investigate several concepts before flowing Pb-Li compatibility tests are conducted. Prior work has shown that alloys that contain Al or have an Al-rich coating show dramatically lower mass losses in 1kh Pb-Li capsule tests than alloys without Al, Figure 1. However, it has not been possible to aluminize the ODS Fe-14Cr alloy (14YWT) and those CVD results and characterization of the 14YWT specimens after exposure in the CVD reactor are presented here.

Experimental Procedure

The composition of the aluminized alloys is given in Table 1. The results for 14YWT and 754 are preliminary values from other heats and need to be measured for the particular batch of material used in these experiments (SM10) which also had a very fine grain size (~140nm). Composition is being

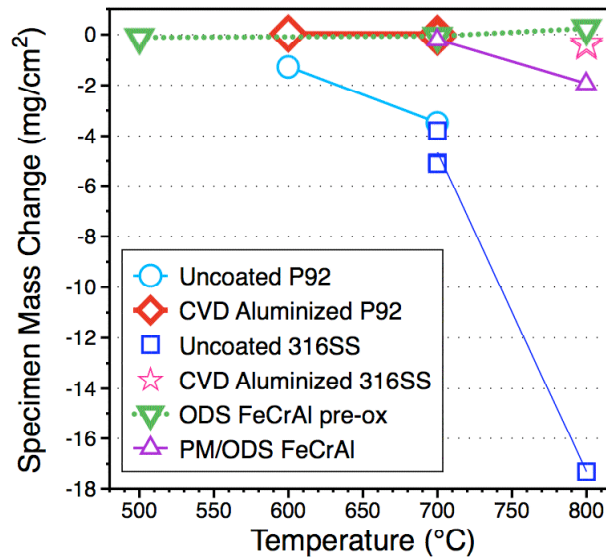


Figure 1. Specimen mass loss as a function of exposure temperature in Pb-Li for 1kh in Mo capsules. Alumina-forming alloys or coatings have much lower mass losses than conventional Fe-base alloys.[4-6]

measured for the new Fe~14Cr ODS alloy, 401 (designated ODM401 by its manufacturer Dour Metal sro). Prior to aluminizing, specimens were polished to a $0.3\mu\text{m}$ alumina finish and cleaned ultrasonically in acetone and alcohol. Aluminizing was performed in a laboratory-scale CVD reactor consisting of an inductively heated alumina tube with flowing H_2 carrying the AlCl_x vapor. The reactor has been described in detail elsewhere.[15,16] Typically, four specimens were hung from two alumina rods and are designated

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

Material	Fe	Ni	Cr	Al	O	C	N	S	Other
14YWT	84.5		14.0	0.04	3940	2440	1540	52	0.2W,0.14Y 0.22Ti,0.16Si
Gr.91 (9Cr-1Mo)	87.8	0.1	9.9		90	2380	1900	14	0.6Mo,0.3V, 0.5Mn,0.4Si,
P92 (9Cr-2W)	87.2	0.1	9.9	0.02	80	5120	2330	87	0.55W, 0.46Mn 0.30Mo,0.32Si
754	0.4	74.9	21.4	0.7	15100	2300	n.d.	20	0.53Ti,0.36Y
740	2.0	46.2	25.3	1.7	60	3650	460	<	19.3Co,2.3Ti,1.2Nb 0.9Si,0.3Mn,0.3Mo
X	18.7	46.5	24.8	0.2	33	3260	1680	<	5.8Mo,1.8Co 0.2W,0.7Mn,0.6Si
N5	0.1	64.8	7.8	13.9	52	2490	<	7	7.3Co,2.1Ta,1.6W 1Re,0.9Mo,0.05Hf,0.003Y

< indicates below the detectability limit of <0.01% or <0.001% for interstitials

front or back with relation to the flowing gas stream. The front specimens typically had 10-30% higher mass gain. An Al-60wt.%Cr powder was added to the reactor to increase the Al activity for some runs at 900°C, but not at 1100°C. The specimen mass change was measured before and after aluminizing with an accuracy of ± 0.01 mg/cm². A summary of the conditions and mass change data for the ODS specimens is given in Table 2. After aluminizing, the specimens were examined by x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDX) analysis. For cross-sectioning, a focused ion beam (FIB) was used.

Results and Discussion

The mass gain data for the two CVD aluminizing temperatures are shown in Figures 2 and 3 and the data for the ODS alloys are summarized in Table 2. (The comparison mass gain data are from a variety of different programs that have made coatings for fossil energy applications in the same CVD reactor.[17-19]) At 900°C, the mass gain for the 14YWT material was much lower than other FM steels (Grades 91 and 92) at 900°C and even lower than the ODS and wrought austenitic Ni-base alloys (754 and X) which have slower Al diffusivity than the ferritic alloys. The mass gain was slightly higher for the 14YWT specimens when Al-Cr powder was added to the reactor but orders of magnitude lower than the all the comparison materials. At 1100°C, the 14YWT specimen lost mass while the Ni-base alloys all gained mass, forming a NiAl coating. (No other Fe-base alloys were aluminized as the coating would be very thick ($>250\mu\text{m}$).[16]) Only one commercial ODS FeCr alloy (401) was recently made available for comparison to 14YWT, therefore, an ODS NiCr alloy, 754 (designated MA754 by manufacturer Special Metals), was included in two runs adjacent to the 14YWT specimen for a direct comparison. At both temperatures, the 754 specimen mass gain was significantly higher than the 14YWT specimen, gaining more mass than the comparable Ni-base alloys at 900° and 1100°C.

In order to determine why the 14YWT specimen did not gain mass during aluminizing, the characterization compared the 14YWT and 754 specimens as both are dispersion strengthened alloys. Figures 4 and 5 show the surface morphology of both materials after aluminizing. For Ni-base alloys, the morphology of 754 after 6h at 1100°C, Figure 5c, is a typical aluminized morphology with NiAl grain boundaries clearly evident and slight ridges forming on most boundaries.[15,17] At 900°C, the aluminide grains appear to be finer on 754 with similar grain boundary ridges, Figure 4c. In contrast, the surface of 14YWT at both temperatures was much different with fewer distinctive features, Figures 4a and 5a. Higher magnification images of the 14YWT surface are shown in Figures 4b and 5b that suggest a much finer grained surface layer, nothing like an aluminide structure.

Table 2. Mass change of ODS specimens in CVD aluminizing for 6h in laboratory reactor.

Specimen	Temperature	Powder	Location	Mass Change (mg/cm ²)
14YWT	1100°C	No	Front	-0.61
	900°C	Al/Cr	Front	0.05
				0.06
				0.15
				0.02
754 (NiCr)	1100°C	No	Back	8.02
	900°C	Al/Cr	Back	1.54
401 (FeCr)	900°C	No	Back	1.30

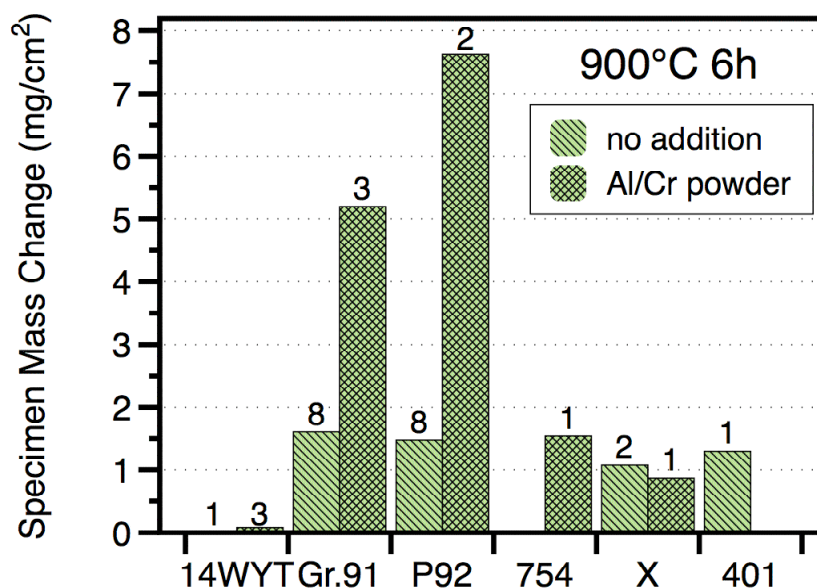


Figure 2. Average specimen mass change after 6h at 900°C in a laboratory-scale CVD reactor with and without Al-Cr powder to raise the Al activity and increase the Al uptake. The numbers mark the number of specimens exposed.

Based on the low mass change for 14WYT, a thin reaction product was expected that could be studied by a surface analytical technique such as XPS. Figure 6 shows sputter depth profiles for 14WYT after CVD exposures at 900° and 1100°C. The sputter depth is estimated based on the sputter crater depth. At 900°C, the surface is rich in Al, O and N with the O signal falling off faster than the N signal. Based on

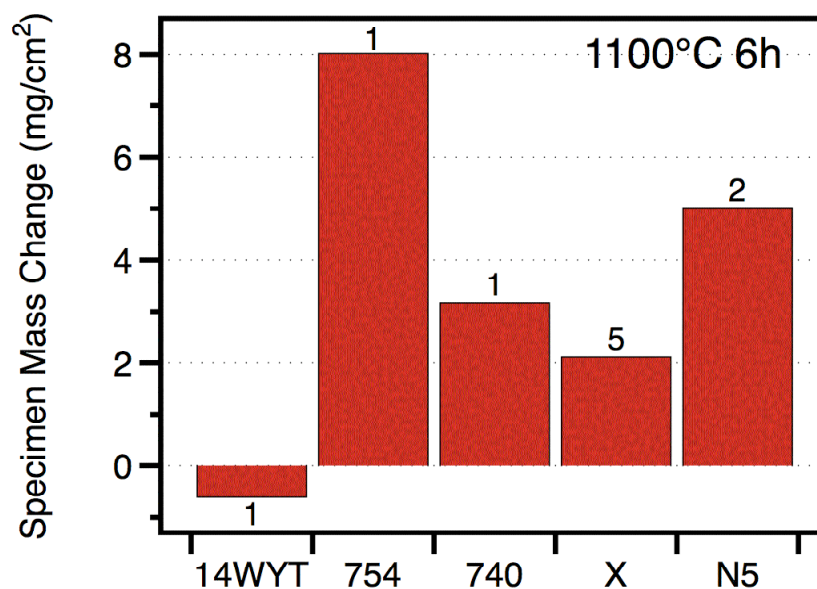


Figure 3. Average specimen mass change after 6h at 1100°C in a laboratory-scale CVD reactor. The numbers mark the number of specimens exposed.

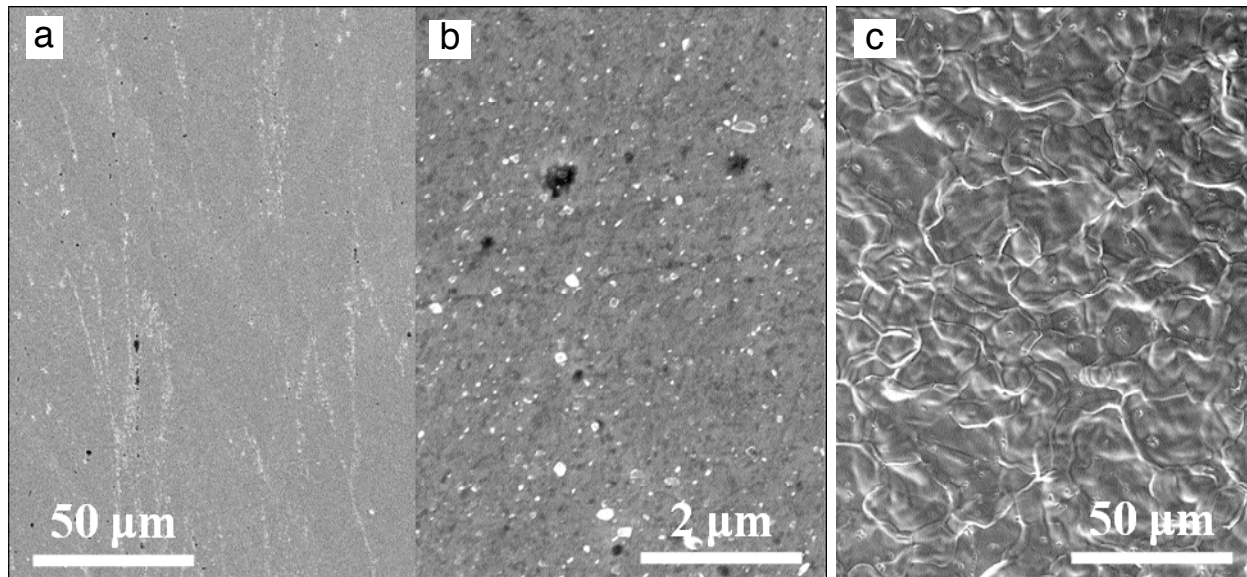


Figure 4. SEM plan view images of the specimen surface after aluminizing for 6h at 900°C with Al-Cr powder (a,b) 14YWT and (c) 754.

the cross-over of the Fe and Al signals, this outer Al-rich oxy-nitride layer appears to be less than 100 nm in thickness. The Al signal drops to background levels by 175 nm. Typically, FM steels aluminized under these conditions would show ~32-36 at.%Al at the surface with an Al profile extending 100 μm into the substrate. These deep Al profiles were observed with coating mass gains of 5-7 mg/cm², Figure 2. At 1100°C, the reaction product on 14YWT was much thicker but appeared to be more concentrated in N than at 900°C, Figure 6b. Again based on the Al-Fe signal cross-over, the surface reaction product appeared

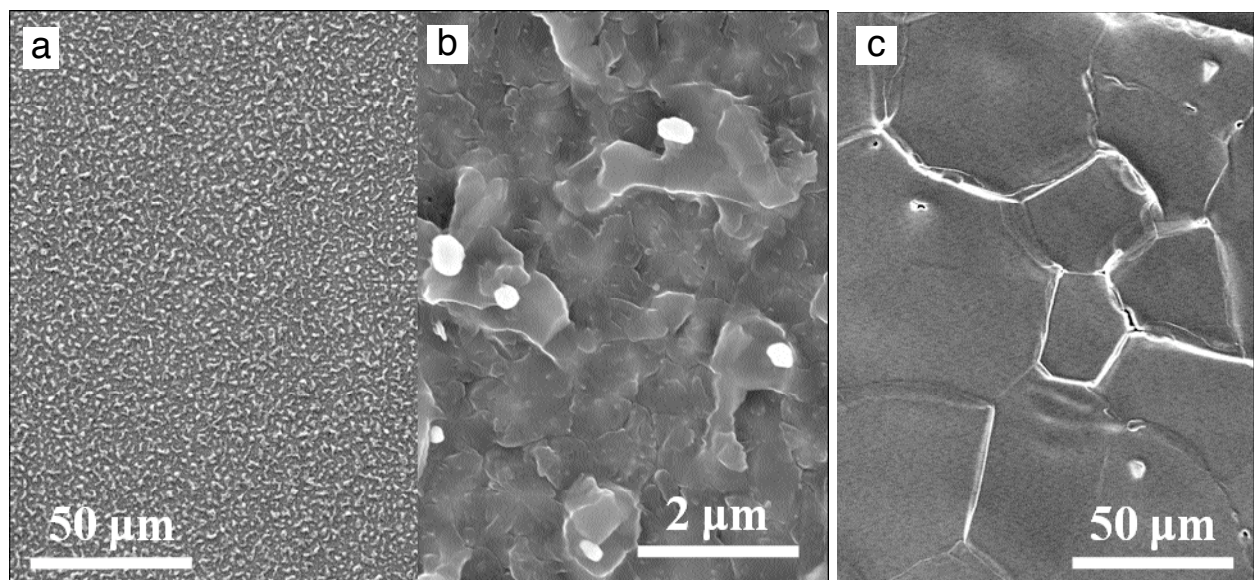


Figure 5. SEM plan view images of the specimen surface after aluminizing for 6h at 1100°C (a,b) 14YWT and (c) 754.

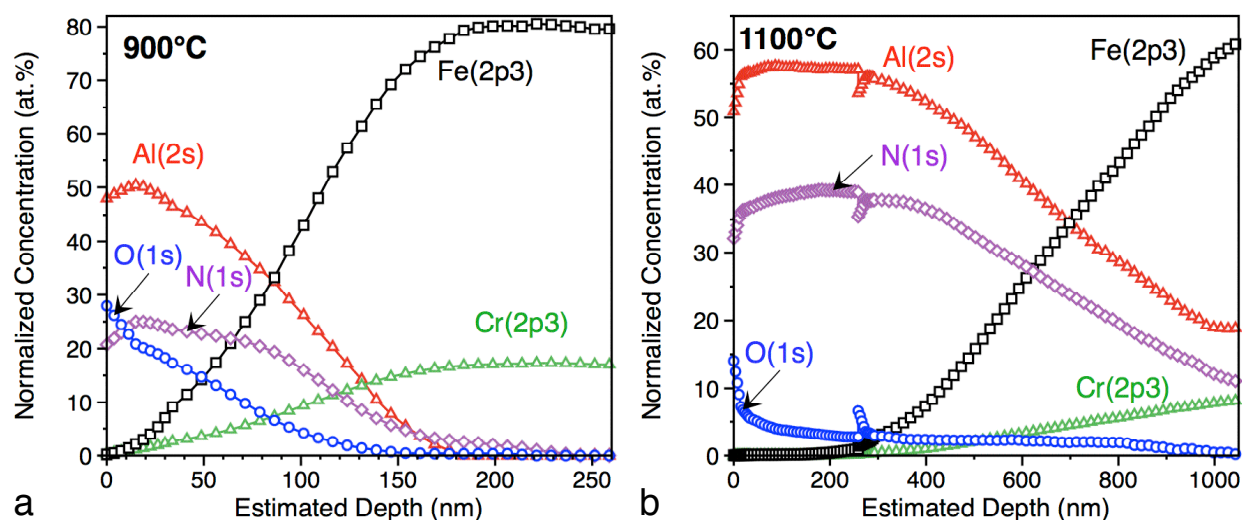


Figure 6. XPS sputter depth profiles of 14YWT after aluminizing (a) 900°C with powder and (b) 1100°C. The outer surface is rich in Al, O and N in both cases. In (b), the signal change at $\sim 250\mu\text{m}$ is where the sputtering was stopped and restarted in the same location.

to be $\sim 700\text{nm}$ thick. The composition change at $\sim 250\mu\text{m}$ depth is where the XPS sputtering was stopped and then restarted at the same location. The formation of this surface AlN layer on 14YWT is not consistent with the mass loss observed after exposure, Table 2. One possibility is that some Fe was removed from the surface by the Cl in the environment, as suggested by Kung and Rapp.[20] The surface of the aluminized 754 specimens also was sputtered by XPS for comparison. Figure 7 shows that after both CVD temperatures, a $\sim 10\text{nm}$ oxide layer was detected on the surface of the aluminide layer with

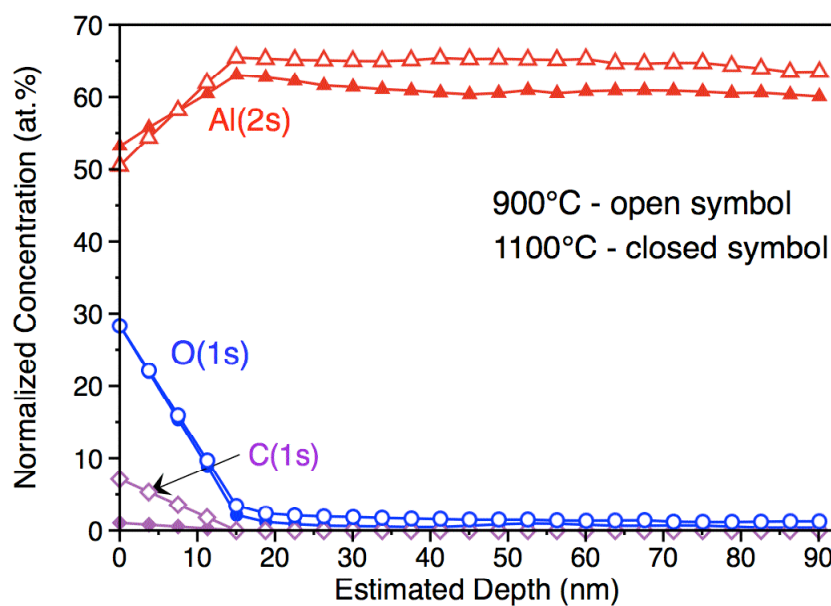


Figure 7. XPS sputter depth profiles of 754 after aluminizing, the 900°C data are shown with open symbols and the 1100°C data with closed symbols.

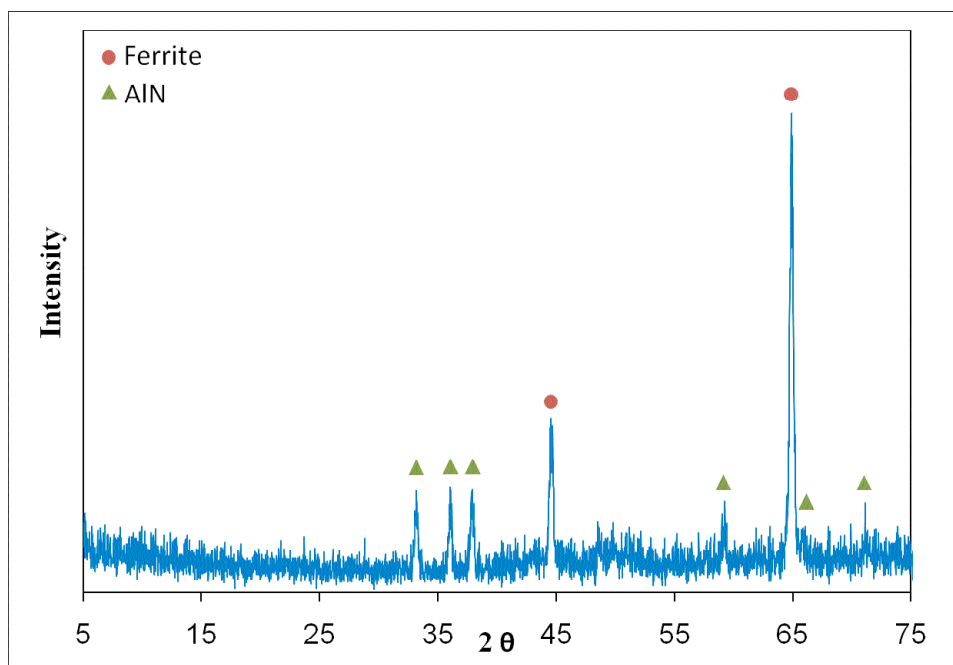


Figure 8. XRD spectra from 14YWT after CVD exposure at 1100°C.

some C present. This is more typical of the native oxide expected on a CVD aluminized substrate.

The reaction layer on 14YWT after the 1100°C CVD exposure was further characterized by XRD and FIB sectioning. In the XRD spectra, the ferritic matrix and the AlN peaks are labeled, confirming the presence of a nitride layer, Figure 8. Figure 9 shows a cross-section of the reaction product prepared by FIB sectioning. A W coating was deposited on the surface to protect the reaction product during sectioning by the ion beam. In this region, the reaction product appears to be continuous and at least 250 nm thick, less than that suggested by the XPS sputtering profile. However, quantifying the sputtering rate can be difficult and may have over estimated the AlN thickness. Also, the layer thickness may not be uniform on the specimen.

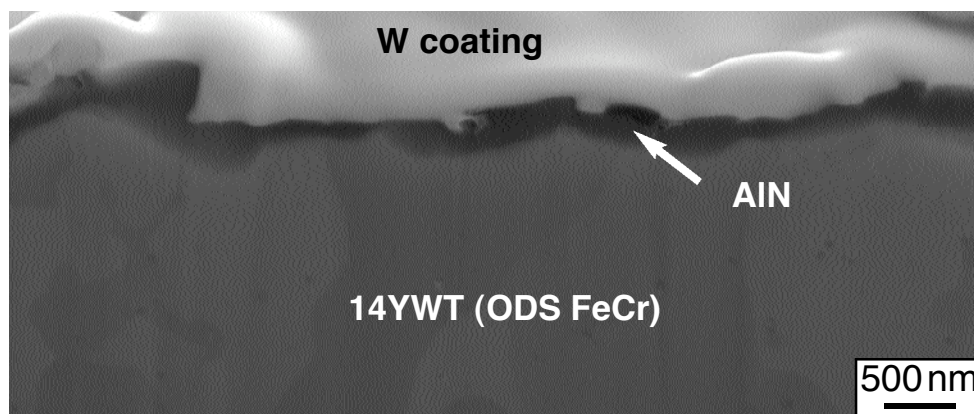


Figure 9. SEM image of FIB cut cross-section of 14YWT after aluminizing at 1100°C. The surface was coated with a layer of W for protection.

The N content in 14YWT is the likely source of N to form the AlN layer as no nitride layer was observed on aluminized 754 or on other FM specimens. Table 1 shows that the nominal N content in 14YWT is not expected to be higher than levels in other FM steels. With these N levels, FM steels routinely form acicular AlN precipitates in the coating which coarsen with exposure time,[16,19,21] but there is no indication of a continuous surface layer as was observed for 14YWT specimens. The source of the AlN precipitates in aluminized FM steels was clearly shown to be the N in the alloy by low-N model alloy experiments.[22] Nickel-base alloy X was chosen for comparison because it also contains a high N content which does not inhibit aluminizing. The reason 14YWT behaves differently than FM steels in aluminizing may be due to the combination of N and O in the alloy. Of course, all ODS alloys have high N and O contents compared to conventional alloys due to the nature of the powder metallurgy process used for fabrication. Neither 754 (NiCr) nor 401 (FeCr) showed a similar problem as 14YWT. One reported unique aspect of 14YWT is the high density of Y-Ti oxide “nano-clusters”. If the O distribution is different in 14YWT than other ODS alloys, the fine dispersion may more readily allow the rapid formation of an Al-rich oxide layer in the CVD environment that could inhibit Al uptake in this alloy. Both XPS profiles suggest a high O concentration at the surface. After the Al-rich oxide layer forms, the N content in the alloy could then continue to react with Al forming the underlying AlN layer at a rate dependent on the temperature.

Regardless of the mechanism, a different strategy may be needed for protecting 14YWT from dissolution in Pb-Li. Now that it is apparent that 14YWT will not be coated by the CVD process used for other materials on this project, uncoated 14YWT specimens are being prepared for Pb-Li capsule exposures.

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DISLOCATION BIAS REVISITED, S.I. Golubov (Oak Ridge National Laboratory, *University of Tennessee*), A.V. Barashev (The University of Liverpool, UK), B.N. Singh (*Risø National Laboratory, Denmark*) and R.E. Stoller (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this work is to investigate the underlying mechanisms that control damage accumulation in irradiated materials. The current focus is on the impact of anisotropic diffusion on the fate of self-interstitial atoms (SIA) and SIA clusters as they diffuse and react under the influence of internal stress fields associated with extended defects such as dislocations and grain boundaries.

SUMMARY

A diffusion-based model has been developed to predict how anisotropic diffusion influences the SIA-dislocation bias, and comparisons have been made between the behavior of defects that exhibit 1-D and 3-D diffusion. The dislocation capture radius for SIAs undergoing a mixture of 1-D and 3-D diffusion corresponds to higher interaction energy than the thermal energy, as in the case of pure 3-D diffusion. This leads to reduced dislocation bias factors and suggests that it may be possible to categorize the damage accumulation tendency of metals according to relative stability of the SIA crowdion and dumbbell configurations.

PROGRESS AND STATUS

I. Introduction

Greenwood, Foreman and Rimmer [1] suggested in 1959 that a preferential absorption of SIAs by dislocations could cause radiation-induced dimensional changes in reactor materials. The phenomenon of void swelling was then discovered by Cawthorne and Fulton [2] in 1967, and the preferential absorption was incorporated into the theoretical model for void swelling, sometimes called the Standard Rate Theory (see [3] for a review), via an empirical parameter, B_D , that came to be known as the ‘dislocation bias factor’. To reproduce experimentally observed swelling rates, the bias factor, the relative excess of SIAs over vacancies absorbed by dislocations, is required to be an order of the order of several percent [4].

The first attempt to determine B_D by using the elasticity theory for the point defect - dislocation interaction, by solving the diffusion equation with a drift term have been made by Foreman [5], who concluded that the bias was significantly larger than the empirical estimate. Later, Heald [6] obtained an analytical expression for the bias (see next Section) using the solution of Ham [7] in the form presented by Margvelashvili and Saralidze [8].

The estimates [6,9-12] produced using this approach confirmed much higher B_D values, e.g. ~15% for the bcc iron and ~30% for the fcc copper. Note that, with these bias factors, the maximum swelling rates corresponding to equal sink strengths of voids and dislocations (see next Section), which are equal to $B_D / 4 \approx 4$ and 8 %/dpa (displacements per atom, (dpa)), have never been observed.

It should be emphasised that, in the approaches described above, no distinction was made between different types of irradiation: ~1 MeV electrons, fission neutrons and heavy ions. It was believed

that the initial damage is produced in the form of Frenkel pairs. Now we understand much better the mechanisms operating under different conditions and make clear distinction between electron and neutron / heavy ion irradiations (see, e.g. [13-15] and references therein for some recent advances in the development of the Production Bias Model (PBM)). In the latter case, the displacement cascades produce one-dimensionally (1-D) migrating SIA clusters, which change qualitatively the reaction kinetics between defects. Most estimates of the bias factor used data obtained in reactor irradiations, but the treatment of the data on swelling in electron-irradiated metals also resulted in $B_D \approx 2$ to 4% for fcc copper [13,16,17] (data reported by Glowinski [18] were used in [17]), ~2% for pure Fe-Cr-Ni alloys [19], and an orders of magnitude lower values for bcc metals (see, e.g. swelling data in molybdenum [20]).

A few attempts were made to resolve the contradiction described above since early seventies. It was suggested in [21] that the density of jogs, which are traps for point defects, along dislocation lines is very low, and this could lead to decreasing dislocation sink strength. This might work for vacancies, since they have relatively small binding (formation) energy, ~1.2 eV in copper (e.g. [22]), with the dislocation line and can dissociate from dislocation without being absorbed. The SIAs, however, have high formation energy, ~3.6 eV in copper, and could not escape for any reasonable density of jogs at temperatures of practical importance. As a result, the net flux of SIAs to dislocations, hence the value of the bias factor, could only increase with decreasing jog density and could not explain observations.

Recently, Wolfer [12] suggested that the high values of the dislocation bias factor predicted using the elasticity theory in [6,9-11] are correct, whereas the low swelling rates under neutron irradiations were due to intra-cascade recombination of defects. Thus, he ignored experimental and theoretical knowledge on the principal differences of damage mechanisms operating under neutron and electron irradiations. However, even if the dislocation bias were the main driving force for the microstructure evolution under neutron irradiation, his explanation would contradict the low swelling rates found in electron-irradiated samples, where the intra-cascade recombination is absent (see e.g. [14]).

Another attempts are based on the results of MD simulations using empirical potentials, which demonstrated that, even when the SIA dumbbell configuration is the most stable and the SIAs migrate 3-D in the matrix, in the vicinity of an edge dislocation, the crowdion configuration with the axis along the dislocation Burgers vector become most stable and the SIAs have preference to move 1-D [23-26]. The authors of [25] speculated that this might decrease the dislocation capture efficiency for the SIAs since the SIA migration parallel to the dislocation Burgers vector blocks SIA in its vicinity. They did not provide, however, any mechanism supporting their conjecture.

In this paper, we analyze the applicability of the classical approach of calculating the dislocation bias factor by defining the SIA capture volume as that where the SIA interaction energy with dislocation is higher than thermal energy, $k_B T$ (k_B is the Boltzmann constant and T is the absolute temperature). We argue that it is incorrect when the SIA migration is not pure 3-D with the preference to configurations with the axis parallel to the dislocation Burgers vector and to thermally-activated jumps leading to or preserving such configurations. The critical point is that the SIAs moving this way may escape from the ‘capture volume’, thus reducing the capture efficiency, hence the bias factor.

RESULTS

II. Problem characterisation

In this section we describe the mathematical formulation of the problem as it is in the SRT as formulated in [6-12], which we can use for comparison with the following generalised approach.

The stationary diffusion equation for a vacancy ($\alpha = v$) or SIA ($\alpha = i$) is given by

$$\nabla J_\alpha = 0, \quad (1)$$

where the defect flux near an edge dislocation is

$$J_\alpha = -D_\alpha \nabla C_\alpha - \beta D_\alpha C_\alpha \nabla E_\alpha. \quad (2)$$

Here, $C_\alpha(r)$ is the defect concentration, D_α is the diffusion coefficient of the mobile defect, $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the absolute temperature, and E_α is the interaction energy between the point defect and dislocation. The largest contribution to the long-range interaction arises from the Cottrell size effect [27,28], which, when expressed in polar coordinates (r, φ) , is given by

$$\beta E_\alpha = -L_\alpha \frac{\sin(\varphi)}{r}. \quad (3)$$

Here, the characteristic ranges of the interaction potential, L_α , are given by

$$L_\alpha = \frac{\mu b(1 + \nu) \Delta \Omega_\alpha}{3\pi(1 - \nu) k_B T}, \quad (4)$$

where $\Delta \Omega_\alpha$ is the relaxation volume of the point defect, μ and ν are the shear modulus and Poisson ratio, respectively. The boundary conditions correspond to a steady state, where the concentrations of point defects near the dislocation core, $r = r_0$, and in the midway between dislocations, $r = R \equiv (\rho_D / \pi)^{1/2}$, are kept to be constants, corresponding to the thermal-equilibrium (superscript ‘th’) and volume overage values (superscript ‘0’):

$$C_\alpha(r_0) = C_\alpha^{\text{th}}, \quad (5)$$

$$C_\alpha(R) = C_\alpha^0. \quad (6)$$

The solution of Eqs. (1)-(6) gives the following expression for the capture efficiency, Z_α , and the bias factor, B_D

$$Z_\alpha = \frac{2\pi}{\ln(2R / L_\alpha)}, \quad (\alpha = v, i), \quad (7)$$

$$B_D = \frac{Z_i - Z_v}{Z_v} = \frac{\ln(L_i / L_v)}{\ln(2R / L_v)}. \quad (8)$$

The values of B_D calculated by using this equation for different metals are given in Table 1 in [12]. Note that L_α can be interpreted as the absorption radii for point defects, since the interaction energy at smaller distances is higher than the thermal energy: $|E_\alpha(r < L_\alpha)| > k_B T$. In addition, both Z_v and Z_i are of the order of unity, hence one can use $Z_v = Z_i \approx 1$ everywhere except for the bias.

At relatively high temperature, when the recombination reactions between point defects make negligible contribution to the total defect loss in the system, and if dislocations and voids are the only sinks, the swelling rate driven by the dislocation bias, $dS / d\phi$ ($\phi = Gt$ is the irradiation dose in dpa, G is the damage rate) is given by

$$\frac{dS}{d\phi} \approx B_D \frac{k_C^2 k_{D,v}^2}{(k_C^2 + k_{D,i}^2)(k_C^2 + k_{D,v}^2)}, \quad (9)$$

where

$$k_{D,\alpha}^2 = Z_\alpha \rho_D, \quad (\alpha = i, v) \quad (10)$$

$$k_C^2 = 4\pi \langle R \rangle N, \quad (11)$$

are the sink strengths of dislocations (ρ_D is the edge dislocation density) and voids (cavities) for 3-D mobile point defects ($\langle R \rangle$ being the mean void radius and N the void number density). As can be seen from this equation, the swelling rate depends on the bias factor and some combination of sink strengths of voids and dislocations. The latter assumes its maximum value of 1/4 when $k_C^2 = k_D^2$ and decreases by 2.5 times when the sink strengths of voids and dislocations differ from each other by an order of magnitude. The observations show that the sink strengths are often close to each other. Hence, to explain the observed smaller swelling rates than predicted by Eqs. (8)-(11), the dislocation sink strength has to be smaller by about two orders of magnitude as compared to that given by Eq. (10). Such a decrease cannot be justified by the features of SIA diffusion near dislocation observed in MD studies in [23-26]. The only obvious way is to make values of Z_v and Z_i closer to each other. Taking into consideration the MD results obtained in [23-26], one can expect that the decrease of Z_i (rather than increase of Z_v) should provide the required decrease of the dislocation bias. It is argued below that the 1-D mode of the SIA diffusion does produce such effect.

III. Analysis

The theory described above assumes 3-D mobile SIAs and vacancies. Our current understanding of the relative stability and the migration modes in metals and alloys has changed significantly since it was formulated in seventies. In the following we describe relevant information and analyse the consequences on the bias factor.

A. Properties of SIAs

Quantum mechanical calculations and MD simulations using empirical potentials show that in all nonmagnetic bcc metals the most stable SIA defect configuration has the $\langle 111 \rangle$ symmetry [29] and migrates 1-D along its axis. In metals in group 5B of the periodic table (V, Nb, Ta), the difference in formation energies of the $\langle 111 \rangle$ and $\langle 110 \rangle$ SIA configurations is significant, ~ 0.3 - 0.55 eV, while for the group 6B metals (Cr, Mo, W) it is smaller, ~ 0.01 - 0.3 eV. This in turn is fundamentally different from the ferromagnetic bcc α -Fe, where the $\langle 110 \rangle$ dumbbell configuration is by far (~ 0.7 eV [30,31]) the most stable than the $\langle 111 \rangle$ crowdion. This trend correlates with the observed thermally activated mobility of SIA defects, deduced from the temperatures of the recovery stage 1.

Table 1. Material and point defect parameters: the lattice parameter, a_0 ; shear modulus, μ , and the Poisson's ratio, ν , from [33]; and melting temperature, T_m .

Element	a_0 , nm	μ , GPa	ν	$\Delta\Omega_v$	$\Delta\Omega_i$	T_m , K
bcc Mo	0.315	123	0.305	-0.45	0.85	2890
fcc Cu	0.361	55	0.324	-0.25	1.45	1357

In contrast, in the fcc metals, the dumbbell configuration is energetically favourable and the SIAs migrate 3-D in the matrix (e.g. [22]). It has been found, however, that the crowdion configuration with the axis along the dislocation Burgers vector become stable and the SIAs move 1-D in the vicinity of an edge dislocation [23-26]. Hence, the 1-D mobility governs the behaviour of SIAs near dislocations in fcc metals as well. In the next section we consider in more details the bcc molybdenum (Mo) and fcc copper (Cu). We suppose that the stabilisation effect of edge dislocation on the crowdion configuration has the same origin as that for stronger interaction of dislocations with SIA clusters with the Burgers vector parallel to the dislocation Burgers vector. To keep the analysis simple, we use the isotropic elasticity theory [32] for the stress field of an edge dislocation (see Appendix A) and treat SIAs as infinitesimal dislocation loops containing one SIA. The parameters used in calculations are collected in Table 1.

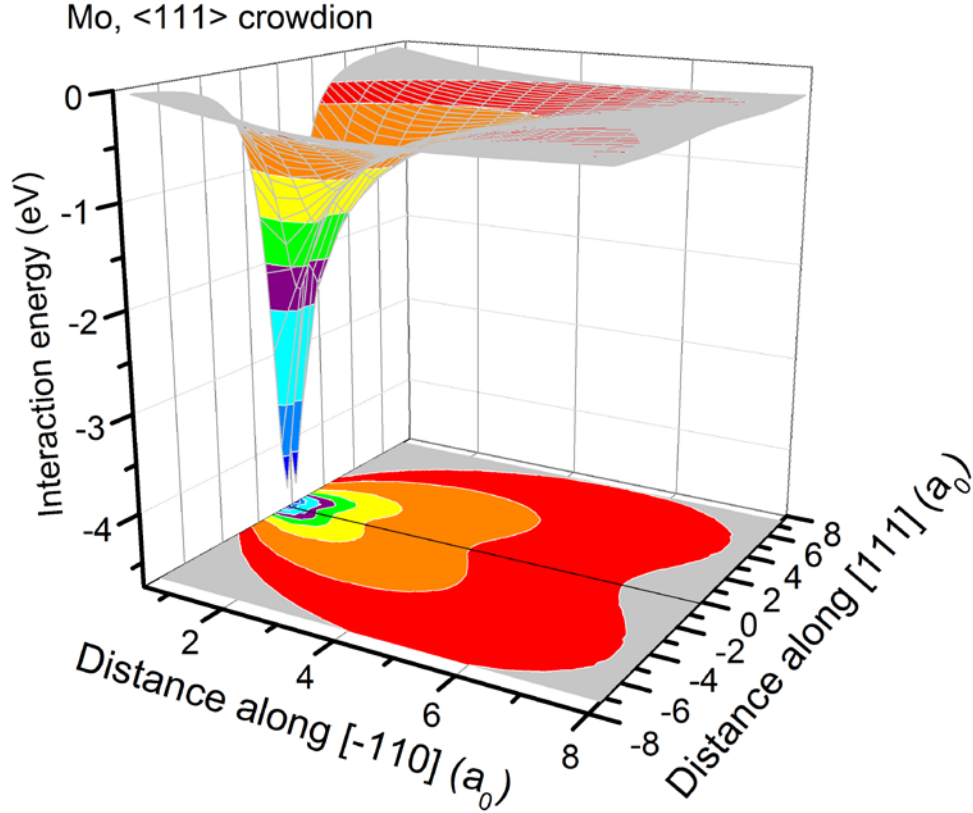


Figure 1. The interaction energy landscape of a $\frac{1}{2}[111]$ crowdion in the expansion region below the line of a perfect $\frac{1}{2}[111](\bar{1}10)$ edge dislocation in molybdenum.

B. Molybdenum

In Mo, the $\frac{1}{2}\langle 111 \rangle$ crowdion configuration of the SIA is more stable than the dumbbell configuration by ~ 0.16 eV [29]. In the vicinity of the dislocation it is even more stable. This can be seen in Figs. 1 and 2, where the interaction energy landscapes of the crowdion and the SIA in the most stable $\langle \bar{1}10 \rangle$ dumbbell configuration in the expansion region, below the dislocation line, of a perfect $\frac{1}{2}[111](\bar{1}10)$ edge dislocation are presented. The interaction energies difference between the crowdion and dumbbell configurations is presented in Fig. 3. As can be seen, it is large except for a narrow area just below the dislocation line, which may be considered as a favourable pass to the dislocation core for migrating dumbbells. However, the realisation of this trajectory is difficult because the dumbbell migrates with changing orientation of its axis, thus deviating from this trajectory. In addition, the configurations with different axes have higher energy (less stable). The energy profiles for the SIAs of different orientations along this pass are presented in Fig. 4. As can be seen, the maximum interaction energy is higher than the thermal energy at a half the melting temperature, $\frac{1}{2}k_B T_m = 0.125$ eV, in the $[\bar{1}10]$ direction at a distance of $\sim 16a_0$ for both $\langle 111 \rangle$ crowdion and $\langle \bar{1}10 \rangle$ dumbbell. The interaction energy of dislocation with dumbbells of other orientations is smaller than that of the most stable $\langle \bar{1}10 \rangle$ configuration, and the difference in the interaction energy increases with decreasing the distance to dislocation. To move towards the dislocation line, the SIA must change from crowdion to dumbbell configuration. If the SIA path towards the dislocation line requires assuming all possible SIA configurations, the activation energy required for such a motion can be estimated as ~ 0.2 eV plus the activation energy of the SIA jump.

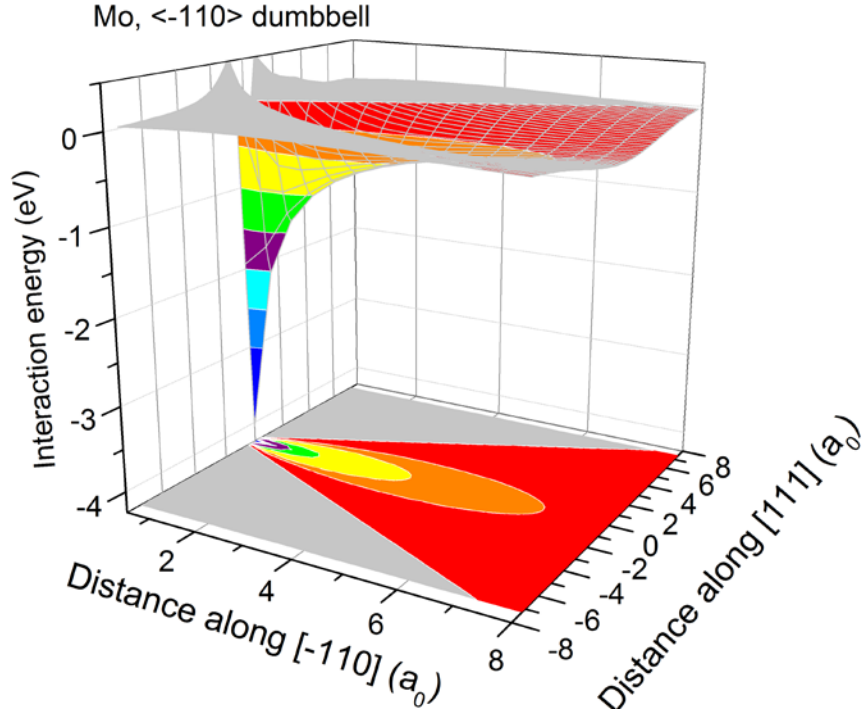


Figure 2. The interaction energy landscape of a $[-110]$ dumbbell in the expansion region below the line of a perfect $\frac{1}{2}[111](\bar{1}10)$ edge dislocation in molybdenum.

The energy landscape for a vacancy calculated using Eq. (3) is shown in Fig. 5. It shows that the interaction energy equal to $\frac{1}{2}k_B T_m$ is achieved at a distance of $\sim 7.5 a_0$ in the $[\bar{1}10]$ direction. For 3-D migrating vacancies, the contour corresponding to this energy level can be interpreted as that separating area of free migration of vacancies from that of certain absorption by the dislocation. The same is not correct for the SIAs which have preference to configurations with the axis direction along the dislocation Burgers vector.

The difference in formation energies of the crowdion and dumbbell SIAs far away from dislocation is not so significant and, depending on the temperature, the SIAs can move 3-D with 1-D parts executed while in the crowdion configuration. Near the dislocation, the crowdion configuration parallel to the dislocation Burgers vector is stabilised, which makes it difficult for the SIA to join the dislocation line (see Fig. 4). To estimate the time required for an SIA to be incorporated into dislocation, one needs to know precise details of the SIA migration, which can be obtained by comprehensive studies using combination of first principle, MD and kinetic Monte Carlo (kMC) methods. Below we make some estimates to illustrate the effect.

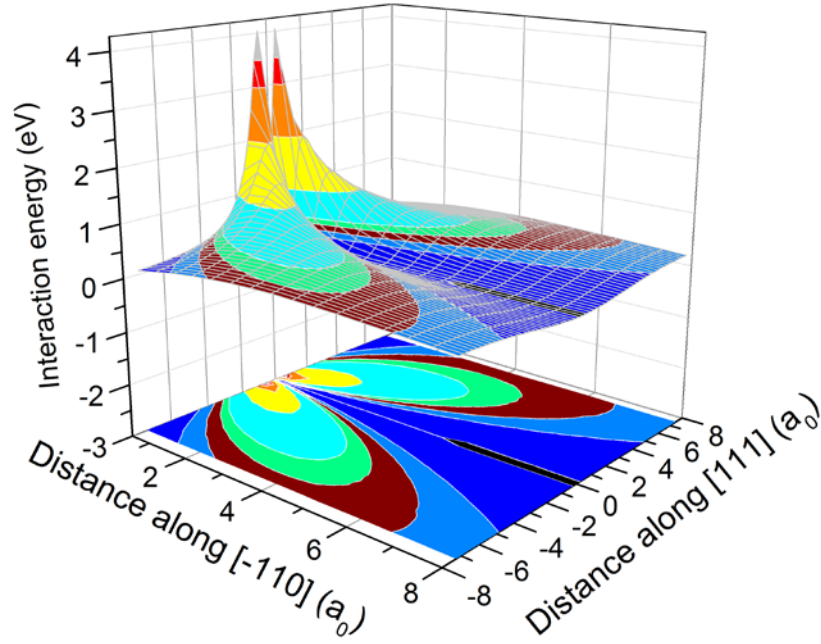


Figure 3. Excess of the interaction energy landscape of a $\frac{1}{2}[111]$ crowdion compare to that of a $[-110]$ dumbbell in the expansion region below the line of a perfect $\frac{1}{2}[111](\bar{1}10)$ edge dislocation in molybdenum.

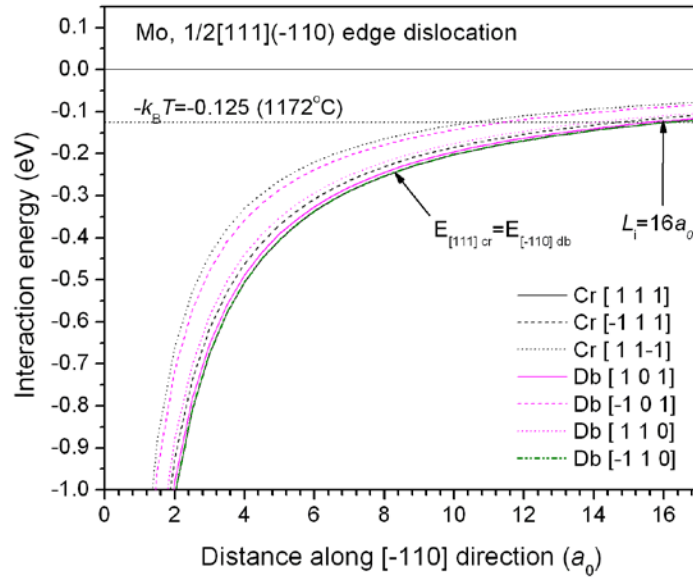


Figure 4. The interaction energy of SIAs of different configurations near $\frac{1}{2}[111](\bar{1}10)$ edge dislocation in Mo as a function of the distance along $[\bar{1}10]$ direction.

The SIAs with the Burgers vector parallel to the dislocation Burgers vector can migrate 1-D without being absorbed by the dislocation for a long time. Simple estimates show that this time is not long enough to recombine with incoming vacancies. The mean time, t_v , between vacancy arrival to a particular point of the dislocation line can be determined from $Gt_v \approx n\rho_D\Omega$, where Ω is the atomic volume and n is the linear density of jogs. For $G=10^{-3}$ dpa/s, $\Omega=10^{-29}$ m³, $\rho_D=10^{13}$ m⁻² and $n=0.01/a_0$, $t_v=3\times 10^{-6}$ s. This is much longer than the mean time of the SIA conversion from the crowdion to the dumbbell configuration and migrating towards and absorption by the dislocation line, estimated as

$$t_{ab} \approx \nu_0^{-1} \exp \left[\beta (E_{db}^f - E_{cr}^f + E_{db}^m) \right], \quad (12)$$

where ν_0 is the attempt frequency $\sim 10^{12} \text{ s}^{-1}$, E_{db}^f and E_{cr}^f are the dumbbell and crowdion formation energies, respectively, and E_{db}^m is the dumbbell migration energy (all energies should be influenced by the proximity to the dislocation). For $k_B T = 0.05 \text{ eV}$ and $E_{db}^f - E_{cr}^f + E_{db}^m = 0.3 \text{ eV}$, $t_{ab} \sim 10^{-10} \text{ s}$. This time can also be significantly longer than the time required for the SIA in the crowdion configuration to leave the dislocation region, which can be found from

$$t_{leave} \approx \nu_0^{-1} \exp(\beta E_{cr}^b), \quad (13)$$

where $E_{cr}^b = -E_{cr}^{disl}$ is the binding energy of dislocation with the crowdion (a precise equation can be found in [34]). So, $t_{leave} < t_{ab}$ estimated above if $E_{cr}^b < E_{db}^f - E_{cr}^f + E_{db}^m = 0.3 \text{ eV}$.

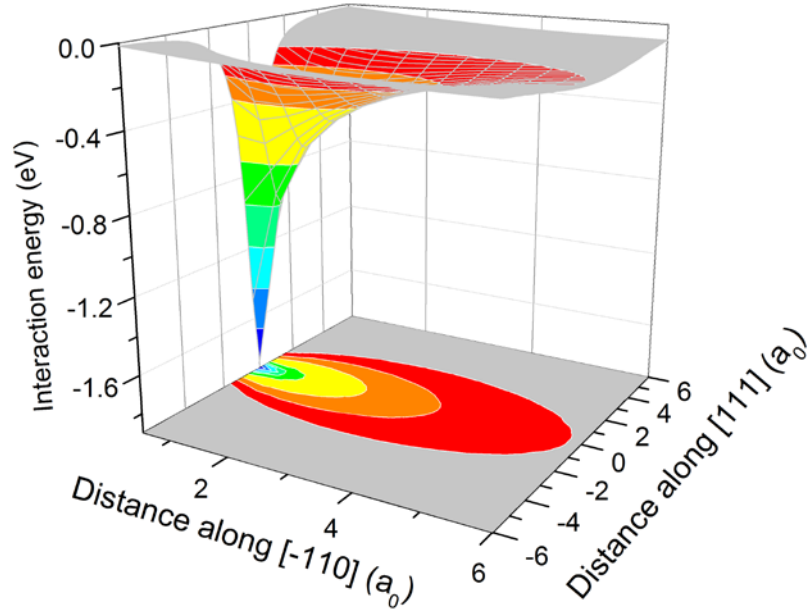


Figure 5. The energy landscape for a vacancy near the $\frac{1}{2}[111](\bar{1}10)$ edge dislocation in Mo.

As a final note to this Section, let us show that supposition made in [21] that a low density of jogs on the dislocation line can affect significantly the sink strength of dislocations is wrong. Assume a vacancy (or an SIA) is already near the dislocation line but it has to move a distance n^{-1} towards nearest jog. It would take approximately $(n)^{-2} / 6D_v$ to reach this point. The time required to dissociate from dislocation line to the matrix is $\left(\frac{L_v}{\lambda} \right)^2 \exp(-\beta E_v^f) / 6D_v$. So, for $L_v \approx 10 a_0$ and $E_v^f = 2 \text{ eV}$, these times are equal to each other if the distance between jogs is of the order of $n^{-1} \approx 6 \times 10^5 a_0 = 50 \mu\text{m}$ for $T = 820^\circ\text{C}$, and even longer for lower temperature, which is unrealistic. The results obtained in [21], in particular Figure 2 on page 1400 which suggests high sensitivity of swelling rate to the jog density in the region of $n^{-1} \approx 50 a_0$, must be erroneous.

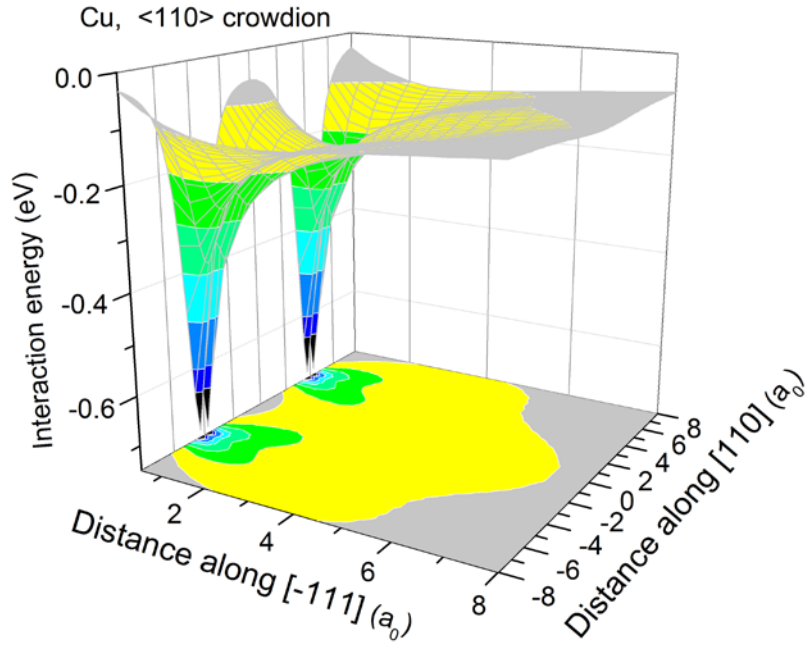


Figure 6. The interaction energy landscape of a $\frac{1}{2}[110]$ crowdion in the expansion region below the line of a perfect $\frac{1}{2}[110](\bar{1}11)$ edge dislocation in copper.

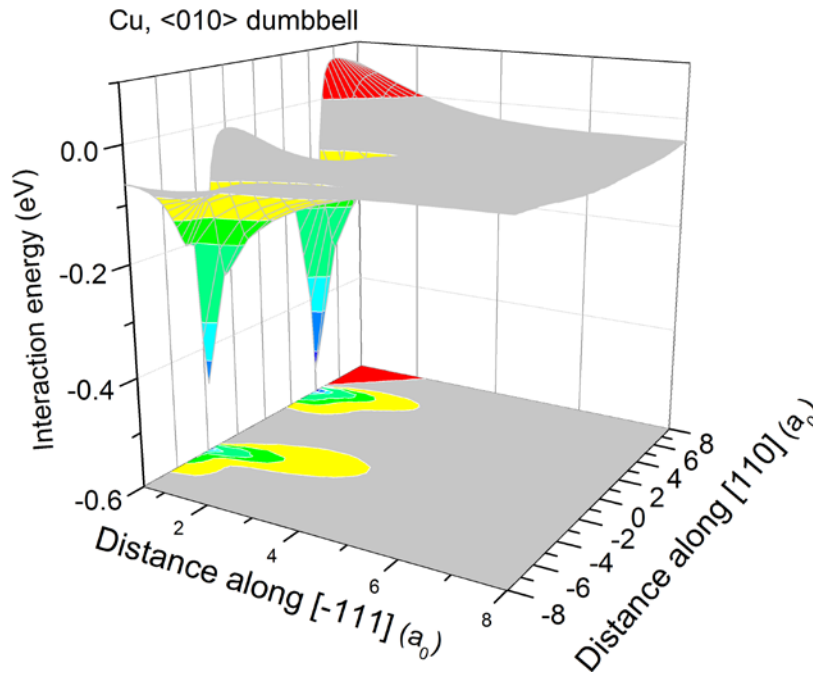


Figure 7. The interaction energy landscape of a $[010]$ dumbbell in the expansion region below the line of a perfect $\frac{1}{2}[110](\bar{1}11)$ edge dislocation in copper.

C. Copper

For Cu, the situation is similar with two exceptions. First, the $\frac{1}{2}\langle 110 \rangle (111)$ edge dislocation is extended due to relatively small stacking-fault energy, $\sim 40 \text{ mJ/m}^2$: the two partials being separated by about $11b$ (see [35], pp.87-89). Second, the $\langle 100 \rangle$ -dumbbell configuration in pure crystal is more stable than the $\frac{1}{2}\langle 110 \rangle$ crowdion configuration. The difference should not be very large and the SIA will frequently assume the crowdion configuration and migrate along its axis. Hence, in the vicinity

of dislocation core there should be difficult for the SIA to jump towards the dislocation line and the SIA may leave the dislocation region in crowdion configuration.

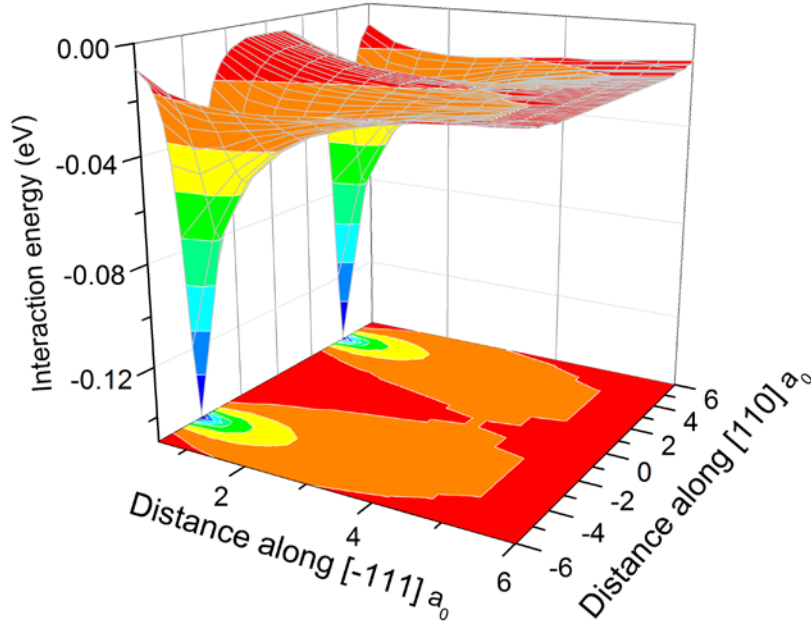


Figure 8. The interaction energy landscape of a vacancy in the compression region above the line of a perfect $\frac{1}{2}[110](\bar{1}11)$ edge dislocation in copper.

Figure 6 shows the interaction energy landscape for the crowdion configuration with the axis parallel to the dislocation Burgers vector. As can be seen, the interaction energy is much smaller in Cu than in Mo. This fact (generally for the fcc compared to bcc lattices) has already been noticed by Kuramoto in [24] and is because of the extended dislocation and smaller shear modulus (see Table 1). Thus, although the values $\mu\Delta\Omega_i$ are similar in Cu and Mo and the interaction energy is predicted by Eq. (4) to be similar, it is, in fact, weaker in Cu due to dissociation of dislocation. This is valid for the vacancies as well (see Fig. 8). In addition, similar to Mo, the interaction energy of dislocation with the most stable dumbbell configuration (see Fig. 7) is smaller than that for the crowdion. This shows a qualitative difference in the mechanisms controlling the dislocation bias from those in the conventional theory. Note that despite the stronger interaction of the SIAs with dislocations in Mo, the bias factor in Mo may be smaller than that in Cu due to higher stability of crowdions compared to dumbbells and the 1-D mobility of crowdions along the dislocation Burgers vector.

IV. Generalised diffusion equations

A way of writing equations for the concentrations of SIAs for a simplified scenario, which account, however, for the existence of different SIA configurations is as follows. Let us assume that dumbbells migrate along the x coordinate towards the dislocation located at $x=0$, while crowdions migrate along transverse y coordinate parallel to the dislocation Burgers vector (see Fig. 6). Then, in the framework described in Section 2 (absence of the generation term and with the boundary conditions described by Eqs. (5) and (6)), the concentrations of dumbbells, C_{db} , and crowdion configurations, C_{cr} , are described by the usual continuity equations containing additional term describing mutual transformations

$$\frac{dC_{db}}{d\phi} = -(\nu_{db \rightarrow cr} C_{db} - \nu_{cr \rightarrow db} C_{cr}) - \nabla J_{db}, \quad (14)$$

$$\frac{dC_{cr}}{d\phi} = (\nu_{db \rightarrow cr} C_{db} - \nu_{cr \rightarrow db} C_{cr}) - \nabla J_{cr}, \quad (15)$$

where J_{db} and J_{cr} are the corresponding fluxes of SIAs, and $\nu_{db \rightarrow cr} \propto \exp[-\beta(E_{db}^f - E_{cr}^f)]$ is the rate by which a dumbbell is transformed into crowdion, and $\nu_{cr \rightarrow db} \propto \exp[-\beta(E_{cr}^f - E_{db}^f)]$ is the rate of the reverse reaction.

Let us consider limiting cases. If the dumbbell configuration is much more stable than the crowdion configuration, then $C_{cr} = 0$ and $\nu_{db \rightarrow cr} = 0$, hence the first terms in the right-hand side of Eq. (14) and Eq. (15) itself are zero. The remaining terms represent usual continuity equation in the system of migrating dumbbell SIAs, as in the case considered by Heald [6] (see Section 2).

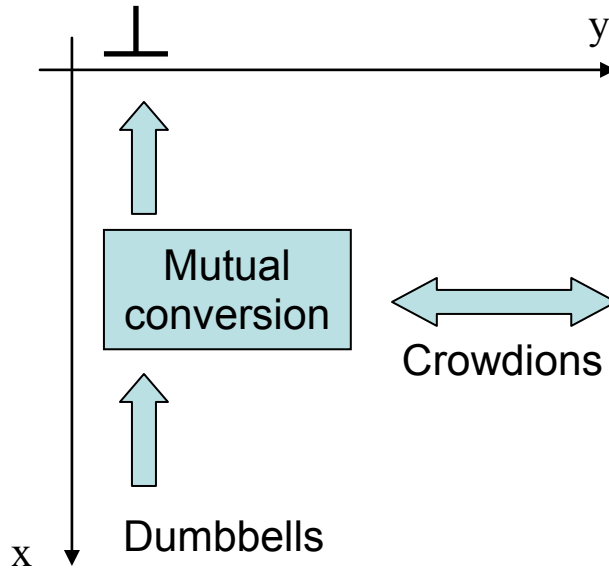


Figure 9. Diagram illustrating a simplified scenario of SIA diffusion near dislocation, which includes mutual conversions of SIA dumbbell and crowdion configurations.

In the case, when the dumbbell configuration is still more stable than the crowdion configuration in the matrix but with crowdion configuration stabilized near the dislocation line, the dumbbells may be converted into the crowdion configuration and leave the region, i.e. escape to the matrix, without being absorbed by the dislocation. In this situation, not all dumbbells entering the region, where the interaction energy with the dislocation is greater than the thermal energy, join the dislocation line: some would escape in crowdion configuration. The effective capture radius of dislocation for the SIAs is smaller in this case than that defined by the equality of the interaction energy to the thermal energy. And the dislocation bias factor is smaller than that defined by Eq. (8).

If the crowdion configuration is much more stable than the dumbbell configuration, then the SIA diffusion is pure 1-D. This situation is described by the PBM [13-15], where the dislocation capture distance for an SIA, r_D , defines zone of spontaneous absorption, and is, hence, much smaller than L_i (see [36], page 99). In addition, after some irradiation dose, a saturation of swelling may be achieved for the void radius $r_{Void} \approx 2\pi r_D$ for a random void arrangement. In this case, the

transformation of crowdion to dumbbell configuration may increase the dislocation capture radius for the SIAs. This is in contrast to the situation when the dumbbells are more stable, and their transformation to crowdion configuration leads to a decrease of the effective capture radius. In both the cases, however, the capture radius is smaller than L_i while the dislocation bias smaller than that given by Eq. (8).

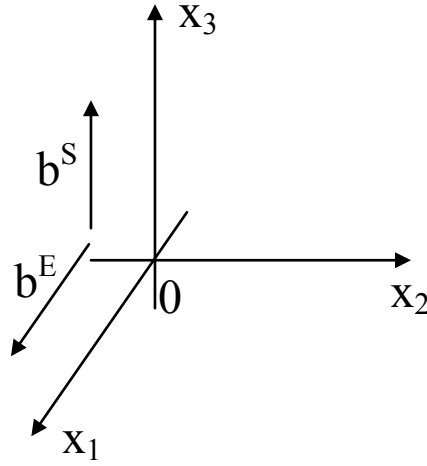


Figure 10. Coordinate system for calculating stress field around a dislocation with the edge, $\mathbf{b}^E$, and screw, $\mathbf{b}^S$, components of the Burgers vector.

SUMMARY of RESULTS

The main results can be summarized as follows:

1. Large dislocation bias factors as compared to those derived from the swelling rates observed in the framework of the conventional theory are a consequence of the assumption that the SIAs migrate 3-D in the vicinity of dislocation line and correspond to maximum values in the cases when the assumption is correct.
2. An assumption of the low density of jogs on dislocation line cannot resolve the contradiction.
3. The 1-D migration of the crowdions with axes parallel to the dislocation Burgers is a process controlling the SIA absorption by the dislocation, hence, the damage accumulation driven by the dislocation bias. The key aspect is an increased probability for the SIAs to escape from the capture region to the matrix, hence decreasing the effective capture radius.
4. The dislocation capture radius for SIAs is determined by the relative stability of the crowdion and dumbbell configurations. The corresponding energy criterion is stronger than the equality of interaction energy to the thermal energy, as in the case of pure 3-D diffusion. This leads to reduced bias factors as required by experiments.
5. Dissociation of dislocations in the fcc metals may be an additional reason for the reduced values of the dislocation bias.
6. The analysis suggests categorizing metals according to relative stability of the SIA crowdion configuration and sheds light on possible reasons for the higher swelling levels observed in fcc compared to bcc materials.
7. Different metals have wide range of relative stability of the crowdion and dumbbell SIA configurations. The diffusion-reaction kinetics in these metals may, thus, vary from that corresponding to pure 1-D migration to that of 3-D diffusion of irradiation-produced defects. The former should be similar to that under neutron irradiation, where the displacement cascades produce 1-D migrating SIA clusters, and described by the PBM (see, e.g. [13,15]).

It is worthy to emphasize that the analysis presented illuminates similarity of the damage mechanisms operating under electron and neutron / heavy ion irradiations: in both cases the 1-D migration of interstitial defects plays key role in the microstructure evolution. In this context, the decoration of dislocations with the cascade-produced SIA clusters may be viewed as a magnified analogy to the behaviour of single SIAs near dislocation. While here we have shown that the presence of 1-D diffusion reduces the dislocation bias factor, in [37] we argue that the decoration may even account for the damage saturation observed in metals. Here we presented a very general analysis of the problem. A combination of first principle, MD and kMC calculations is required to investigate details of point-defect interaction with dislocations and calculate dislocation bias factors in different materials under different conditions.

Finally, let us note that, the very use of metallic alloys as structural materials for nuclear applications becomes possible due to existence of crowdions. Otherwise, high swelling rates would eliminate this possibility. In the latter case, the bias factors would be so large that, despite intra-cascade recombination and clustering, it would be dominant driving force for the damage accumulation even under neutron irradiation (see [15], section 2), and lead unacceptable swelling rates.

ACKNOWLEDGEMENTS

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APPENDIX A. Long-range forces between dislocation loop and edge dislocation

When a straight dislocation lies along x_3 direction with the screw component of the Burgers vector, $\mathbf{b}^S$, along x_3 and the edge component, $\mathbf{b}^E$, along x_1 (see Fig. 1), then the components of the stress tensor are given by the relations [32]:

$$\sigma_{11} = \frac{-Dx_2(3x_1^2 + x_2^2)}{(x_1^2 + x_2^2)^2}, \quad \sigma_{12} = \frac{Dx_1(x_1^2 - x_2^2)}{(x_1^2 + x_2^2)^2} \quad (\text{A1})$$

$$\sigma_{22} = \frac{Dx_2(x_1^2 - x_2^2)}{(x_1^2 + x_2^2)^2}, \quad \sigma_{13} = \frac{-Sx_2}{x_1^2 + x_2^2}, \quad (\text{A2})$$

$$\sigma_{33} = \frac{-2\nu Dx_2}{x_1^2 + x_2^2}, \quad \sigma_{23} = \frac{Sx_1}{x_1^2 + x_2^2}, \quad (\text{A3})$$

where

$$D = \mu \mathbf{b}^E / 2\pi(1 - \nu) \text{ and } S = \mu \mathbf{b}^S / 2\pi, \quad (\text{A4})$$

where μ is the shear modulus and ν is Poisson's ratio. The remaining components obey the rule, $\sigma_{ij} = \sigma_{ji}$, where σ_{ij} is the stress in the i direction on an area perpendicular to the j axis.

If stress components are constant over the area of a small loop, the interaction energy is the sum of each of the stress components multiplied by both the loop area resolved in the appropriate direction and the displacement produced by the loop:

$$E = A' \sum \sigma_{ij} b'_i n'_j, \quad (\text{A5})$$

where b'_i is the component of the loop Burgers vector in the i direction and $A'n'_j$ is the area of the loop resolved onto a plane perpendicular to the j direction.

ATOMISTIC STUDIES OF PROPERTIES OF HELIUM IN BCC IRON USING THE NEW HE-FE POTENTIAL—David M. Stewart, Stanislav Golubov (Oak Ridge National Laboratory and the University of Tennessee), Yuri Ostesky, Roger E. Stoller, Tatiana Seletskaya, and Paul Kamenski (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this work is to use molecular dynamics techniques to increase understanding of the behavior of transmutation-produced helium in reduced-activation ferritic/martensitic steels that are candidate materials for fusion reactors. As there is no suitable iron-carbon-helium interatomic potential, simulations are performed using helium in pure iron.

SUMMARY

We have performed atomistic simulations of helium behavior in iron using a new 3-body Fe-He inter-atomic potential combined with the Ackland iron potential. With the ORNL potential, interstitial helium is very mobile and coalesces to form interstitial clusters. If the He cluster is sufficiently large the cluster can push out an Fe interstitial, creating a Frenkel pair. The resulting helium-vacancy cluster is not mobile. The ejected SIA is mobile, but is weakly trapped by the He-V cluster. If more helium atoms join the He-V cluster, more Fe interstitials can be pushed out, and they combine to form an interstitial dislocation loop. In the reverse process, multiple helium atoms can be trapped in a single vacancy, and if there are few enough, the vacancy can recombine with an Fe interstitial to create a helium interstitial cluster. These mechanisms are investigated together in larger simulations that examine the nucleation of He defects. Helium bubbles of sizes 1–6 nm are also studied. In order to estimate the amount of helium present from an observed bubble size distribution, it is necessary to understand the relationships between bubble size, pressure and helium content. Extensive atomistic simulations of such bubbles are compared to show effect of temperature, interatomic potentials used and helium concentration.

PROGRESS AND STATUS

Introduction

Helium produced in neutron irradiated iron affects the mechanical properties. Predicting the growth, migration and coalescence behavior of helium bubbles is very sensitive to the assumed properties of individual He interstitials and helium-vacancy clusters [1]. A new He-Fe inter-atomic potential has been developed at ORNL, based on extensive fitting to first-principles calculations of point defects and clusters [2–4]. This potential has been used to investigate the properties of helium, helium-vacancy clusters and helium bubbles in MD and MS simulations.

Helium diffuses very fast in the matrix, but is easily trapped in vacancies [5]. It is possible for a self-interstitial to recombine with the vacancy, knocking the helium back into an interstitial position. Previous calculations [6] showed that recombination is possible not only for a single substitutional He, but even when the vacancy contains multiple Helium atoms.

Previous calculations [6] also showed that the reverse process (i.e. Frenkel pair formation) can happen—an iron atom is pushed out of its lattice site, creating a He-V cluster and an SIA. As more helium joins the cluster, more Frenkel pairs are formed, creating larger defects. The He-V defects nucleated in this manner are nascent bubbles. Helium bubbles are more stable than voids and continue to grow as more helium and vacancies diffuse to the bubble.

Simulation Method

The general procedure followed is: Generate perfect BCC lattice. Introduce the defect(s) to be studied. Relax at constant volume using a mixture of conjugate gradient and simulated annealing, and save the atom positions in units of the lattice constant. Start the MD simulation.

The MD simulations used NVE (constant number of atoms, constant volume and constant energy) dynamics. The lattice constant and initial velocities were chosen to give close to zero pressure and the desired initial temperature. The boundary conditions are periodic in X, Y and Z, which are $\langle 100 \rangle$ directions. The velocity Verlet algorithm with a timestep of 0.3 fs is used. As volume and temperature correction are not used, when processes that release energy are simulated the temperature and pressure both rise during the simulation.

Coalescence

Previous He coalescence simulations [6–8] were run at two different concentrations: 125 helium atoms in a $31 \times 31 \times 31$ BCC iron matrix (60,000 iron atoms) and 125 helium atoms in a $40 \times 40 \times 40$ BCC iron matrix (128,000 iron atoms). These give concentrations of 2089 and 976 appm He respectively. New, much larger simulations have now been run at two concentrations: 1000 and 500 helium atoms in a $80 \times 80 \times 80$ BCC iron matrix (1,024,000 iron atoms). These give concentrations of 976 and 488 appm He respectively. For all four simulations, the concentration of vacancies created is plotted as a function of time in Figure 1.

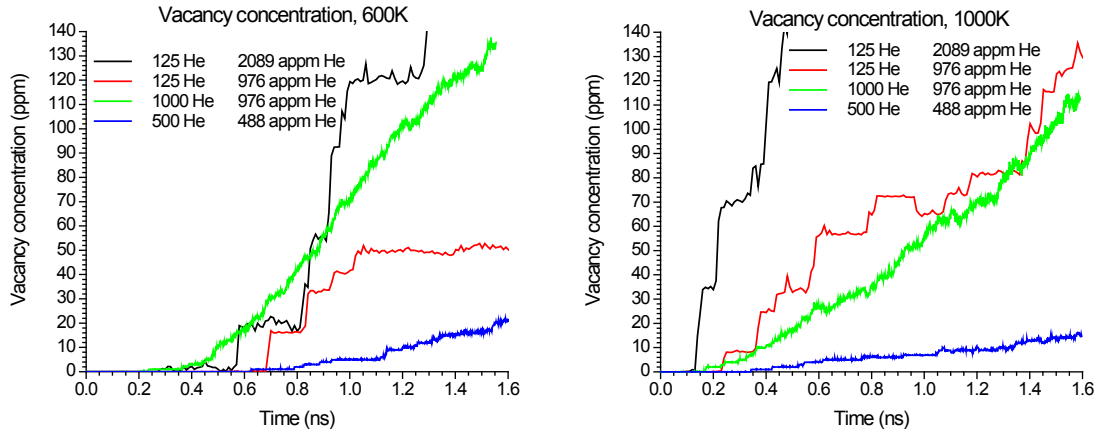


Figure 1. Coalescence for different concentrations at (a) 600 K and (b) 1000 K.

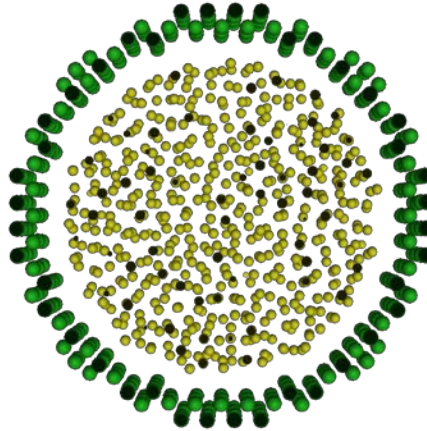


Figure 2. 4 nm 0.5 He/V bubble at 100 K.

Helium bubbles

The He–V defects nucleated in the coalescence simulation are nascent bubbles. We have also simulated larger ones. Bubbles of diameters of 1, 1.5, 2, 4 and 6 nm were investigated. They consist of helium atoms in a spherical void containing 59, 169, 339, 2741 or 9577 vacancies

respectively. Figure 2 shows a cross-section of a 4 nm (2741 vacancy) bubble with a helium to vacancy ratio of one half.

In a void, the surface matrix atoms move inwards slightly. For a helium bubble, the pressure from the helium pushes them back outwards again. We define a bubble as under-pressurized, equilibrium or over-pressurized, if the net effect is to move the matrix atoms inwards, stationary or outwards respectively.

The equilibrium He/V ratio (i.e. the ratio that results in no dilation [7]) is calculated for bubbles of different sizes and temperatures and plotted in Figure 3. The plots show that the ratio decreases with temperature, and larger bubbles show a stronger temperature variation. This is expected as the helium is liquid (as will be shown in a later section) and has a larger coefficient of thermal expansion than iron.

The plots also show that the equilibrium ratio as a function of size has a peak. The size where the peak occurs is temperature dependant, decreasing with increasing temperature. For all but very low temperatures the peak is near 1.5 nm. Above peak size, the equilibrium ratio decreases with size because the pressure goes as $2\gamma/r$. Below peak size, the equilibrium ratio decreases with size because the space available for helium decreases rapidly due to the increasing fraction of the volume accounted for by the He-free gap.

Trinkaus [9] classified He–V clusters and bubbles into three size categories: bubble nuclei, non-ideal gas bubbles and ideal gas bubbles. The boundary between bubble nuclei and non-ideal gas bubbles is given as a diameter of 2 nm, close to the size where we observe the peak equilibrium ratio.

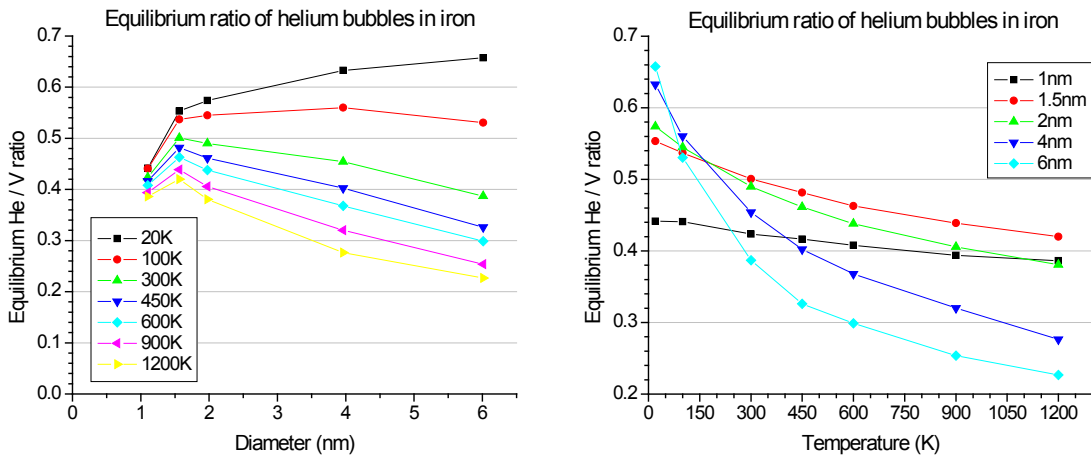


Figure 3. Equilibrium He/V ratio as a function of a) bubble size and b) temperature.

We have performed simulations of helium bubbles using different combinations of Fe–He and He–He potentials. Fe–He potentials used are ORNL [2–4], Juslin–Nordlund [10] and Wilson [11]. He–He potentials used are Aziz [12], Beck [13] and Wilson [11]. All calculations used the Ackland Fe–Fe potential [14].

Figure 4 shows dilation of a bubble as a function of He/V ratio for different temperatures. The graph on the left uses the ORNL potential with the Aziz potential and the graph on the right uses the Wilson potential. With the Wilson potential the curves cross the zero (equilibrium) line at a significantly larger (15–25% higher) He/V ratio at all temperatures, and also show a larger spread with temperature.

Figure 5 shows equilibrium ratios calculated using five different combinations of potentials. The results fall into two groups, one consisting of ORNL+Aziz and ORNL+Beck, and the other consisting of JN+Aziz, Wilson and Wilson+Aziz.

The choice of helium–helium inter-atomic potential did not significantly affect helium bubble equilibrium ratio results. The Wilson and Juslin–Nordlund iron–helium potentials both produced the same equilibrium ratios. Results from the ORNL potential are significantly different than the other Fe–He potentials. With the ORNL potential the bubble has a larger gap, leading to lower He/V ratios at a given size and temperature.

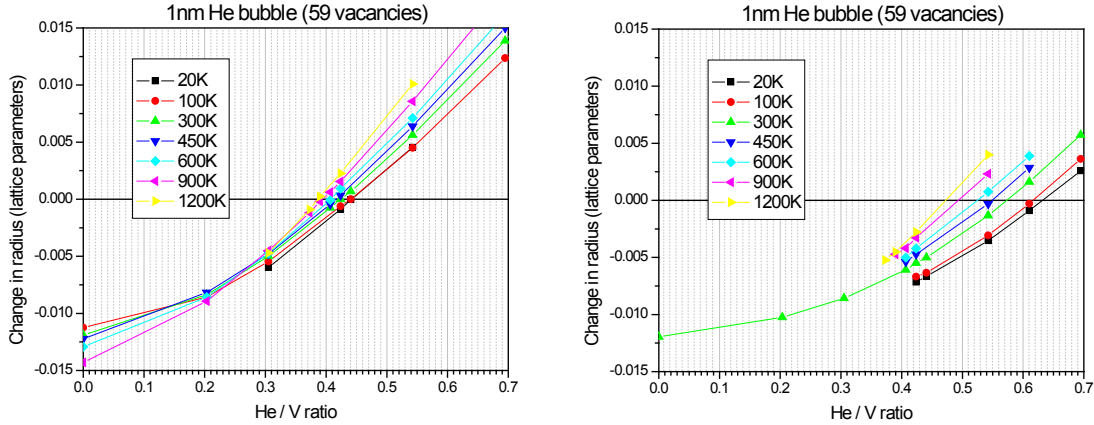


Figure 4. Dilation of 1 nm bubble. (a) Ackland97+ORNL+Aziz. (b) Ackland97+Wilson

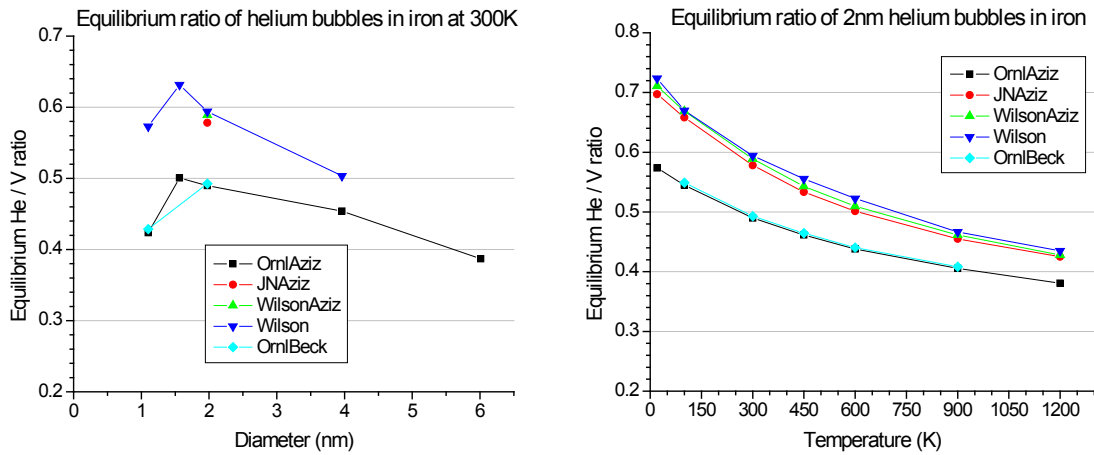


Figure 5. Equilibrium He / V ratio as a function of a) size and b) temperature for different potentials

The pressure of the helium bubble is fit to three theoretical models for the equation of state of a gas and shown in Figure 6. The ideal gas law and the Van der Waals equation do not fit. The hard sphere equation of state [15] fit to bubbles 1.5 nm diameter and above, i.e. the size that Trinkaus [9] classes as non-ideal gas bubbles.

The pressure is calculated as Virial per unit volume. However, since the bubble contains a gap between the iron and the helium, there are two different volumes to consider. The graph on the left is calculated using only the volume actually occupied by helium. The graph on the right is calculated using the volume of the bubble, including the gap.

Also included on the graphs is the Laplace pressure, i.e. the pressure expected from surface energy considerations. This is calculated in two ways also; using the facet-averaged standard iron surface energy density value for iron of 1.82 J/m^2 and using molecular static calculations to determine the surface energy of the bubble size in question.

The hard sphere equation of state has one parameter, the diameter d of the hard spheres. At 300 K, The helium volume calculation fit with $d = 0.2017 \text{ nm}$, and bubble volume calculation fit with $d = 0.259 \text{ nm}$. At 600 K, The helium volume calculation fit with $d = 0.193 \text{ nm}$, and bubble volume calculation fit with $d = 0.244 \text{ nm}$.

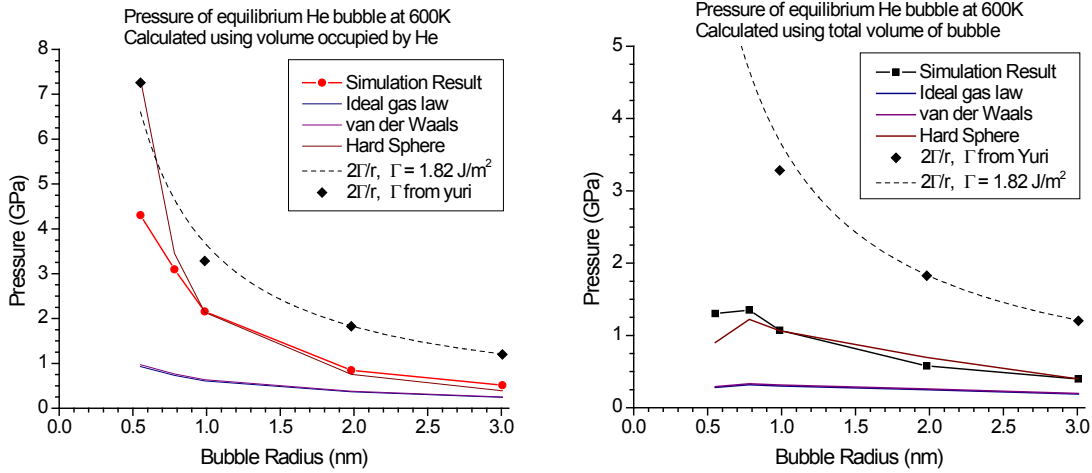


Figure 6. Pressure of He bubble fit to equations of state and surface energy.

The trajectory decomposition method described in [8] and [16] was used to calculate the diffusion coefficient of the helium atoms in a bubble. As the helium atoms cannot escape the bubble, the time segments cannot be too long or the diffusion coefficient will be underestimated. Here we decomposed the atom trajectory into segments of up to 15 ps. For each segment size, the average of the diffusion coefficients of each segment is calculated. This calculation is done for segment sizes of 7.5ps to 15 ps in increments of 0.3 ps, and the average of these is calculated. This is then repeated for 100 (or all, if less than 100) atoms in the bubble and the final value is the average of these atoms.

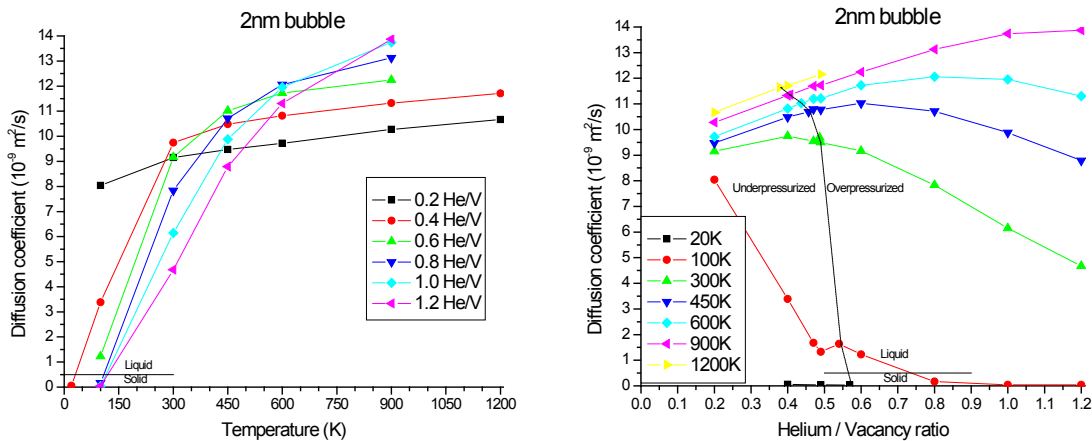


Figure 7. Diffusion coefficient of He atoms in bubble shows state.

The results are plotted in Figure 7. A diffusion coefficient near or below $0.5 \times 10^{-9} \text{ m}^2/\text{s}$ indicates that the helium in the bubble is solid [17]. The graphs show that most of the bubbles studied are liquid; solid helium only occurs in bubbles at very low temperatures or very high He/V ratios.

The diffusion coefficient increases with temperature as expected, but saturates at high temperatures. This saturation is likely due to the confinement of the atom within the bubble, i.e. it is an artifact of the choice of segment lengths to study. A shorter time segment would have been better for these high temperatures but not as good for lower temperatures.

The D vs. ratio plot includes the equilibrium ratios, dividing the space into areas representing underpressurized and overpressurized bubbles.

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AN ATOMISTIC STUDY OF HELIUM RESOLUTION IN bcc IRON - Roger E. Stoller¹ and David M. Stewart^{1, 2} - ¹*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6138, USA;* ²*Center for Materials Processing, The University of Tennessee, Knoxville, TN 37996-0750, USA*

Objective

This research is part of a larger effort intended to reveal the fundamental mechanisms by which helium influences microstructural evolution and mechanical properties in irradiated metals and alloys.

Summary

The evolution of gas-stabilized bubbles in irradiated materials can be a significant factor in the microstructural processes that lead to mechanical property and dimensional changes in structural materials exposed to high-energy neutrons. Helium generation and accumulation is particularly important under DT fusion irradiation conditions. Although the process of ballistic resolution of gas from bubbles has been long-discussed in the literature, there have been few computational studies of this mechanism. Resolution could limit bubble growth by ejecting gas atoms back into the metal matrix. A detailed atomistic study of ballistic He resolution from bubbles in bcc iron has been carried out using molecular dynamics. A newly-developed Fe-He interatomic potential was employed, with the iron matrix described by the potential of Ackland and co-workers from 1997. The primary variables examined were: irradiation temperature (100 and 600K), iron knock-on atom energy (5 and 20 keV), bubble radius (~0.5 and 1.0 nm), and He-to-vacancy ratio in the bubble (0.25, 0.5 and 1.0) in order to obtain an assessment of this dynamic resolution mechanism. The results presented here focus on the 5 keV cascades which indicate a modest, but potentially significant level of He removal by this process.

Progress and Status

Introduction

The evolution of gas-stabilized bubbles in irradiated materials is inherently a dynamic process, involving a balance of growth and shrinkage mechanisms. Simplistically, the bubble volume will grow in units of atomic volume by absorbing vacancies and shrink by either emitting vacancies or absorbing interstitials. Addition or emission of gas atoms will also change the volume, with the relative change dependent on the ratio of gas atoms to vacancies in the bubble. The kinetics of bubble evolution due to reactions with point defects and mobile gas atoms has been extensively investigated using various models of cluster dynamics [1-5]. However, the potentially important mechanism of dynamic ejection of gas due to elastic collisions with energetic knock-on atoms has received much less attention, even though it has been discussed in

the literature for many years [6-13]. Such resolutioning could limit bubble evolution by ejecting gas atoms back into the material matrix.

There are two related mechanisms by which gas atoms can be removed from bubbles and returned to the material matrix; these are schematically illustrated in Fig. 1. The so-called track resolutioning mechanism shown in Fig. 1a is primarily discussed in the context of nuclear fuel in which a highly energetic (up to ~ 100 MeV), heavy fission fragment deposits its kinetic energy over a short mean free path, μ_{FF} . All bubbles atoms that fall within a cylinder defined by this mean free path and an effective track diameter, R , are assumed to be dissolved due to the high energy density in the fission track and all (or some fraction of) the gas atoms contained in these bubbles is returned to the matrix. Ballistic resolutioning, as shown in Fig 1b, is a result of direct collisions between energetic particles and individual gas atoms. The energetic particle could be a fission fragment, a matrix atom recoiling from a collision with a high energy neutron, or (much less frequently) a neutron. Modern computational tools make the ballistic resolutioning mechanism well suited for investigation by molecular dynamics (MD). Recently the effects of ballistic resolutioning of helium from bubbles in UO_2 was examined in an MD study by Parfitt and Grimes [13]. In addition to the two mechanisms just mentioned, they identified a “damage assisted resolution” mechanism in which helium was incorporated into disordered regions of the lattice adjacent to the initial bubble.

Because of the importance of helium generation and accumulation under fusion irradiation conditions, a detailed atomistic study of dynamic He resolutioning from bubbles in bcc iron has been carried out using MD. The primary variables examined were: irradiation temperature (100 and 600K), iron knock-on atom energy (5 and 20 keV), bubble radius (~ 0.5 and 1.0 nm), and He-to-vacancy ratio in the bubble (0.25, 0.5 and 1.0) in order to obtain an assessment of this dynamic resolutioning mechanism. Varying the He to vacancy ratio is equivalent to varying the pressure in the bubble.

Computational Method and Approach

The basic computational approach employed in this investigation follows that published previously for simulation displacement cascades in iron using the MOLDY MD code [14-16]. A newly-developed Fe-He interatomic potential has been employed [17-19], with the iron matrix described by the potential of Ackland and co-workers from 1997 [20]. Constant pressure, periodic boundary conditions were employed in a cubic simulation cell of 70 or 80 lattice parameters, corresponding to 686k or 1024k atoms. Before initiating a ballistic event, a bubble of the desired size was created by removing the necessary number of adjacent iron atoms in an approximately spherical volume (see Table 1), and the number of helium atoms required to obtain the desired He-to-vacancy ratio (Table 1) were placed within the volume. Then, the atom block was thermally equilibrated at the specified temperature for approximately 25 ps. Consistent with the strong He-He and He-vacancy binding observed in previous work with these potentials, no thermal resolutioning was observed. The equilibrated atom configuration was saved and used as the starting point for the subsequent simulations. The ballistic cascade simulations were initiated by giving one of the Fe atoms located near the bubble a defined amount of kinetic energy and an initial direction oriented toward the bubble. As illustrated in Fig. 2, the distance from this primary knockon atom (PKA) to the bubble boundary was between 2 and 10 lattice parameters. Based on previous experience with the statistical nature of cascade

simulations, between ten and twenty simulations were carried out for each of the conditions listed in Table 1, with variability ensured by the different PKA locations and in some cases by further equilibration of the starting configuration. Since no temperature damping was done, a cell size large enough to minimize PKA-induced heating was used, 250k and 1024k atoms for 5 keV and 20 keV simulations, respectively.

Each MD cascade simulation was continued until variables such as the number of defects, and the average kinetic and potential energy had stabilized for a few ps. The time required to reach this new pseudo-equilibrium depended on the PKA energy and irradiation temperature, varying between about 15 to 25 ps. The final atom configuration was then characterized by locating the He atoms and measuring the distance between any ejected He atoms and the initial bubble, and by counting the number and distribution of the point defects (vacancies and interstitials) created by the cascade. The approach used to identify point defects is described in Refs. 14-16.

Results of Simulations

The results presented here will primarily focus on the 5 keV cascade simulations for which a greater level of characterization has been completed. Further simulations are still in progress to develop a more completely symmetric database than that shown in Table 1, which will permit comparisons at both 100 and 600K, and 5 and 20 keV with a range of bubble sizes and He/vacancy ratios. The bubble sizes chosen for this initial study are typical of those observed at low doses in irradiated materials, and values of the helium-to-vacancy ratio will produce conditions from under- to over-pressurized bubbles [17].

In addition to the He resolution behavior, the impact of the bubbles on defect creation is also of interest. The extensive database on cascades in perfect crystal iron developed using a similar interatomic potential [14-16] provide a basis for comparison. Results for the 5 keV cascades are summarized in Fig. 3, where the number of surviving Frenkel pair and the fraction of the interstitials found in clusters are shown. The data points indicate the mean values for a population of cascades at each condition and the error bars show the standard error about the mean. The open symbols in Fig. 3 represent data taken from the perfect crystal database and the filled symbols are the current results in simulation cells containing bubbles. For these particular conditions, there does not appear to be a systematic effect of the bubbles on primary damage formation. Defect survival is somewhat higher, and the interstitial clustering somewhat lower in the cascades with 0.5 nm bubbles at 100K. The larger error bars for the cascades with bubbles at this temperature indicates that the interaction with the bubbles introduces more variability than in perfect crystal material. In contrast, defect survival is unchanged by 0.5 nm bubbles at 600K while the interstitial clustering fraction is somewhat higher. Note that there appears to be less impact of the bubbles on the cascade statistics at 600K where effect of temperature already introduces greater variability than at the lower temperature. The larger, 1.0 nm bubbles also do not influence defect survival at 600K, but do influence interstitial clustering. Clustering is reduced for when the He/vacancy ratio is 0.5, but increased for a He/vacancy ratio of 1.0 as it was for the 0.5 nm bubbles.

The number of He atoms ejected by the 5 keV cascades, and the average distance (in Fe lattice parameters) is shown in Fig. 4. There is a modest effect of temperature, with fewer atoms ejected at 600K for the 0.5 nm bubbles. Although the data are not shown, a temperature effect was observed in 20 keV cascades with 1.0 nm bubbles. The effect of bubble size and He/vacancy

ratio are much stronger. For a He/vacancy ratio of 1.0, average number of He atoms ejected increases from 0.75 to 2.4 when the bubble size increases from 0.5 to 1.0 nm. Reducing the He/vacancy ratio by a factor of two in the larger bubbles reduces the number of He atoms ejected by more than a factor of two, 2.4 to 1.0. The average distance the He atoms are ejected is also slightly reduced at 600K compared to 100K for the 0.5 nm bubbles, and a strong effect of bubble size is observed at 600K. The average ejection distance increases by about a factor of two from the 1.0 nm bubbles, and does not appear to be significantly influenced by the He/vacancy ratio. The numbers shown in parentheses in Fig. 4 are the number of He atoms ejected by more than 5 lattice parameters. This value was chosen to give a simple measure of the tendency for rather long ejections to occur. It appears most sensitive to He/vacancy ratio. Although the average ejection distance was not affected, the number that were displaced over long distances increased from 7 to 18 when the He/vacancy ratio went from 0.5 to 1.0 in the 5 keV cascades at 600K with 1.0 nm bubbles.

The effect of He/vacancy ratio on He ejection from 1.0 nm bubbles is shown in Fig. 5 for 5 and 20 keV cascades at 600K. There is a systematic increase with He/vacancy ratio (bubble pressure) for both cascade energies, and the degree of He resolution is lower for the higher energy.

Discussion and Summary

The simulations completed demonstrate that a number of factors influence ballistic resolution of gas atoms from bubbles in a metal matrix. Some of these are consistent with one's intuition, e.g. more helium atoms are displaced from larger bubbles (Fig. 4) and from bubbles that have a higher He/vacancy ratio or bubble pressure (Figs. 4 and 5). The slightly reduced He resolution at 600K relative to 100K (Fig. 4) is probably an effect of the increased thermal motion which may reduce the probability of direct, high-energy-transfer collisions. This is similar to the reduction in stable defect formation at 600K shown in Fig. 3 for perfect material [17]. The reduction in He resolution for 20 keV cascades compared to 5 keV cascades shown in Fig. 5 is consistent with the lower scattering cross section for higher energy ions.

In the study reported in Ref. [13] of cascade-induced He resolution from bubbles in a UO_2 matrix, an additional He resolution mechanism (besides the purely ballistic process) was reported. The authors described a lower energy process that they call damage assisted resolution which involves He atoms that escape into and are trapped in the regions of heavily damaged crystal near the bubble. Analysis of animated visualization of the cascades in iron did not reveal any significant resolution of this type. This may be a result of the differences between a metal and a covalently-bonded oxide matrix, or the difficulty in determining the nature of the resolution mechanism for He atoms that were found within a few lattice parameters of the bubble. Further analysis of the simulations discussed here, as well as additional simulations that are in progress is planned to investigate this difference. As pointed out in Ref. [13], the number of He atoms removed on typical MD timescales ($\sim$ tens of ps) may be an over-estimate of what would remain in the matrix over longer times. It is likely that He atoms located within a few lattice parameters of the original bubble will be recaptured. This was the motivation for indicating the number of He atoms that were ejected over longer distances in Fig. 4.

Ultimately, the motivation for this work is to provide input to coarser length scale models such as mean field reaction rate theory and Monte Carlo models that can be used to simulate

radiation-induced microstructural evolution over longer times [21]. Initial parametric studies (unpublished) of He bubble evolution using a mean field cluster dynamics model indicated that He resolutioning could have a significant impact on the bubble size distribution. While this preliminary MD study revealed a relatively modest degree of dynamic resolutioning for 5 and 20 keV cascades, a more thorough investigation is required for quantitative assessment and to develop a fundamental understanding of the underlying mechanisms. A change in interatomic potentials could alter the quantitative results presented here. However, the interatomic potential choice is unlikely to have a significant impact on the high-energy ballistic mechanism, although it may influence the rate at which ejected helium is recaptured by a bubble once the system as re-equilibrated, e.g. see the evaluation of potentials discussed in Ref. 19.

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Table 1. Simulation conditions investigated.

Temperature (K)	Cascade energy (keV)	Bubble size		He to vacancy ratio
		Number of vacancies	Radius (nm)	
100	5	40	0.48	1
	20	339	1.0	1
600	5	40	0.48	1
	5	339	1.0	0.5, 1
	20	339	1.0	0.25, 0.5, 1

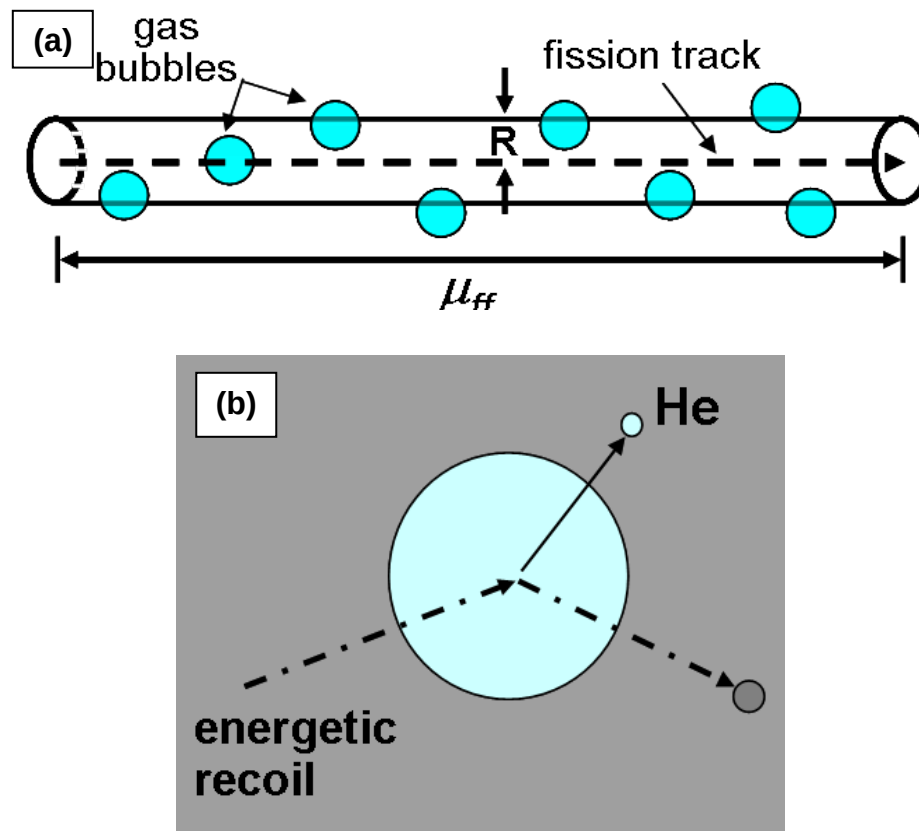


Fig. 1. Schematic diagram of gas resolution mechanisms: (a) “track” resolution with bubble dissolution, and (b) ballistic resolution from a bubble by an energetic recoil.

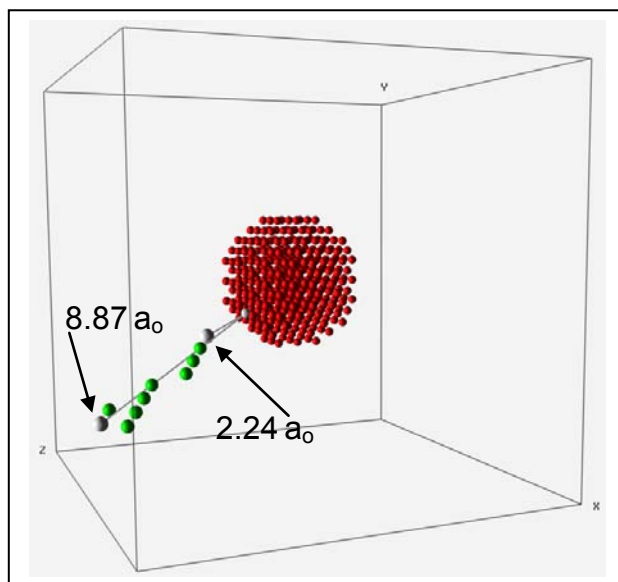


Fig. 2. Illustration of typical initial PKA locations relative to bubble formed by 339 vacancies, radius ~ 1 nm, in Fe matrix.

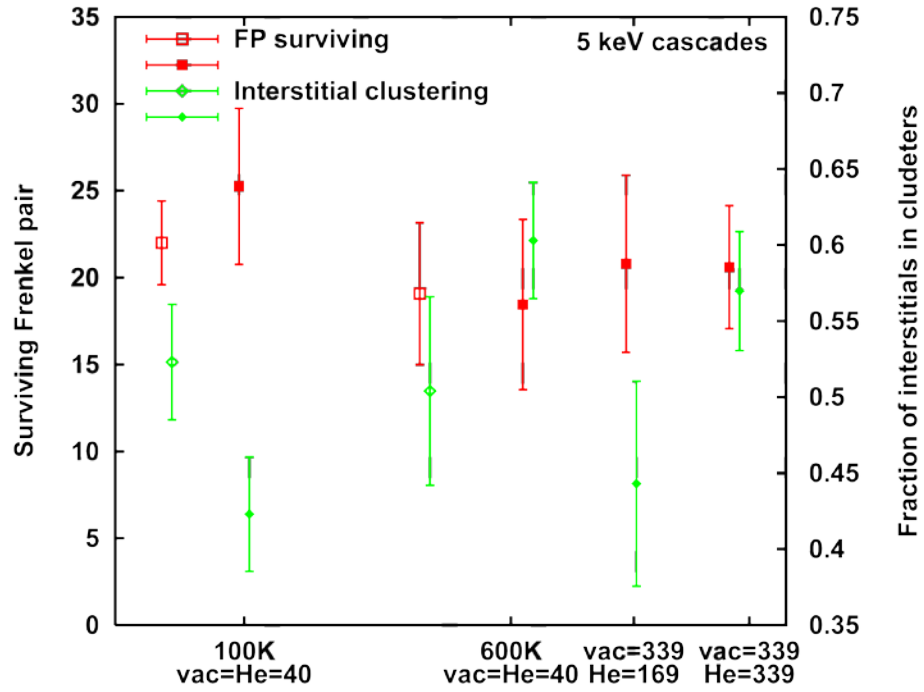


Figure 3. Impact of He bubbles on primary damage formation from 5 keV cascades. Open symbols are from perfect crystal database and filled symbols are current results in simulation cell containing bubbles.

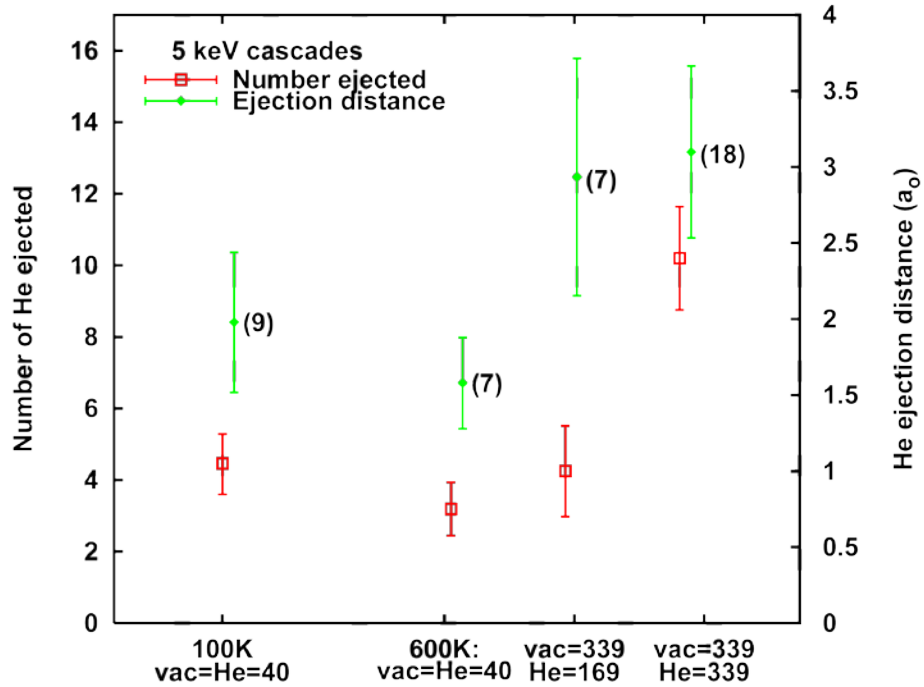


Figure 4. Number of He atoms ejected and average ejection distance from bubbles as a result of 5 keV cascades. Values shown in parentheses 4 are the number of He atoms ejected by more than 5 lattice parameters

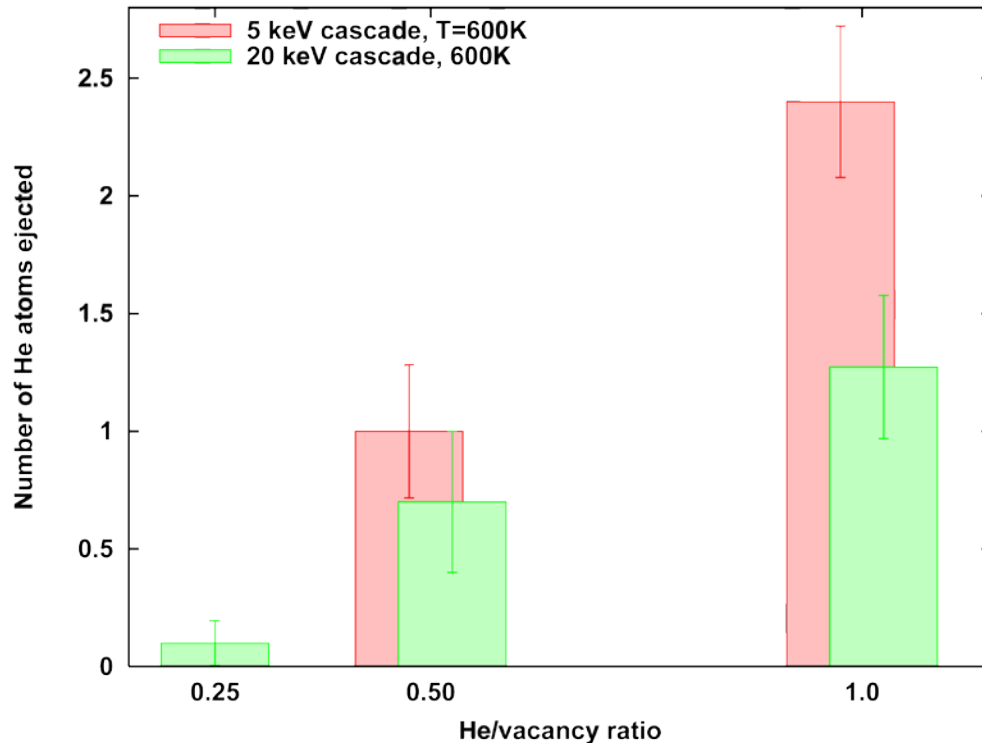


Figure 5. Influence of He/vacancy ratio on the number of He atoms ejected from 1.0 nm bubbles as a result of 5 and 20 keV cascades at 600K.

NEUTRON FLUENCES AND RADIATION DAMAGE PARAMETERS FOR THE HFIR-MFE-RB-14J EXPERIMENT – L. R. Greenwood (Pacific Northwest National Laboratory),
D. C. Glasgow and C. A. Baldwin (Oak Ridge National Laboratory)

OBJECTIVE

The objective is to provide neutron fluences and radiation damage parameters for experimental samples irradiated in the HFIR-MFE-RB-14J experiment.

SUMMARY

The 14J experiment was conducted in the unshielded removable beryllium (RB) position of HFIR.[1] The irradiation of the assembly occurred for two separated time periods. The first irradiation was from June 3, 1999 to August 27, 1999. The second irradiation period was from January 27, 2000 until June 6, 2000. The total exposure was for 14293 FPD (full power days). Reactor dosimetry capsules were analyzed and the activation data were used to provide the best estimates of the neutron fluences and radiation damage parameters as a function of height relative to midplane of the reactor.

PROGRESS AND STATUS

Neutron Activation Measurements and Fluence Calculation

Ten reactor dosimetry capsules were fabricated containing small segments of Fe, Ti, Cu, Nb, and 1% Co-V alloy wires. Following irradiation, the capsules were opened and the activities in each of the wires were measured at Oak Ridge National Laboratory. Due to a delay between the end of irradiation and the gamma counting, no data was measurable for the Ti monitors. Additionally, a few of the wires were not recovered for the gamma counting of the samples. The measured activities are listed in Table 1.

Table 1 – Measured Activities for the HFIR-14J Irradiation
Data are corrected to the end of irradiation date, June 6, 2000

Height cm	ID	1% Co-V Monitor		Fe Monitor		Nb-monitor		Copper Monitor	
		Co-60		Mn-54		Nb-94		Co-60	
		Bq/mg	Error	Bq/mg	Error	Bq/mg	Error	Bq/mg	Error
39.7	RO					3.61E+3	8.09E+1		
-12.85	8A	9.80E+7	5.79E+5	1.76E+6	5.35E+4	8.58E+4	2.01E+3	2.15E+4	3.11E+2
8.4	RL	1.07E+8	6.43E+5					3.57E+4	5.57E+2
-8.72	OV	1.00E+8	5.18E+5	1.93E+6	5.86E+4	9.82E+4	3.65E+3		
12.52	X7	8.81E+7	5.28E+5			8.13E+4	1.93E+3	2.58E+4	3.92E+2
-20.97	BC			1.16E+6	3.51E+4	5.99E+4	1.40E+3	5.47E+4	7.92E+2
20.65	HF	5.81E+7	3.89E+5	1.17E+6	3.44E+4	5.04E+4	1.20E+3	1.59E+4	2.32E+2
36.5	2E	8.96E+6	7.81E+4	2.13E+5	6.72E+3	7.72E+3	1.88E+2	3.74E+3	5.72E+1
27.6	5I	3.81E+7	2.52E+5	6.58E+5	1.93E+4	2.93E+4	6.94E+2	9.45E+3	1.42E+2
24.4	A5	4.71E+7	3.27E+5					1.36E+4	2.12E+2

The activities listed in Table 1 are produced by the $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$, $^{54}\text{Fe}(n,p)^{54}\text{Mn}$, $^{93}\text{Nb}(n,\gamma)^{94}\text{Nb}$, and $^{63}\text{Cu}(n,\alpha)^{60}\text{Co}$ nuclear reactions. The reaction rates were calculated for each of the measured data in Table 1 by correcting for the irradiation history, atomic weight, isotopic percentage, gamma absorption, and decay during irradiation. The decay during irradiation correction was determined by calculating the growth and decay of each activation product over the entire irradiation history as shown in reference 1 and summarized above. The measured activation rate for the $^{63}\text{Cu}(n,\alpha)^{60}\text{Co}$ reaction at -20.97 cm does not fit the rest of the data so this data point was not used in the subsequent analyses and the $^{54}\text{Fe}(n,p)^{54}\text{Mn}$ data was judged to be more reliable at this location.

The STAY'SL [2] computer code was then used to adjust the neutron energy spectrum at each location using the calculated reaction rates and uncertainties as input. The starting neutron spectrum was adopted from prior measurements in the unshielded RB positions of HFIR. [3] STAY'SL performs a least-squares adjustment to determine the most likely neutron spectrum at each position taking into account the uncertainties and covariances of all of the input data whenever possible. The neutron activation cross sections and covariances were taken from the IRDF2002. [4] An example of the adjusted neutron energy spectra is shown in Figure 1 and the adjusted neutron fluences and uncertainties are listed in Table 2.

Table 2 – Adjusted Neutron Fluences for the HFIR-14J Irradiation

Height cm	ID	Thermal < 0.5 eV		Epithermal 0.5 eV to 0.11 MeV		Fast > 0.1 MeV		Fast > 1 MeV	
		n/cm ²	±%	n/cm ²	±%	n/cm ²	±%	n/cm ²	±%
39.7	RO	3.55E+20	10						
-12.85	8A	9.29E+21	8	8.83E+21	12	5.48E+21	12	2.12E+21	12
8.4	RL	1.03E+22	10						
-8.72	OV	1.09E+22	8	1.08E+22	12	5.94E+21	13	2.20E+21	13
12.52	X7	8.31E+21	10			5.43E+21	15	2.06E+21	15
-20.97	BC	6.10E+21	10	5.89E+21	15	3.45E+21	15	1.29E+21	15
20.65	HF	5.13E+21	9	4.92E+21	14	3.11E+21	15	1.26E+21	15
36.5	2E	7.18E+20	12	8.92E+20	15	6.10E+20	15	2.26E+20	15
27.6	5I	3.34E+21	8	2.66E+21	15	1.81E+21	12	7.07E+20	12
24.4	A5	4.09E+21	10			2.84E+21	15	1.07E+21	15

The neutron fluences above 1 MeV were fit with a polynomial to help determine fluences at other locations or where data are not available. The polynomial is of form:

$$F(x) = a (1 + bx + cx^2 + dx^3) \quad (1)$$

a is the fluence at midplane = 2.40E+21 n/cm²

b = - 5.7523e-3, c = -1.0520e-3, and d = 1.4092e-5

Equation 1 can be used to predict the fast neutron fluence and radiation damage parameters discussed later at any height above midplane in the assembly. Neutron fluences calculated with

equation 1 agree with the measured fluences listed in Table 2 within 10% at all of the measured locations. However, the measured values listed in Table 2 are of course more reliable at those locations than using the polynomial fit to the data.

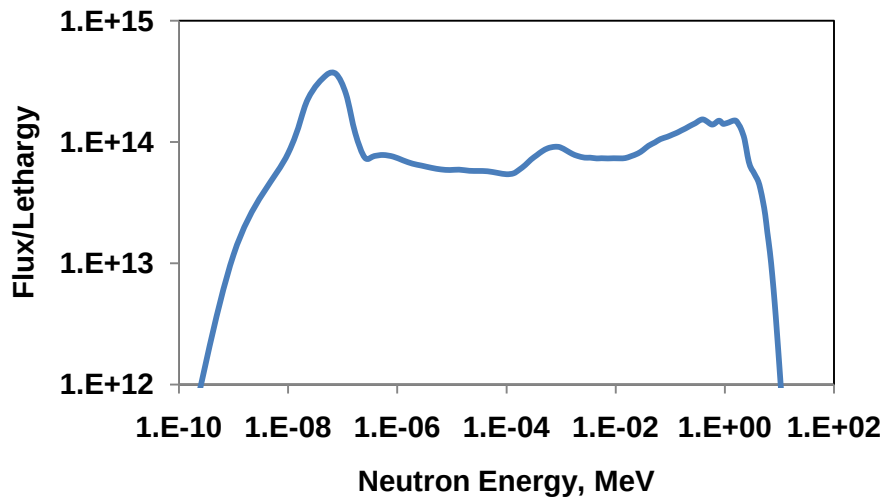


Figure 1 – Adjusted Neutron Spectrum for HFIR-14JP

Radiation Damage Calculations

The adjusted neutron spectrum as shown in Figure 1 was used to calculate radiation damage parameters using the SPECTER computer code.[5] Displacement per atom (dpa) and helium production in appm (atomic parts per million) for several important elements are listed in Table 3. Calculations for nickel include the additional helium production and dpa from the in growth of ^{59}Ni , which has a significant thermal neutron cross section for the production of helium.[6] Table 4 lists calculated dpa and helium production in 316 stainless steel, also taking into account the extra helium and damage from the ^{59}Ni reaction.

Table 3 – Calculated Radiation Damage Parameters for the HFIR-14J Irradiation at Midplane

Element	dpa	He,appm
C	4.54	4.45
Al	7.23	1.74
V	4.94	0.059
Cr	4.12	0.43
Fe	3.64	0.77
Mn	4.78	0.36
Ni Fast	4.12	11.3
Ni-59	1.62	919.4
Ni-Total	5.74	930.7
Cu	4.89	0.65

Table 4 – Calculated Radiation Damage in 316 Stainless Steel for HFIR-14J

Height,cm	dpa	He,appm
-20.97	2.04	37.7
-12.85	3.53	98.6
-8.72	3.91	116.9
0	4.00	121.6
8.4	3.42	93.0
12.52	2.98	73.3
20.65	1.97	35.2
27.6	1.11	12.4
36.5	0.27	0.9
39.7	0.08	0.1

The calculated dpa in 316 stainless steel is shown as a function of height above midplane in Figure 2.

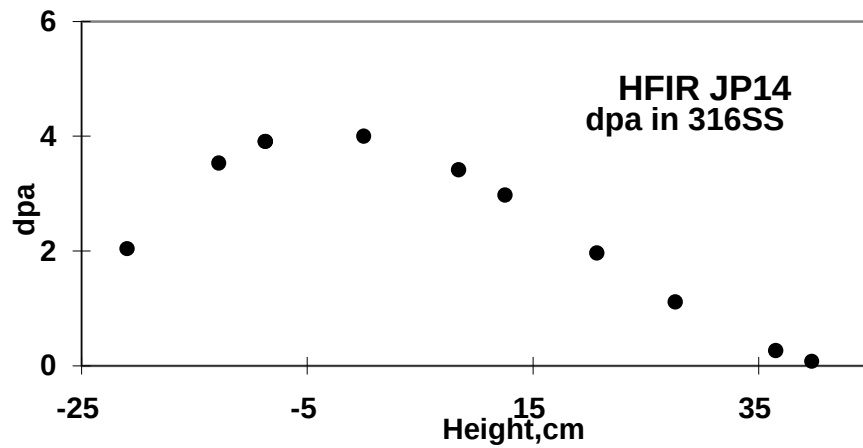


Figure 2 – Calculation of dpa vs. height above midplane

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NEUTRON FLUENCES AND RADIATION DAMAGE PARAMETERS FOR THE HFIR-MFE-RB-17J EXPERIMENT – L. R. Greenwood (Pacific Northwest National Laboratory).

D. C. Glasgow and C. A. Baldwin (Oak Ridge National Laboratory)

OBJECTIVE

The objective is to provide neutron fluences and radiation damage parameters for experimental samples irradiated in the HFIR-MFE-RB-17J experiment.

SUMMARY

The 17J experiment was conducted in the removable beryllium (RB) position of HFIR with a Eu_2O_3 shield.[1,2] The irradiation was conducted from April 27, 2004, to May 18, 2005. The total exposure was for 353.6 FPD (full power days). Reactor dosimetry capsules were analyzed and the activation data were used to provide the best estimates of the neutron fluences and radiation damage parameters as a function of height relative to midplane of the reactor.

PROGRESS AND STATUS

Neutron Activation Measurements and Fluence Calculation

Four reactor dosimetry capsules were fabricated from vanadium tubing containing small segments of Fe, Ti, Cu, Nb, and 1% Co-V alloy wires. Following irradiation, the capsules were opened and the activities in each of the wires were measured at Oak Ridge National Laboratory. Due to a delay between the end of irradiation and the gamma counting, no data were measurable for the Ti monitors. The measured activities are listed in Table 1.

Table 1 – Measured Activities for the HFIR-17J Irradiation

Data are corrected to the end of irradiation date, May 18, 2005

		1% Co-V Monitor		Fe Monitor		Nb-monitor		Copper Monitor	
Height		Co-60		Mn-54		Nb-94		Co-60	
cm	ID	Bq/mg	Error	Bq/mg	Error	Bq/mg	Error	Bq/mg	Error
-18.52	J	3.82E+6	5.06E+4	8.75E+5	2.69E+4	1.41E+4	3.30E+2	1.32E+4	1.72E+2
-3.61	D	6.52E+6	8.67E+4	1.33E+6	4.19E+4	2.31E+4	5.58E+2	2.12E+4	2.78E+2
8.83	2X	5.59E+6	7.43E+4	1.24E+6	3.83E+4	2.07E+4	4.86E+2	1.93E+4	2.47E+2
18.26	11	3.62E+6	4.76E+4	8.26E+5	2.59E+4	1.37E+4	3.36E+2	1.32E+4	1.68E+2

The activities listed in Table 1 are produced by the $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$, $^{54}\text{Fe}(n,p)^{54}\text{Mn}$, $^{93}\text{Nb}(n,\gamma)^{94}\text{Nb}$, and $^{63}\text{Cu}(n,\alpha)^{60}\text{Co}$ nuclear reactions. The saturated reaction rates were calculated for all of the measured data in Table 1 by correcting for the irradiation history, atomic weight, isotopic percentage, gamma absorption, and decay during irradiation. The decay during irradiation correction was determined by calculating the growth and decay of each activation product over the entire irradiation history as summarized above.

The STAY'SL [3] computer code was then used to adjust the neutron energy spectrum at each location using the calculated reaction rates and uncertainties as input. The starting neutron spectrum was adopted from prior measurements in the RB position of HFIR with the Eu_2O_3 shielding.[4] The effect of the Eu_2O_3 can be seen in Figure 1, which shows the adjusted neutron flux spectrum at -3.61 cm. The thermal and epithermal flux regions are seen to be greatly depressed by the shield. Information was not available regarding the burnout of the Eu_2O_3 which gradually loses its effectiveness during prolonged irradiations, as shown in reference 3. However, the STAY'SL adjustment of the neutron spectrum should produce the best estimate of the time-averaged neutron spectrum over the entire irradiation history. STAY'SL performs a least-squares adjustment to determine the most likely neutron spectrum at each position taking into account the uncertainties and covariances of all of the input data whenever possible. The neutron activation cross sections and covariances were taken from the International Reactor Dosimetry File, IRDF2002 [4] An example of the adjusted neutron energy spectra is shown in Figure 1 and the adjusted neutron fluences and uncertainties are listed in Table 2.

Table 2 – Adjusted Neutron Fluences for the HFIR-17J Irradiation

		Thermal		Epithermal		Fast		Fast	
Height		< 0.5 eV		0.5 eV to 0.11 MeV		> 0.1 MeV		> 1 MeV	
cm	ID	n/cm ²	±%	n/cm ²	±%	n/cm ²	±%	n/cm ²	±%
-18.52	J	7.06E+19	17	2.26E+21	8	2.60E+21	10	9.51E+20	12
-3.61	D	1.17E+20	17	3.75E+21	8	4.21E+21	10	1.49E+21	12
8.83	2X	1.03E+20	17	3.33E+21	8	3.77E+21	10	1.36E+21	12
18.26	11	6.77E+19	17	2.18E+21	8	2.47E+21	10	8.90E+20	12

The neutron fluences above 1 MeV were fit with a polynomial to help determine fluences at other locations or where data are not available. The polynomial is of form:

$$F(x) = a (1 + bx + cx^2 + dx^3) \quad (1)$$

where a is the fluence at midplane = 1.505E+21 n/cm², b = - 7.880e-4, c = -1.150e-3, and d = 1.783e-6

Equation 1 can be used to predict the fast neutron fluence and radiation damage parameters discussed later at any height above midplane in the assembly. Neutron fluences calculated with equation 1 agree with the measured fluences listed in Table 2 within 5% at all of the measured locations. However, the measured values listed in Table 2 are of course more reliable at those locations than using the polynomial fit to the data.

Radiation Damage Calculations

The adjusted neutron spectrum as shown in Figure 1 was used to calculate radiation damage parameters using the SPECTER computer code.[6] Displacement per atom (dpa) and helium production in appm (atomic parts per million) for several important elements are listed in Table 3. Calculations for nickel include the additional helium production and dpa from the in growth of

^{59}Ni , which has a significant thermal neutron cross section for the production of helium.[7] Table 4 lists calculated dpa and helium production in 316 stainless steel, also taking into account the extra helium and damage from the ^{59}Ni reaction. The ^{59}Ni contributions are not significant for this experiment due to the use of the Eu_2O_3 shield to suppress the thermal neutron flux.

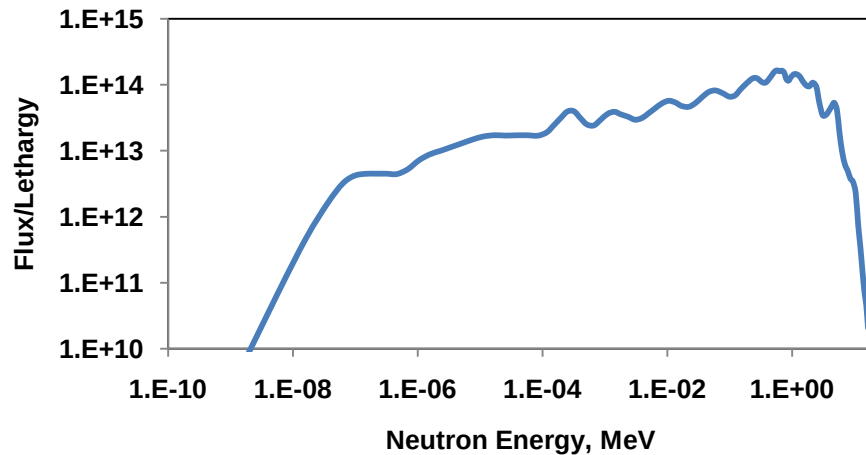


Figure 1 – Adjusted Neutron Flux Spectrum for HFIR-17JP

Table 3 – Calculated Radiation Damage Parameters for the HFIR-17J Irradiation at Midplane

Element	dpa	He,appm
C	3.08	3.56
Al	4.91	1.22
V	3.15	0.048
Cr	2.68	0.32
Fe	2.40	0.52
Mn	2.91	0.25
Ni Fast	2.67	7.85
Ni-59	0	1.11
Ni-Total	2.67	8.96
Cu	3.23	0.44

Table 4 – Calculated Radiation Damage in 316 Stainless Steel for HFIR-17J

Height,cm	dpa	He,appm
-18.52	1.50	0.91
-3.61	2.46	1.54
8.83	2.19	1.37
18.26	1.44	0.87

The calculated dpa in 316 stainless steel is shown as a function of height above midplane in Figure 2.

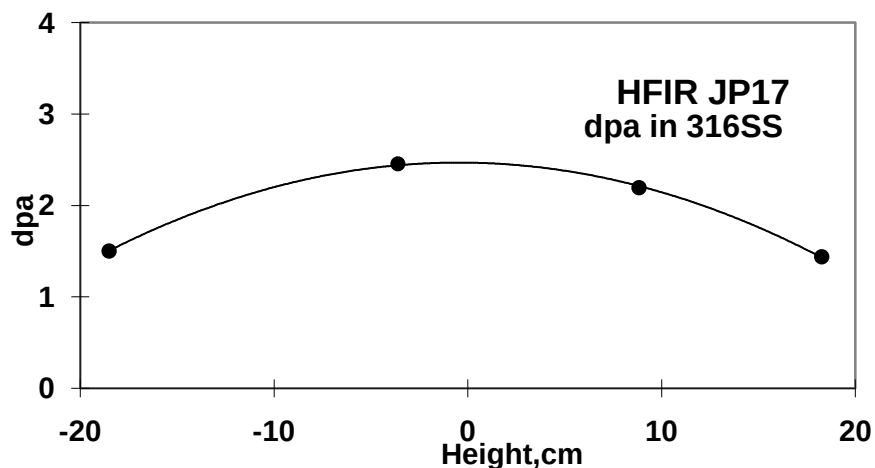


Figure 2 – Calculation of dpa vs. height above midplane

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DILATOMETRY OF IRRADIATED SILICON CARBIDE AS A METHOD FOR DETERMINATION OF IRRADIATION TEMPERATURE —Y. Katoh, A. Clark, K. Ozawa (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this work is to evaluate applicability of temperature dependent dimensional evolution of cubic silicon carbide for determination of irradiation temperature.

SUMMARY

Dilatometry-based thermometry using SiC appeared to be consistent with the result of conventional electrical resistivity-based technique within the irradiation conditions examined in this work, ~673K (~400 °C) to ~1073K (~800°C). The maximum difference in irradiation temperatures determined by these two methods was ~20K. This method appeared to be as reliable as the conventional electrical resistivity-based technique within the irradiation conditions examined in this work.

PROGRESS AND STATUS

Introduction

Thermal expansion of irradiated SiC will be affected by defect annealing when heated beyond the temperature at which the sample was irradiated. Linear thermal expansion measurement may be used for passive thermometry of reactor irradiation, if the onset of such annealing can be explicitly determined.

Benefit of dilatometry-based thermometry will be the fact that the irradiation temperature may be determined in one measurement run which typically can be completed within a day or over-night. The conventional thermometry method involving repeated isochronal annealing processes and electrical resistivity measurement at a fixed temperature typically takes weeks to complete.

Moreover, there have been only very limited reports on the effect of irradiation on the thermal expansion behavior of SiC. The result obtained here may be scientifically and technologically valuable.

Experiment

The material used was high purity (manufacturer-claimed purity >99.999%, nitrogen as the primary impurity) chemically vapor-deposited (CVD) SiC manufactured by Rohm & Haas Advanced Materials (now Dow Chemical Co.). The irradiated samples used in this study were a part of fixture, called “retainer,” used in the bend stress relaxation irradiation creep experiment performed in the fusion US-Japan TITAN program. The nominal irradiation temperatures and doses are shown in [Table I](#).

[Table I](#): Summary of nominal irradiation conditions, swelling, and the dilatometric annealing onset temperatures.

Capsule ID/ Specimen	Tirr (nominal)	Dose (dpa)	Linear Swelling	Ramp Rate (K/min.)	Defect Ann. Temp. per Dilatometry	Defect Ann. Temp. per ER*
M02	300°C	0.11	0.50%	2.5	~400°C	~390°C
				0.25	~380°C	
M05	500°C	0.94	0.46%	2.5	~540°C	~540°C
M07	800°C	1.38	0.25%	2.5	~760°C	~740°C

*ER: Electrical resistivity

The original length of the retainers was 40 mm. Linear swelling values in the above table were determined by measuring the change in length.

The dilatometry was performed up to about 1250K at a constant ramp rate of 2.5 K/min. for one sample from each capsule. Then a replicate sample from M02 (M02-2 hereafter) was measured to about 750K at the ramp rate of 0.25 K/min.

The other CVD SiC piece from the fixture, called “hub,” was subjected to the routine thermometry analysis. The pair of retainer and hub were irradiated side-by-side both pressed to the internal surface of the same molybdenum sleeve during irradiation. Therefore their irradiation temperatures are expected to be exactly same. The routine thermometry analysis is based on measurement of electrical resistivity at room temperature following isochronal annealing. The annealing time at each temperature step was 30 minutes.

Results and Discussion

All samples exhibited clear deflections in the length-temperature plots, Figs. 1 (a) through (c), approximately corresponding to the nominal irradiation temperatures. Specifically, the onset temperatures of apparent defect annealing during heating were 673, 813, and 1033K (400, 540, and 760°C) as compared to the nominal irradiation temperatures of 573, 773, and 1073K (300, 500, and 800°C) for M02, M05, and M07, respectively. The results are summarized in Table I.

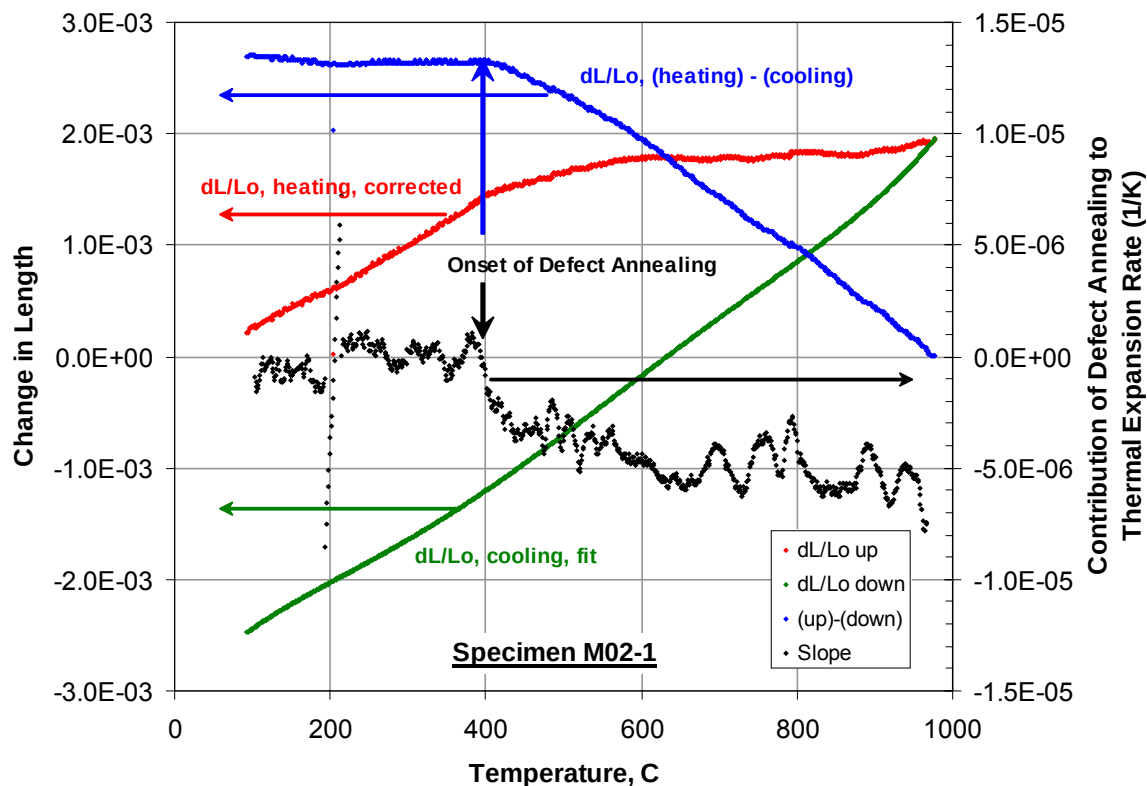


Figure 1: (a) Fractional change in length of M02 CVD SiC sample as a function of temperature at a constant ramp rate of 2.5 K/min. Red: initial heating; Green: cooling after initial heating; Blue: difference between initial heating and cooling; Black: derivative of the differential length change.

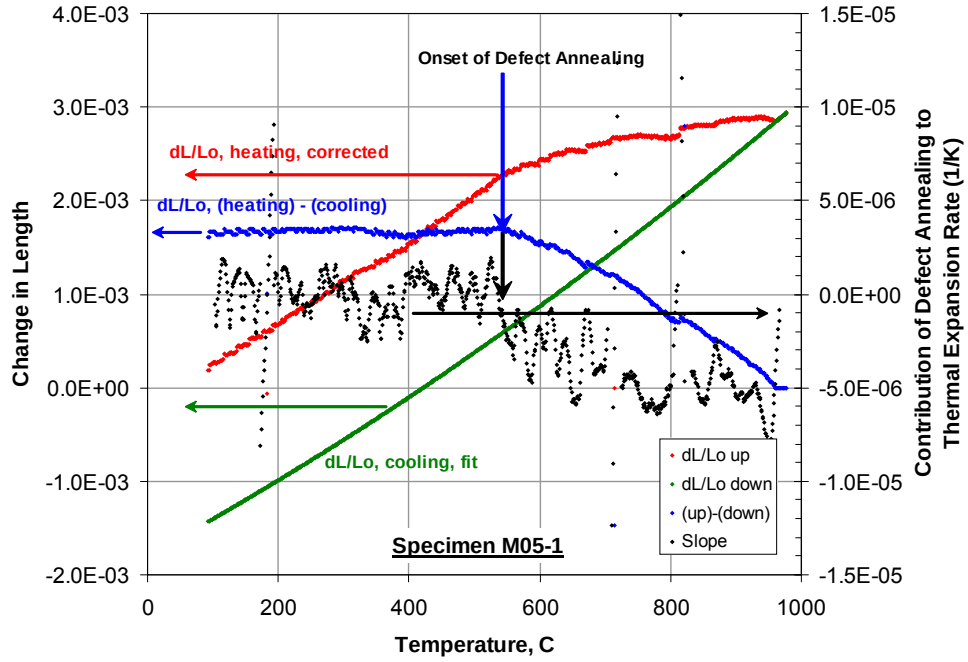


Figure 1: (b) Fractional change in length of M05 CVD SiC sample as a function of temperature at a constant ramp rate of 2.5 K/min. Red: initial heating; Green: cooling after initial heating; Blue: difference between initial heating and cooling; Black: derivative of the differential length change.

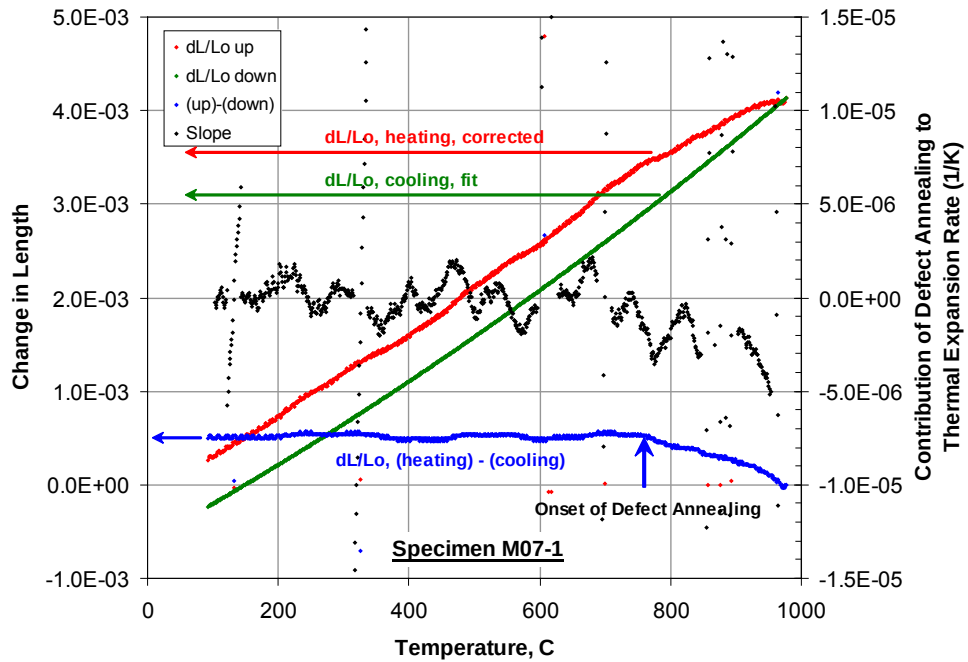


Figure 1: (c) Fractional change in length of M07 CVD SiC sample as a function of temperature at a constant ramp rate of 2.5 K/min. Red: initial heating; Green: cooling after initial heating; Blue: difference between initial heating and cooling; Black: derivative of the differential length change.

Figure 2 shows the result of dilatometry run at the slower ramp rate, 0.25 K/min., using the M02-2 sample. The onset of defect annealing in this case appeared slightly less clear due to the noise, but it is certainly in the vicinity of 653K (380°C). This indicates about -20K difference from the annealing onset temperature at a ramp rate 2.5 K/min.

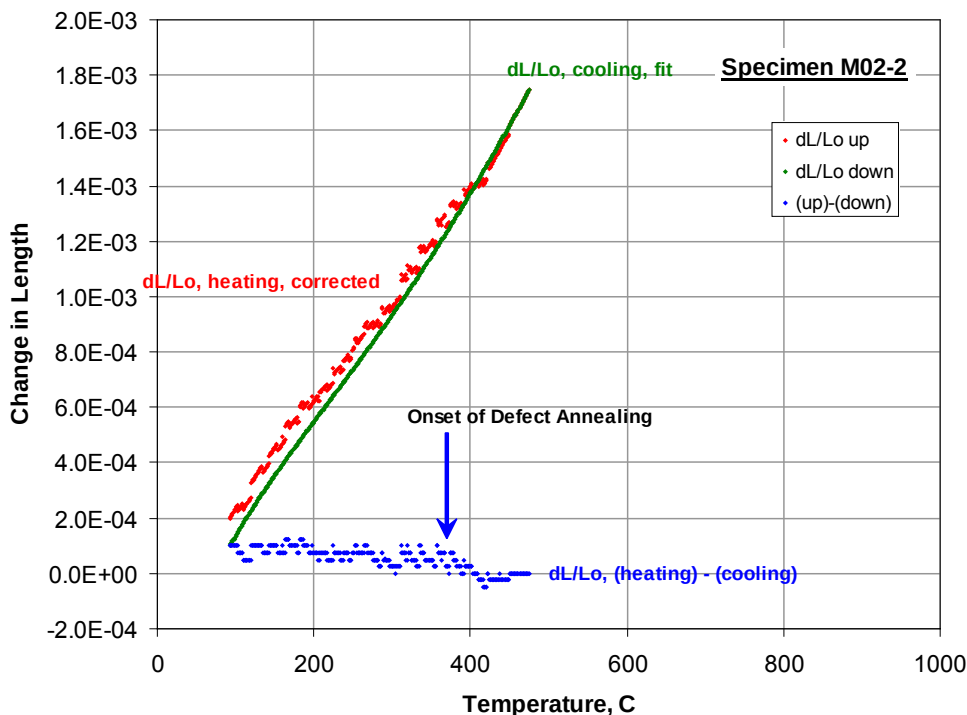


Figure 2: Fractional change in length of M02-2 CVD SiC sample as a function of temperature at a constant ramp rate of 0.25 K/min. Red: initial heating; Green: cooling after initial heating; Blue: difference between initial heating and cooling.

Figure 3 shows the electrical resistivity at room temperature as a function of annealing temperature. The onset temperature of defect annealing in this process appeared to be ~390°C for M02, which falls between the defect annealing onset at ramp rates 2.5 K/min. and 0.25 K/min. during dilatometry. The onset temperatures of defect annealing for M05 and M07 were determined to be ~813K (~540°C) and ~1013K (~740°C), respectively, by the electrical resistivity at room temperature. These are also within ± 20 K of the onset defect annealing determined by dilatometry, Fig. 4.

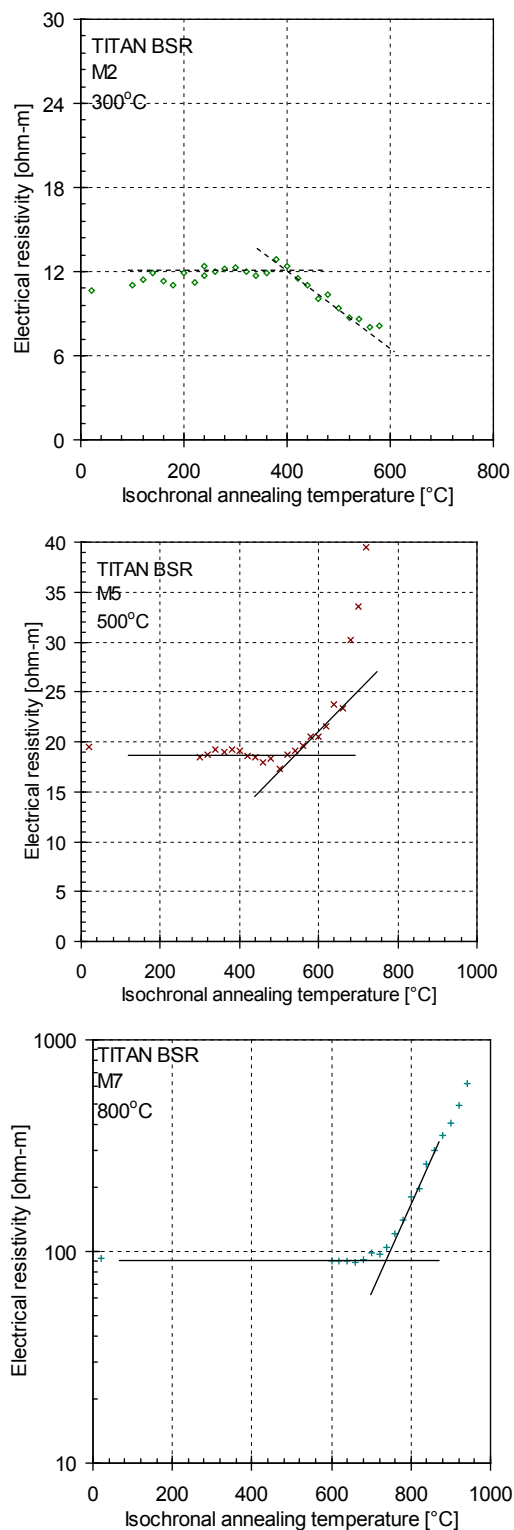


Figure 3: Isochronal annealing of room temperature electrical resistivity of CVD SiC samples, top: M02, showing defect annealing onset at ~663K (~390°C); middle: M05, ~813K (~540°C); bottom: M07, ~1013K (~740°C).

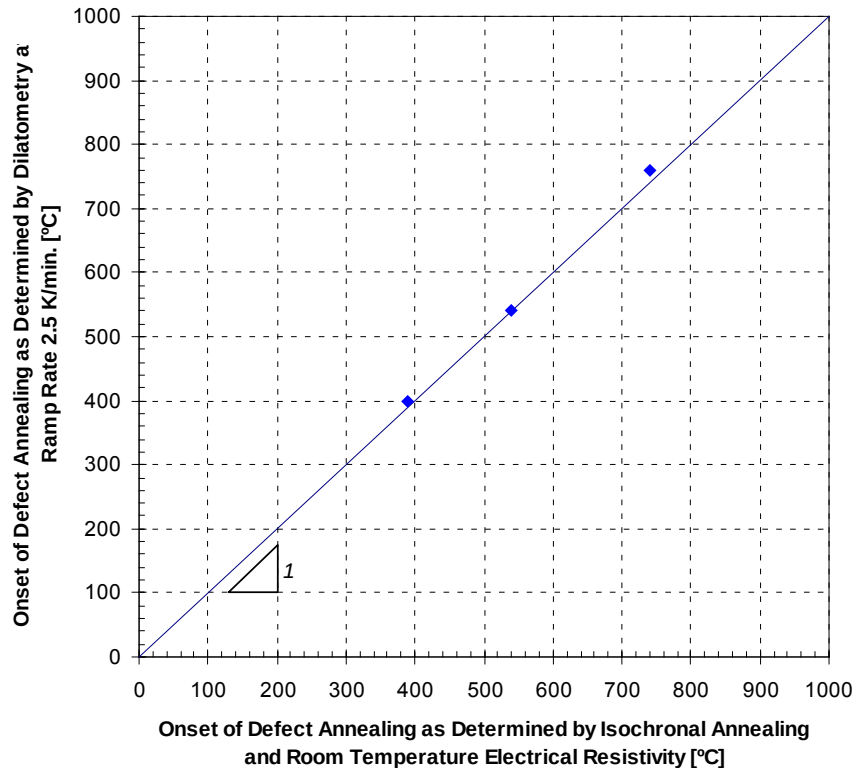


Figure 4: Correlation between the irradiation temperatures determined by dilatometry and isochronal annealing with intermittent room temperature electrical resistivity measurement.

The time required for thermal equilibration of the entire specimen housing is typically <5 minutes for the dilatometer used, thus the potential maximum shift in annealing temperature at the ramp rate of 2.5 K/min. will be 12.5K as compared to the pseudo-static annealing. The influence of ramp rate on defect annealing behavior is not known but may be contributing as well. In the routine thermometry practice, the isochronal annealing time is 30 minutes. In the present dilatometry runs, the temperature changes during 30 minutes are 75K at 2.5 K/min. and 7.5K at 0.25 K/min. However, assuming as an example that the responsible annealing process has an activation energy of 1.5 eV, temperature increase by 50K in the temperature range 573-673K will increase the annealing rate approximately by an order. Thus the difference in ramp rate between 2.5 and 0.25 K/min. may impose a significant shift in the apparent temperature dependent annealing behavior, although it is unlikely that the shift reaches many tens of Kelvin in most cases. On the other hand, typical error in determining the annealing onset temperatures from charts (Figs. 2 and 3) is anticipated to be within 10K. Therefore, it is reasonable to assume that the observed ~20K difference in the annealing onset temperature between the two ramp rates is contributed by all of the equipment thermal equilibration time, the rate of defect annealing in relation with the equilibration time, and the error in reading the onset temperature.

Anticipated error range in determining irradiation temperature based on the conventional electrical resistivity-based passive thermometry is typically $\pm 20\text{K}$ of the actual irradiation temperature.[1] To achieve similar accuracy with this dilatometry-based thermometry technique, ramp rates smaller than $\sim 2.5 \text{ K/min.}$ are recommended. Limited yet significant improvement in accuracy may be achieved by further decreasing the ramp rate.

Reference

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HFIR IRRADIATION EXPERIMENTS – F. W. Wiffen (Oak Ridge National Laboratory)

The current status of Fusion Materials Program irradiation experiments in the HFIR reactor is tabulated.

Table - Summary of Recent, Current and Planned Fusion Materials Program Experiments in the High Flux Isotope Reactor (HFIR)

Experiment Designation	Primary Materials	Specimen Types*	Irradiation Temperature (°C)	Max Exposure (dpa)	Number of Reactor Cycles	Irradiation Period (month/year)
<i>Beryllium reflector (RB) irradiation positions</i>						
RB-15J	F82H	T, F, FT	300, 400	6	10	6/08 – 12/09
<i>Target zone capsules</i>						
JP-25	F82H	T, FT	300, 500	20	10	2/99 - 1/10
JP-26	F82H	T, FT	300,400,500	9	5	12/03-11/04
JP-27	F82H	T, FT	300, 400	21	13	12/03 - 1/08
JP-28	F82H	T, FT	300,400,500	80-?	50	1/05 – 6/13
JP-29	F82H	T, FT	300,400,500	80	50	1/05 - 6/13
<i>Target zone rabbit capsules</i>						
F8A-1	F82H	T, FT	300	50	28	2/09 – 6/13
F8A-2	“	“	“	“	“	“
F8B-1	“	“	“	“	“	“
F8B-2	“	“	“	“	“	“
<i>Target zone rabbit capsules</i>						
JCR-1	SiC/SiC	Bend bars	800	30	15	10/04 – 1/09
JCR-2	“	“	“	“	“	“
JCR-3	“	“	“	“	“	“
JCR-4	“	“	“	“	“	“
JCR-5	“	“	“	>50	>25	10/04 - ??
JCR-6	“	“	“	“	“	“
JCR-7	“	“	“	“	“	“
JCR-8	“	“	“	“	“	“
JCR-9	“	“	500	30	15	10/04 – 1/09
JCR-10	“	“	“	“	“	“
JCR-11	“	“	“	“	“	“
JCR-12	“	“	“	“	“	“

*T = Tensile, F = Fatigue, FT = Fracture Toughness. Most experiments also contain TEM disks, other special purpose specimens, and monitors occupying a small portion of the available volume.