DOE-ER-0313/68 Distribution Categories UC-423, -424

# FUSION MATERIALS SEMIANNUAL PROGRESS REPORT FOR THE PERIOD ENDING

June 30, 2020

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

DATE PUBLISHED: August 2020

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

## FOREWORD

This is the sixty-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, 2020. This report focuses on research addressing the effects on materials properties and performance of exposure to the neutronic, thermal and chemical environments anticipated in the chambers of fusion experiments and energy systems. This research is a major element of the national effort to establish the materials knowledge base for an economically and environmentally attractive fusion energy source. Research activities on issues related to the interaction of materials with plasmas are reported separately.

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

This report has been compiled by Stephanie Melton, Oak Ridge National Laboratory. Her efforts, and the efforts of the many persons who made technical contributions, are gratefully acknowledged.

Daniel Clark Research Division Office of Fusion Energy Sciences

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FERRITIC/MARTENSITIC STEEL DEVELOPMENT 1.

**1.1 SURVEY OF CASTABLE NANOSTRUCTURED ALLOYS FOR THEIR FURTHER DEVELOPMENT**—L. Tan, T. Graening, X. Hu, W. Zhong, Y. Yang, Y. Katoh (Oak Ridge National Laboratory)

# OBJECTIVE

To understand the radiology of castable nanostructured alloys (CNAs) as reduced-activation ferriticmartensitic (RAFM) steels and the advantages of the two types of CNAs, from which to advance further development of CNAs as the US-RAFM steel.

### SUMMARY

Either carbide- or carbonitride-strengthened CNAs were developed and examined in recent nearly five years. Systematical comparisons in different aspects for the two types of CNAs are important for the further development of CNAs. Radiological analysis indicated that the increased N in the carbonitride-CNAs leads to higher activity at ≥ 50 years, and thus to the disposal concern under the current NRC regulation. However, the calculation using the Fetter's evaluation leads to reduced waste disposal rating (WDR) of down to 0.25 depending on the damage dose from ~0.05 wt% N, and thus less concern on the waste disposal. The other increased elements, such as V, Si, Ti, and Mn, in CNAs do not have significant effect on the specific activity, contact dose rate, or decay heat. By comparing the seven-aspect performance in precipitates, yield strength, creep resistance, Charpy impact toughness, He management, deuterium retention, and phase transmutation resistance, carbide-CNAs showed some advantages over the carbonitride-CNAs in terms of the uniformly distributed higher density of carbide nanoprecipitates, greater Charpy impact upper shelf energies, less deuterium retention and swelling, and potentially less transmutation-induced composition changes and consequently thermodynamically more stable carbides. The carbide-CNAs showed the best-balanced high performance, in contrast to the significantly varied performance of oxide-dispersion-strengthened (ODS) alloys and the generally lower performance of current RAFM steels.

### PROGRESS AND STATUS

### Introduction

Carbonitride is a common type of MX used in the current RAFM steels such as Eurofer97 and F82H. Other than carbonitride, carbide MX is also used in CNAs to study their effects on microstructures and properties.

### **Experimental Procedure**

Comprehensive microstructural characterization and a variety of tests such as tensile, Charpy impact, creep, deuterium implantation and desorption, and He implantation, together with transmutation calculations, were conducted.

### Results

Here are two examples of the survey results. Figure 1 shows the radiological analysis result of the carbonitride-CNA (CNA1) and carbide-CNA (CNA3), compared with Eurofer97-2 and F82H-BA12. It indicates the comparable contact dose rates among the alloys, suitable for different waste recycling methods with different cooling times. The carbide-CNA tends to have slightly lower contact dose rates.



**Figure 1.** Contact dose rate of Eurofer 97-2, F82H-BA12, CNA1, and CNA3 after a five-year DEMO reactor service of the damage dose of 55 dpa (solid symbols) and 200 dpa (open symbols). [*After W. Zhong, L. Tan, Radiological analysis and transmutation calculation of representative castable nanostructured alloys, Fusion Engineering and Design 160 (2020) 111899.*]

Following the developed scoring method, the seven-aspect performance comparison of the carbide- and carbonitride-CNAs with Eurofer97/F82H, and ODS 14YWT is presented in Figure 2. The seven-aspect evaluates precipitate density and dispersion, yield strength at 600°C, creep Larson-Miller parameter at 100 MPa, Charpy impact toughness, He-induced swelling, deuterium retention, and phase transmutation under neutron irradiation. Unlike the first four aspects having the larger values for higher scores, the later three aspects favor lower values for higher scores. Figure 2 indicates the best-balanced performance of carbide-CNAs compared with the mostly varied performance of ODS 14YWT and the generally lower performance of Eurofer97/F82H. The systematic survey suggests carbide-CNAs as the further developmental direction.



**Figure 2.** Seven-aspect performance comparison of carbide- and carbonitride-CNAs with Eurofer 97 (E97), F28H, and ODS 14YWT. [*After L. Tan, T. Graening, X. Hu, W. Zhong, Y. Yang, S.J. Zinkle, Y. Katoh, Effects of carbonitrides and carbides on microstructure and properties of castable nanostructured alloys, Journal of Nuclear Materials 540 (2020) 152376.*]

1.2 PERFORMANCE IMPROVEMENT OF MODIFIED 3Cr BAINITIC STEEL WELDMENTS-Y. Yamamoto (Oak Ridge National Laboratory)

## OBJECTIVE

This work aims to develop new bainitic steels, based on 3Cr-3WV(Ta) steels originally developed at ORNL. The goal is mechanical properties of both base metal and weldments superior to those of existing commercial bainitic steels or ferritic-martensitic (F-M) steels, together with no requirement for post-weld heat treatment (PWHT). The target applications are high-temperature structural components in fusion reactors such as helium cooled vacuum vessels operating up to 450°C and blanket support structures up to 550°C. Improvements of creep performance and room-temperature toughness are targeted via optimization of alloy composition and thermo-mechanical treatment.

### SUMMARY

Preparation of newly modified 3Cr-3WVTa base bainitic steel containing high Mn and low C contents (ID: MLC02T) was initiated, which targeted a proposed alloy design strategy to maintain high hardenability and reduce the as-normalized hardness, in order to minimize the property inhomogeneity across the weldment. Computational thermodynamics guided down selecting the alloy composition. By comparing with the original 3Cr-3WVTa steel, MLC02T showed relatively low hardness in the as-normalized condition and small variation of the hardness after applying tempering in the range of 660 to 860°C, as expected. The heat affected zone in the as-welded MLC02T showed significantly less change in the hardness, and therefore reduced hardness inhomogeneity across the weldment compared to the original 3Cr-3WVTa steel, indicating that newly modified steel successfully achieved the targeted design strategy. Preparation of property evaluations including uni-axial creep-rupture tests and Charpy impact toughness tests of both base metal and cross-weld samples are currently in progress.

## **PROGRESS AND STATUS**

A new heat of modified 3Cr-3WVTa base steel was proposed and prepared. The heat (ID: MLC02T) contains higher Mn and lower C than the original 3Cr-3WVTa steel to expect maintaining high hardenability and reducing the as-normalized hardness, targeting a reduced property inhomogeneity across the weldment in as-welded (no PWHT) condition. The nominal compositions of the original and newly modified steels are summarized in Table 1. Note that MLC02T heat contains less Si content than previously evaluated MLSC2 heat (0.16 wt.% vs. 0.5 wt. %), in order to avoid temper-embrittlement due to high Si content.

Name	Alloy composition, wt.%	*A1,°C	*A3,°C	Remarks
Original	3Cr-3W-0.2V-0.16Si-0.4Mn-0.1Ta-0.1C	790.6	899.7	Reference
MLC02T	3Cr-3W-0.2V-0.16Si-2.0Mn-0.1Ta-0.05C	737.7	854.9	New heat
MSLC2	3Cr-3W-0.2V-0.50Si-2.0Mn-0.1Ta-0.05C	745.1	873.8	Previously evaluated

Table 1. Nominal and analyzed compositions of the steels

\*calculated by JMatPro v.9

The modified alloy composition was selected with a guidance from thermodynamic calculation. The calculated phase equilibria and transformation kinetics of the original 3Cr-3WVTa and MLC02T are shown in Figure 1. There are two major changes by alloy modification;

(1) the phase transformation temperatures (A1 and A3) are ~50°C lower than the original steel, and

(2) the amounts of M<sub>6</sub>C and M<sub>23</sub>C<sub>6</sub> in the target operation temperature range (450-550°C) reduce significantly but Laves-Fe<sub>2</sub>W appears instead.

The former would result in lowering the bainitic transformation start temperature and therefore increase the hardenability. It should be noted that less Si content compared to MSLC2 also lowered the transformation temperature, as summarized in Table 1, which would positively affect to increase the hardenability compared to MSLC2 as well. The latter indicates that less amount of the strengthening carbides in MLC02T could be compensated by the formation of Laves phase as a substituting strengthening second-phase. The high Mn addition also resulted in retarding the formation of ferrite and pearlite in the continuous cooling transformation (CCT) diagrams, even with the low C content in MLC02T, which also positively worked to extend the range of the cooling rate for full bainitic transformation.



**Figure 1**. Phase equilibria (a, b) and CCT diagrams (c, d) calculated by JMatPro v.9; (a, c) original 3Cr-3WVTa, and (b, d) MLC02T.

The hardness of normalized-and-tempered MLC02T showed relatively small variation with respect to the tempering temperature, compared to the original 3Cr-3WVTa steel (Figure 2). As-normalized hardness was ~300HV which was lower than the original 3Cr-3WVTa (~340HV), as expected. After applying isothermal tempering for 1h, the hardness decreased with increasing the tempering temperature up to 780°C, and then increased above that. The original 3Cr-3WVTa steel showed similar dependence, although the hardness variation in MLC02T was nearly a half of the original 3Cr-3WVTa steel. Because of low C content in MLC02T, the effect of C solid solution as well as less carbide formation could be the source of less hardness variation. The results indicate that MLC02T would be more stable to the heat exposure than the original 3Cr-3WVTa steel. The "as-normalized" and "tempered" conditions could be like the "weld metal" and the "heat affected zone (HAZ)" in the as-welded materials, respectively, in terms of microstructure evolution. Therefore, a

small hardness variation across the weldment would also be expected in the modified steel compared to the original 3Cr-3WVTa steel.



**Figure 2**. Vickers hardness of normalized-and-tempered original 3Cr-3WVTa and MLC02T plotted as a function of tempering temperature.

Previous study indicated that the cross-weld specimens of as-welded samples always creep-ruptured at HAZ which was the base metal adjacent to the molten metal and exposed very high temperature during welding process. Therefore, the current study focuses on the microstructure and the hardness at HAZ in the as-welded samples. Figure 3 illustrates the cross-sectional microstructure of the gas tungsten arc welded (as-GTAW) original 3Cr-3WVTa steel and MCL02T. The base plates were both normalized at 1100°C for 30min, and then tempered at 700°C for 1h. The average hardness was ~250HV for both plates, slightly lower than the values obtained from the small samples used in Figure 2, presumably due to slower cooling rate of the large plate samples after tempering. Note that the weld filler metal was made of the original 3Cr-3WVTa steel for both weldments. The HAZ area consists of very fine grains compared to the base metal, since the area was heated above A1 during welding and subjected to phase-transformation to partially or fully austenite region.

The 2D color contour maps on the cross-weld microstructure represent the hardness distribution on the same regions. Note that the hardness data inside the weldment was eliminated because it is out of interest in the present discussion. The HAZ in the original 3Cr-3WVTa steel showed locally high hardness, corresponding to "coarse grain HAZ" which was fully transformed to austenite during heating and therefore very similar to "normalized" condition. On the other hand, the hardness of the "coarse grain HAZ" area in MLC02T was not so high, as expected. The results indicated that the alloy design of MLC02T to reduce the cross-weld property inhomogeneity was successfully achieved.

# FUTURE PLANS

To evaluate the property improvement of the modified steel "MLC02T", uni-axial creep-rupture tests and Charpy impact toughness tests of both base metal and cross-weld samples will be conducted. The specimen machining has been completed in June 2020, and short-term creep-rupture tests targeting up to  $\sim$ 2,000h life will be initiated in July 2020. The results will be compared with the original 3Cr-3WVTa steel.



**Figure 3**. Cross-sectional micrograph montages across the weldment, together with 2D color contour maps illustrating the hardness distribution inside the heat affected zone (HAZ) and the base metal, in the as-GTAW bainitic steels (with a filler metal made of original 3Cr-3WVTa); (a) original 3Cr-3WVTa, and (b) MLC02T.

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**1.3 DISLOCATION LOOP EVOLUTION OF IN-SITU DUAL ION IRRADIATED Fe AND Fe-10Cr ALLOY**—Yan-Ru Lin, Steven John Zinkle (University of Tennessee), Wei-Ying Chen (Argonne National Laboratory)

# OBJECTIVE

The objective of this task is to study the dose dependence of the irradiation-induced dislocation loop and cavity evolution at fusion reactor-relevant He/dpa conditions for high purity Fe and Fe-10%Cr using simultaneous dual ion beams (heavy ion plus implanted He). Although the dislocation loops in neutron and ion irradiated bulk Fe-Cr material have been widely studied since the early 1960s[1], relatively few studies have employed in-situ TEM facility (high-voltage electron and ion irradiation) to dynamically investigate the formation and growth of dislocation loops in Fe-Cr thin foils. In addition, dynamic observations of the loops are valuable for understanding the mechanisms responsible for the formation and evolution of <100> loops and  $\frac{1}{2}$ <111> loops in bcc Fe that have intrigued researchers for decades [2].

## SUMMARY

The dose dependence of the irradiation-induced dislocation loop and cavity evolution was examined up to 20 dpa in high purity Fe and Fe-10%Cr during simultaneous dual beam (Kr ion plus implanted He) in-situ irradiation at 435°C. The He production rate was approximately 10 appm/dpa. The dynamic evolution of black dot loops, loop coarsening, loop strings, loop decoration, dislocation networks, and cavities were studied. During ion irradiation at 435°C, the interaction and coalescence of  $\frac{1}{2}$ <111> loops were more prominent than <100> loops. With increasing dose,  $\frac{1}{2}$ <111> loops became the dominant type of loop. It is notable that different microstructure features were observed near grain boundaries. In addition, the dislocation pinning process was only found in the Fe-10Cr foil.

# PROGRESS AND STATUS

We have completed preliminary characterization of in-situ dual beam (1 MeV Kr and 12 KeV He) irradiation of high purity Fe and Fe-10Cr applying the IVEM facility at Argonne National Laboratory [3]. Figure 1 shows the microstructural evolution of simultaneous dual beam ion irradiated Fe thin foil at 435°C with displacement damage up to 20 dpa. The corresponding dpa value and accumulated irradiation time are indicated in the upper right corner of each TEM bright-field image. The 0 dpa (unirradiated) and 0.5 dpa images were taken in a relatively thin area (<50nm). Images of 1 dpa to 20 dpa were taken in the same area with an average thickness of 78 nm. Small black dot dislocation loops (~2 nm in diameter) first appeared at dose of about 0.02 dpa (29 seconds). During the irradiation, the formation of loops with elliptical and edge-on projections could be observed. The loop size increased with increasing dose and irradiation time. Based on the crystal structure of Fe and diffraction contrast of loops (g b criteria) [4], the visible projected dislocation loop excited by g001 near the [100] zone axis should follow the map as shown in Figure 1 (top-left corner). For this imaging condition, 1/2[111] and 1/2[-111] loops would be elliptical loops, while [001] and [010] loops are edge-on loops. At 0 to 3 dpa, most of the loops were homogeneously distributed. Below 1 dpa, loop decoration was observed around a primitive dislocation. From 0.5-3dpa, a small amount of loop strings was observed lined up mostly along the <100> direction. Above 3dpa, the dislocation loops grow via merging of other loops and gradually develop into island-shaped loops (5, 8.5, and 10 dpa) and dislocation networks (15 and 20 dpa). The loop decoration phenomenon was not obvious at doses between 3-8.5 dpa. However, at 8.5-10 dpa, the dislocation decoration phenomenon appeared where coarse finger-shaped loops were adorned with black dot loops. It is worth to notice that different microstructure features were observed near grain boundaries. As shown in the 3 dpa TEM image in Figure 1, a defect denuded zone with a width of ~300nm was present next to the grain boundary. Within the denuded zone, only [001] and [010] loops were observed. Several <100> edge-on loops (some could be

primitive dislocations) were observed at doses of 3 dpa to 8.5 dpa under TEM images. The <100> loop population dramatically increased at 10 dpa and evolved into ladder-shaped dislocation networks.



**Figure 1.** Sequence of snapshots showing the dynamic evolution of dislocation loops and dislocation network in dual beam (Kr+He) irradiated Fe foil. All are bright-field images taken with g=011 near the [100] zone axis. (The g vector was slightly deviated during the irradiation.)

The dynamic observation of defects in irradiated Fe-10Cr is shown in Figure 2 for the same [100] zone axis and a similar diffraction contrast condition as in Fe (Figure 1). The 0-1dpa images were taken at a foil thickness of ~58nm, and the 3-10dpa images were taken at areas with thickness of ~84nm. The 15-20dpa image was taken at a relatively thicker regime (~101nm). Like the case in irradiated pure Fe, the black-dot defects appeared at ~0.02dpa (31 seconds). Even at low dose with a low population of defects, the black dot loops in Fe-10Cr were mostly immobile and could only move to another adjacent black dot. The maximum migration distance of black dot loops in Fe-10Cr at 1dpa was ~ 30nm, which is roughly 5 times smaller than in pure Fe. Even though black-dot loops, loop strings, elliptical loops, and dislocation networks were observed in both pure Fe and Fe-10Cr foil, the microstructural evolution in Fe-10Cr took much more time (dose) than in Fe. The elliptical loops started to show up at ~1dpa (20 minutes) for Fe, whereas only a small proportion of elliptical loops were found in Fe-10Cr even for doses above ~5dpa (90 minutes). The Fe-10Cr loop size grew with increasing dose (time), but the average size was smaller compared to Fe at all corresponding doses. In addition, the population of <001> loop strings were much higher in Fe-10Cr than in Fe. For the elliptical loop to dislocation network transformation, the transition happened at around 5dpa (1.5 hours) and 10dpa (3 hours) for Fe and Fe-10Cr, respectively. It is worth to notice that, at 5-8.5dpa, the pinning of dislocations by the irradiation induced loops was observed in Fe-10Cr but not in Fe. In addition, unlike the heterogeneous microstructural features in Fe, the defects in Fe-10Cr had no significant difference between the near-grain boundary area and the in-grain area. The <100> edge-on loops were not found near the Fe-10Cr grain boundaries.



**Figure 2.** Sequence of snapshots showing the dynamic evolution of dislocation loops and dislocation network in dual beam (Kr+He) irradiated Fe-10Cr foil. All are bright-filed images taken with g=011 near the [100] zone axis. (The g vector was slightly deviated during the irradiation.)

Cavities were also observed in the Fe and Fe-10Cr foils in under-focused TEM images (Figure 3). While cavities were observed in Fe at ~10dpa, the white contrast cavities were observed in Fe-10Cr only for doses approaching 20dpa. In addition, cavities in Fe were found in both the near-grain boundary area (even gathered in the grain boundary) and in-grain area. However, for the Fe-10Cr foil, cavities were observed only at the in-grain area. At 20dpa, the average radius of cavities in Fe was larger than those in Fe-10Cr. The cavity density, in contrast, was lower in the pure Fe foil.



**Figure 3.** Cavities observed at 435°C with dose of 20dpa in dual beam irradiated (a) Fe and (b) Fe-10Cr foils.

# FUTURE PLANS

In order to further discuss the mechanisms responsible for the presence and competition of <100> loops and  $\frac{1}{2}$ <111> loops, the evolution of the loop size and density, relative fraction of  $\frac{1}{2}$ <111> vs <100> loops, and size and density evolution of cavities are planned to be quantitatively summarized.

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**1.4 EFFECT OF Cr ON DISLOCATION LOOPS IN HEAVY ION IRRADIATED ULTRA-HIGH PURITY Fe-Cr ALLOYS**—Yao Li, Steven John Zinkle (University of Tennessee), Ling Wang, Arunodaya Bhattacharya (Oak Ridge National Laboratory)

## OBJECTIVE

The objective of this task is to study the effect of Cr additions on dislocation loop size, density and type in high-purity Fe and Fe-Cr model alloys after heavy ion irradiation at different temperatures.

### SUMMARY

Transmission electron microscopy (TEM) was used to characterize the size, density, and type of loops after 8 MeV Fe ion irradiation to 0.35 dpa at 350 and 450 °C in high-purity Fe and Fe-Cr alloys. By using detailed Burgers vector analysis g·b method, we are examining the effect of temperature and Cr concentration on the formation of dislocation loops under conditions where surface effects and implanted ion effects are minimal.

#### PROGRESS AND STATUS

Dislocation loops were examined in ultra-high purity (UHP) iron and several Fe-Cr alloys containing 3,5,8, and 12 wt% of Cr after irradiation by 8MeV Fe ions to midrange doses of 0.35 dpa at 350°C and 450 °C. Analysis was done in the midrange of irradiated region (700-1200nm deep, named safe analysis region in following text). Damage and ion distribution profiles vs depth are shown in Figure 1. In the SRIM calculations, ion distribution and quick calculation of damage method (K-P model) was applied and displacement energy was set as 40 eV. Table 1 summarizes the irradiation conditions examined in this study.



Figure 1. SRIM calculation of 8MeV Fe ions in Fe-Cr alloy (K-P model).

	Fe	Fe-3Cr	Fe-5Cr	Fe-8Cr	Fe-12Cr
350°C 0.35 dpa 10 <sup>-4</sup> dpa/s	$\checkmark$	$\checkmark$	$\checkmark$	-	-
450°C 0.35 dpa 10⁻⁵ dpa/s	-	-	$\checkmark$	$\checkmark$	$\checkmark$

 Table 1. Alloys and irradiation conditions

 $\sqrt{2}$ : samples have been characterized and presented in this report.

-: samples have not been characterized yet.

As one of the most precise nano-fabrication tools at present, focused ion beam (FIB) is a popular technique for TEM sample preparation. However, the FIB sputtering process is essentially low energy ion irradiation and therefore can introduce displacement damage artifacts near the sample surfaces. Dense FIB damage may mask real irradiation damage and interfere with quantitative analysis. Flash polishing technique is designed to remove FIB-damage near-surface by electropolishing for millisecond time frames. The key flash polishing steps are: Immerse thick (>100 nm) FIB lamellae into electrolyte. Apply a pulsed voltage for a prescribed time, removing FIB damage and thinning lamellae down to suitable thickness for TEM. Rinse polished lamellae in ethanol. The general features of heavy ion damage are visible in Figure 2a but are not very clear due to dense FIB damage. Also, beyond the irradiated region, FIB damage contrast is still visible. In Figure 2b, an ion-irradiated Fe-3Cr (350 °C, 0.35 dpa, and 10<sup>-4</sup> dpa/s) lamella was prepared by flash polishing. It is totally FIB damage free. This is an important step for our case. Based on the analysis, the average size of loops in 3Cr lamella was 9 nm in diameter. The size of black spots by FIB are ~10 nm in diameter. If the black spot damage due to FIB damage occurred in the 3Cr lamella, the measured size distribution and density could change, leading to inaccurate results.



**Figure 2.** TEM images of ion irradiated Fe-3Cr lamellae at 350 °C, 0.35 dpa, and 10-4 dpa/s (a) by FIB only and (b) after flash polishing.

# Irradiation-induced Microstructure After 0.35 dpa Midrange Dose

All the remaining samples discussed in this report were prepared by flash polishing method. The electrolyte was 70% perchloric acid (4 ml) mixed with ethanol (96 ml). Polishing temperature was -50 °C. Voltage increased from 12 to 20 V with increasing Cr concentration. Polishing time was ~60 minutes. The first ethanol rinse was at -30 °C, and the second and third rinse were at room temperature. Each rinse was for 2 mins. Based on TEM analysis, dislocation loops were the only defects observed in the ion irradiated Fe-

Cr alloys at 350°C and 450°C. Petal shaped loop clusters were observed in Fe-5Cr, Fe-8Cr and Fe-12Cr samples irradiated at 450 °C, while distributed loops in the matrix and loop decoration along preexisting dislocation lines were observed in samples irradiated at 350 °C.

## Loop Microstructure at 350°C (10<sup>-4</sup> dpa/s)

Isolated dislocation loops rarely appeared in the matrix of the UHP Fe irradiated at 350°C, 0.35 dpa. Most visible loops were in the vicinity of preexisting dislocations. Loop diameter in UHP Fe was up to ~60 nm. Nanosized voids were observed and their average diameter was 4 nm, as shown in Figure 3.



**Figure 3.** (a)under-focus and (b)over-focus micrograph of nanosized voids in UHP Fe. (c) Loop distribution in UHP Fe. (d) large loops near dislocation line. Irradiation was at 350 °C, 0.35 dpa 10<sup>-4</sup> dpa/s.

Dislocation decoration also appeared in irradiated Fe-3Cr. In contrast with UHP Fe, loops were also distributed in the matrix in Fe-Cr alloys. No void was observed in the Fe-Cr alloys for the examined low dose irradiation conditions at 350 and 450°C. Five different reflection vectors were applied for g·b analysis. Among identified loops in Fe-3Cr (350 °C, 0.35 dpa), 51 were  $a_0 < 100 >$  type and 14 were 1/2 $a_0 < 111 >$ . Average loop diameter was 9 nm. Volumetric number density was  $1.75 \times 10^{21}$  m<sup>-3</sup>. As shown in the inset images of Figure 4, in Fe-3Cr some loops were arranged in two-loop rafting, two loops aligning in a row.

are the invisible conditions for different loops.						
	diffraction vector (g)					
	[(	[011] zone axis			[001] zone axis	
Burgers vector (b)	200	2 -1 1	0 -1 1	-1 1 0	-1-1 0	
111	2	2	0	0	-2	
1 1-1	2	0	-2	0	-2	
1-1 1	2	4	2	-2	0	
-11 1	-2	-2	0	2	0	
100	2	2	0	-1	-1	
010	0	-1	-1	1	-1	
0 0 1	0	1	1	0	0	

**Table 2.** Applied g vectors for loop identification in body centered cubic (BCC) Fe-Cr system. Red cells are the invisible conditions for different loops.

June 30, 2020

001Z g=1-10

# 001Z g=110

011Z g=200



**Figure 4.** Fe-3Cr at 350 °C, 0.35 dpa 10<sup>-4</sup> dpa/s. Five loops are marked by circles. In (a) and (b), all of them are visible, marked by solid circles while in (c) loop C and D are invisible. Circle A holds two loops aligned together. The inset images are loops in circle A in higher magnification.

The general features in ion irradiated Fe-5Cr were quite like those in Fe-3Cr. As shown in Figure 5, only three loops were visible in matrix and several loops decorated the preexisting dislocation. Two-loop rafting was barely observed in Fe-5Cr sample. Three preexisting dislocations are shown in Figure 6. The middle one is free of decoration. Based on conventional g·b analysis and vector projection analysis, its Burgers vector and line sense were  $1/2a_0[11-1]$ , i.e. pure screw dislocation. For the other two preexisting dislocations, the left one was identified as  $1/2a_0[111]$  type. Its line sense was neither parallel nor perpendicular to [200] in the upper image of Figure 6. It was identified as mixed dislocation. The dislocation on the right was  $1/2a_0[1-11]$  type. Its line sense was identified as  $1/2a_0[1-11]$  type. Its line sense was a mixed dislocation. Among identified loops in Fe-5Cr at 350 °C, 0.35 dpa, 93 were  $a_0 < 100 >$  type and 17 were  $1/2a_0 < 111 >$  type. The average loop diameter was ~9nm. Volumetric number density was  $1.6 \times 10^{20}$  m<sup>-3</sup>.







**Figure 6.** Micrograph of Fe5Cr at 350 °C, 0.35 dpa, and  $10^{-4}$  dpa/s. The same region under (upper) 200g [011] Z; (middle) -110g [001] Z; and (lower) 110g [001] Z. The projection of [11-1] vector under [001] Z and [011] Z is perpendicular to [2-11] vector and along [110] vector, respectively. The line sense is parallel to its own Burgers vector, so the middle dislocation was identified as pure screw.

Volumetric number density versus Cr concentration for Fe-3Cr and Fe-5Cr (350 °C, 0.35 dpa) is shown in Figure 7. The volumetric number density decreased by roughly one order of magnitude from Fe-3Cr to Fe-5Cr. Loops not decorating preexisting dislocation lines were used for the loop density calculation. The homogeneous loop distribution in Fe-3Cr vs heterogenous loop distribution in Fe-5Cr in our study are similar to the distributions created by neutron irradiations at 300 °C.<sup>[1]</sup> Thickness was measured by electron energy

loss spectrometry (EELS) with log-ratio method (20% uncertainty for thickness measurement).<sup>[2]</sup> The total mean free path of inelastic scattering of iron for 200 keV electrons was taken from lakoubovskii.<sup>[3]</sup>

The  $1/2a_0 < 111 > loop and a_0 < 100 > loop fraction against Cr concentration for Fe-3Cr and Fe-5Cr (350 °C, 0.35 dpa) is shown in Figure 8. The a_0 < 100 > type loops were dominant in both Fe-3Cr and Fe-5Cr (350 °C, 0.35 dpa), with no statistical difference in the loop fraction for these two alloys. The comprehensive trend of <math>1/2a_0 < 111 > loop$  vs Cr concentration is not fully clear yet. Data from UHP Fe and Fe-8Cr samples at this irradiation condition will be updated in the future to determine the overall trend.

The loop size distributions in Fe-3Cr and Fe-5Cr irradiated at 350 °C are shown in Figure 9. Features smaller than 3 nm were not counted since it is possible that they were contamination artifacts. The projections of loops for the selected imaging zone axes were round or elliptical, so all the measurements were performed along the major axes of loop images. The average diameter of loops in both alloys was 9 nm, in contrast to the order of magnitude variation in loop density for the two alloys (Figure 7). Compared with loops in Fe-3Cr, loops in Fe-5Cr had a slightly narrower size distribution.



**Figure 7.** Volumetric number density vs Cr concentration at 350°C 0.35 dpa and 10<sup>-4</sup> dpa/s. Thickness was measured by EELS method. The error bars were mainly due to uncertainties in the EELS measurement of foil thickness.



**Figure 8.** Loop fraction vs Cr concentration at 350°C 0.35 dpa and 10<sup>-4</sup> dpa/s. Error bars are about 95% confidence interval.





# Loop Microstructure at 450°C (10<sup>-5</sup> dpa/s)

Among several types of radiation-induced defect structures in materials, dislocation rafting is a relatively common phenomenon in BCC system<sup>[4-6]</sup>. It refers to several dislocation loops aligning in a row and has been observed in previous ion and neutron irradiation studies. On the other hand, following electron and neutron irradiation experiments at elevated temperatures on different materials, scientists have also reported more complicated 2-D loop clusters in several materials, known as petal-shaped loop clusters.<sup>17-11</sup> It is assumed that these loop clusters only occur under a specific combination of experimental conditions. To our knowledge, the current observation of petal-shape loop cluster is the first observation in an ion irradiation experiment.

As shown in Figure 10, in Fe-5Cr irradiated at 450°C, 0.35 dpa, two categories of features were visible during imaging along low-index zone axes: long black lines and petal-like clusters. By full g·b analysis, these features were identified as edge-on and inclined (or plan view) dislocation loop clusters with predominantly one type of Burgers vector. The structure of outlined edge-on loops in Figure 10b are shown in Figure 10a and Figure 10c, respectively. On average, the diameter of the loop cluster was 220 nm and each cluster contained 34 loops in Fe-5Cr sample. In the Fe-8Cr sample, on average, the loop cluster

diameter was 240 nm and each cluster contained 26 loops. Only one loop cluster in 5Cr sample was identified as a  $1/2a_0 < 111$  loop while 37 were  $a_0 < 100$  type. In the Fe-8Cr sample, no  $1/2a_0 < 111$  type loop cluster was observed.



**Figure 10.** On zone STEM-BF: the same region viewed under (a) [011] Z, (b) [001] Z, and (c) [101] regions show different perspectives of the same loop cluster. (d) Kikuchi map of body centered cu structure. Fe-5Cr 450°C, 0.35dpa, and  $10^{-5}$  dpa/s.

The loop microstructure of Fe-12Cr irradiated at 450°C, 0.35 dpa is show in Figure 11 for imaging conditions near [001] Z. Under this zone axis,  $a_0 < 100 >$  type loops are either edge-on or invisible. It can be seen in Figure 11a that most of the loops are  $a_0 < 100 >$  type. A few loop clusters shown In Figure 11b are open-structure, indicating they are  $1/2a_0 < 111 >$  type. Most of the dislocation loops in Figure 11b are associated with a preexisting dislocation. Considering that  $1/2a_0 < 111 >$  is the only energetically favorable Burgers vector of dislocations in BCC system without irradiation effect, it is likely that the nucleation of  $1/2a_0 < 111 >$  petal shaped loop cluster is directly related to preexisting dislocation line, as shown in Figure 11.



**Figure 11.** STEM-BF micrograph of Fe12Cr at 450°C, 0.35dpa, and 10<sup>-5</sup> dpa/s: (a)low magnification of irradiated region under [001] Z;(b) high magnification of marked region in (a).

The length of the major axis of the loop cluster was defined as the diameter for size measurements. Since the petal shaped loop clusters were huge, some clusters were partially destroyed in sample preparation, as shown in the yellow box in Figure 10. In order to make measurement accurate, only intact or slightly damaged clusters whose major axes were distinguishable were measured for data shown in Figure 12. Compared with the cluster distribution in Fe-5Cr, the distribution in Fe-8Cr was narrower while the average cluster sizes were similar in the two alloys. Due to all loops in a single cluster sharing the same Burgers vector, cluster completeness was not a concern for Burgers vector analysis. 37 and 35 loop clusters were identified in safe analysis region in Fe-5Cr and Fe-8Cr ( $450^{\circ}$ C, 0.35 dpa), respectively. All clusters not linked to preexisting dislocations were  $a_0 < 100 >$  type, as shown in Figure 13.



Figure 12. Fe-Cr loop cluster distributions. Irradiation was at 450°C, 0.35dpa, and 10<sup>-5</sup> dpa/s.



**Figure 13.** The fraction of <100> type loop cluster in matrix (clusters not linked to preexisting dislocations). Irradiation was at  $450^{\circ}$ C, 0.35dpa, and  $10^{-5}$  dpa/s.

## Discussion

In most published papers, authors have assumed, without any loop nature determination, that all the loops in Fe-Cr system created by energetic (>1 MeV) ion irradiation are interstitial type. This may not be true for all irradiations. Jenkins reported vacancy type loops were created by 40 to 240 keV ion irradiation,<sup>[12]</sup> indicating that vacancy loop formation is possible under some conditions. This has traditionally been attributed to the shallow depth of these low energy ion irradiations, which could favor preferential loss of interstitials to the nearby surface, thereby producing a supersaturation of vacancies. For higher energy (2 MeV) self-ion irradiation in a bulk sample, Haley recently reported vacancy loops in a Fe-9Cr model alloy<sup>[13]</sup>. However, due to the shallow implanted ion range, implanted ions acting as excess SIAs should suppress the nucleation and growth of vacancy clusters. Gilbert <sup>[14]</sup> conducted molecular statics simulation and showed that void is energetically favorable than vacancy loop in BCC iron. In contrast, Zinkle<sup>[15]</sup> applied elasticity theory and calculated the specific energies of vacancy cluster, indicating vacancy loop is preferable in BCC iron. For neutron experiments, different groups [16-18] reported nanosized voids in Fe at 300°C. Our observation of nanosized voids in pure iron irradiated at 350°C agrees with their results. The exact reason why vacancy loops have formed in above literatures was not fully clear vet. Calculation by Zinkle<sup>[19]</sup> indicated that coating by impurity atoms in vacancy clusters had observable impact on the specific energies of vacancy cluster. This may stabilize those reported vacancy loops and make them visible.

As shown in Figures 4, 5, and 6, loops were homogenously distributed in the matrix regions of Fe-3Cr and dislocations were decorated with a higher density of loops. In Fe-5Cr at 350°C. 0.35dpa, and 10<sup>-4</sup> dpa/s, the loop number density is quite low. On the other hand, the average size of dislocation loops in Fe-3Cr and Fe-5Cr are comparable. The dislocation loop size is weakly dependent on Cr concentration once Cr is >2%, and the increasing Cr concentration leads to higher loop number density.<sup>[20]</sup> We have observed the average loop size barely changed in Fe-Cr samples but the loop density decreased with increasing Cr concentration at 350°C, 0.35dpa, and 10<sup>-4</sup> dpa/s. The observation that higher number density of loops occurs in higher Cr alloys may fail at low damage level. Once the Cr concentration is greater than 1%, Cr atoms in Fe-Cr alloys should reduce the mobility of SIA clusters<sup>[21]</sup>. It has also been checked in atomistic simulation that the mobility of SIA clusters is reduced by Cr atoms.<sup>[22]</sup> However, the interaction between vacancy and Cr atoms is very weak, which has been proven in positron annihilation and resistivity recovery experiments.<sup>[23, 24]</sup> The glide of SIA clusters deterred by Cr atoms in Fe-Cr alloys are surrounded by enormous freely migrating vacancies. Cr deterred SIA clusters from growing and then SIA clusters acted as recombination sites for vacancies, further suppressing the growth of SIA clusters. At low damage level, more clusters remain in the sizes below the resolution of TEM with increasing Cr concentration, leading to lower number density with increasing Cr concentration in our observation.

# FUTURE PLANS

It is considered likely that petal shaped loop clusters may also be present in pure Fe and other Fe-Cr alloys. As marked in yellow box in Figure 10c, part of that petal-shaped cluster was destroyed during FIB sample

preparation. In order to measure the diameter accurately, the foil normal of future TEM samples would be close to [001], identified by EBSD before FIB session and by on-zone STEM technique to reveal all [001] loop clusters as the data points for size measurement. HRTEM will be applied to verify whether loops in the same cluster reside on several adjacent parallel atomic planes or on the same plane.

So far, the volumetric loop densities of Fe-Cr alloys at 350°C, 0.35dpa, and 10<sup>-4</sup> dpa/s were based on loops in matrix. Decorating loops were excluded for loop density calculation since the loops along dislocation lines overlapped with each other, it was difficult to perform statistical analysis of loops. Additional weak beam dark field image analysis of loops at high magnification will be performed to further quantify these loops. We may have different statistical results afterwards.

To determine the nature of loops in our samples, inside/outside contrast will be carried out. Considering the small size of loops at 350°C, we may perform inside/outside contrast using weak beam dark field techniques.

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**1.5** ATOM PROBE CHARACTERISATION OF SEGREGATION DRIVEN Cu AND Mn-Ni-Si CO-PRECIPITATION IN A NEUTRON IRRADIATED 9Cr TEMPERED-MARTENSITIC STEEL—T. P. Davis, M. P. Moody, D. E. J. Armstrong (Oxford University), N. Almirall, G. R. Odette (University of California, Santa Barbara)

# **OBJECTIVE:**

The objective of this work was to characterize the Cu-Ni-Mn-Si precipitates that lead to significant irradiation hardening in 9Cr tempered martensitic steels.

## SUMMARY

Reduced activation 9Cr tempered-martensitic steels (TMS) are leading candidate structural alloys for fusion power reactors. At low temperatures (300 to 400°C) fission neutron irradiation hardens and embrittles these steels. In this study, a T91 steel was separately neutron irradiated to 2.14 dpa at 327°C and 8.82 dpa at 377°C in the Idaho National Laboratory Advanced Test Reactor. Atom probe tomography was used to investigate the segregation driven formation of Mn-Ni-Si-rich (MNSPs) and Cu-rich (CRP) co-precipitates. The precipitates increase in size and, slightly, in volume fraction at the higher irradiation temperature and dose, while their corresponding compositions were very similar, falling near the Si(Mn,Ni) field in the Mn-Ni-Si projection of the Fe-based quaternary phase diagram. While the structure of the precipitates has not been characterized, this composition range is distinctly different than that of the typically cited G-phase. The precipitates are composed of CRPs with MNSP appendages. Such features are often observed in neutron irradiated reactor pressure vessel (RPV) steels. However, the Si, Ni, Mn, P and Cu solutes concentrations are lower in the 9Cr TMS like T91 than in typical RPV steels. Thus, in T91 precipitation primarily takes place in solute segregated regions of line and loop dislocations. These results are consistent with the model for radiation induced segregation driven precipitation of MNSPs proposed by Ke et al. Cr-rich alpha prime ( $\alpha$ ') phase formation was not observed.

# PROGRESS AND STATUS

# Background

Note this report is an edited version of a paper that has been submitted for journal publication. It is another product of a longstanding collaboration between UCSB and Oxford Materials. As part of his PhD dissertation, the lead author Tom Davis carried out the APT measurements with the assistance of Oxford co-workers and UCSB. UCSB conducted the ATR-1 irradiation. The analysis and interpretation of the data involved an intense joint effort between Oxford and UCSB.

Neutron irradiation drives microstructural and microchemical evolutions in TMS, like T91, which have detrimental effects on the mechanical properties, thus limiting the lifetime and performance of reactor structural components. Reported microstructural features that result from neutron irradiation of 9-12 wt% Cr tempered-martensitic alloys, such as T91, HT9 and Eurofer97, include the Mn Ni Si precipitates (MNSPs) [13–20] (often described as 'G-phase' – Mn<sub>6</sub>Ni<sub>16</sub>Si<sub>7</sub> [21]), Cr-rich alpha prime ( $\alpha$ ') precipitates [14,17,22–24], voids, dislocation loops, evolved network dislocations, and solute segregation to, and precipitation at, dislocations [19,25–27]. These microstructural changes are due to the excess radiation defect generation and clustering, dislocation climb, radiation-induced segregation (RIS) and radiation enhanced diffusion (RED). These hardening features embrittle the steels, as manifested by elevations of ductile-to-brittle transition temperature, increases in yield stress, decreases in ductility and degradation of fracture toughness [5].

A number of characterization studies of the MNSPs that form during neutron irradiation of T91 steel have been reported previously [13,14,18,28–33]. MNSPs also have been observed in ion [19,30,33–35] and proton [13,36–39] irradiated T91 and HT9 steels also. In all cases, MNSPs were associated with segregation of Mn, Ni, and Si at dislocations and Cu precipitates between temperatures of ~ 270 °C to ~450°C. Jiao et al. [40] investigated MNSPs in a T91 steel neutron irradiated to 17.1 dpa and 35.1 dpa at several temperatures between 376 to 524°C in the Russian BOR60 sodium-cooled fast test

reactor. Segregation and MNSP precipitation were observed in all cases except at the highest temperature of 524°C. Impurity Cu precipitates, primarily on dislocations enhance MNSP formation in 9Cr TMS, likely be promoting nucleation [29,33,38]. Notably, the typical Mn-Ni-Si contents of these alloys are relatively low, lying either near, or below, the thermodynamic solvus boundary. Recently, a cluster dynamics model showed that solute segregation is required for heterogeneous nucleation and growth of MNSPs on dislocations in T91 steel [29].

In contrast to Jiao's results at 524°C, Adisa et al. [33] recently reported very large MNSP mole fraction (f) of  $\approx$  1.4% in T91 that was neutron irradiated at 500°C to 3 dpa. CRPs and solute segregation were also observed. However, in this case the MNSPs include Fe and Cr contents nominally found by CAMECA Integrated Visualization and Analysis Software (IVAS)<sup>®</sup>, the atom probe tomography (APT) reconstruction software, were at a very high concentration of  $\approx 89\%$ . We believe that the Fe and Cr atoms associated with the reported f are APT artefacts, and is discussed in an experimental method section of this study; further, both experimental and first principles assessment of the relevant phases indicated that the relevant MNSP phases did not contain significant amounts of these matrix solvent elements. The Adisa et al. paper also reports application of a cluster dynamics (CD) simulation, developed by H. Ke at al. [41] which was later used by J. Ke et al. (2018) [29] to model precipitation in T91 steel. Adisa et al. reported that the CD model predicts similarly (quite large) f values for G-phase precipitates, based on the trace bulk T91 solute content of Ni, Mn and Si, not accounting for segregation. However, a thermodynamic analysis provided in this study shows that, in this case at low bulk solute concentrations, the system is highly undersaturated; further the predicted Ni in the G-phase MNSPs greatly exceeds the total available in the alloy. Thus, while the results by Adisa et al. [33] presented solute precipitation of trace amounts at 500°C is a useful, our paper clarifies that this observation is also highly driven by solute segregation at dislocations, as modelled by J. Ke et al. [29].

In addition to MNSP observation in Fe-Cr based alloys, neutron irradiation embrittlement of low alloy reactor pressure vessel (RPV) steels has been the subject of extensive basic research for 40 years [42,43]. Embrittlement is caused by irradiation hardening primarily due to precipitation of supersaturated Cu impurities [44-46] and/or Mn Ni Si solute atoms [47-50]. Supersaturated Cu can form Cu-rich precipitates (CRPs) under very long-term thermal aging near RPV service temperatures [51]; however, Cu precipitation kinetics are highly accelerated by neutron irradiation due to radiation enhanced diffusion (RED) [43,47,52]. The formation of so called late blooming MnNiSi precipitates (MNSPs) was first predicted by Odette in 1996 [42]. In Cu bearing steels, MNSPs form as appendages to CRPs and slowly grow to large fractions of the steel Mn+Ni+Si alloying element contents, which are typically 2 to 3 at.% [43]. MNSPs also develop in low Cu steels, although even trace amounts of Cu are known to be potent catalysts for their formation [53]. The first experimental proof of MNSP formation in irradiated RPV steels was reported in 2004 [54]; and, since then, MNSPs have been widely observed [16,47,50,51,55–58]. Notably, CRPs and MNSPs are well predicted by thermodynamic and kinetic modelling [45,46,59]. Kinetic lattice Monte Carlo models recently showed that the co-precipitated morphology observed in APT reconstructions are the result of an interplay between interfacial energies, diffusion paths, such as through the Cu cluster, and ordering energies [46]. Both experiments and physical models show that MNSPs will dominate RPV integrity issues for life extension of light-water reactors [50,53,55]. RPV steel studies have also revealed significant solute segregation to loop and network dislocations. The segregated dislocations are a favoured nucleation sites for heterogeneous nucleation of MNSPs [43,47,50,57,58], as are cascade generated solute cluster complexes. However, apparently random homogeneous nucleation is also frequently observed in RPV steels and is predicted by models at sufficiently high solute contents (supersaturations), particularly Ni.

Thus, the objective of this study is to build on the understanding of precipitation in RPV steels and the corresponding much more limited database for Fe-Cr alloy systems, including model binary alloys and TMS 9-12%Cr steels like T91 and HT9 [5,9,19,60]. The major differences between these two alloy systems are that the solute contents of TMS are typically much lower than in RPV steels (expect Cr), while the dpa doses are much larger and the temperatures somewhat higher. The primary significance of these differences is that solute segregation to and heterogeneous nucleation on dislocations is critically important, due to the low solute content in TMS alloys. Here we focus on APT characterization of TMS T91, irradiated to 2.14 and 8.82 dpa at 327 and 377 °C, respectively. Note, such lower temperature investigations of T91 steel have practical importance because the inlet temperature of a potential liquid metal cooled reactor could be as low as 320–375 °C (the specific temperature range is

reactor design dependent) [5], thus exposing the lower cladding tubes wrapper and structural components to service conditions, associated with maximum TMS irradiation embrittlement [7].

#### **Experimental Methods**

The chemical composition of the T91 steel heat used in this study, which is given in Table 1, meets the required standard. The as-received APT compositions (at.%) are also given in Table 1 (see section 2.3 for the experimental procedure). The C is lower in the APT data, since it primarily resides in unprobed coarse carbides (expect in a later carbide dataset). The other elements are generally similar except for Ni, which is significantly higher in the APT data (due to significant Ni segregation to nanosized features, as later discussed). APT also detects trace amounts of dissolved Cu.

Element	Bulk (wt%)	Bulk (at%)	APT (at%)
С	0.07	0.32	0.02 ± 0.01
Mn	0.47	0.47	0.41 ± 0.02
Р	0.02	0.04	0.02 ± 0.01
S	0.02	0.04	-
Si	0.28	0.55	0.54 ± 0.01
Cr	9.24	9.84	8.81 ± 0.17
Мо	0.96	0.55	0.41 ± 0.09
Ni	0.16	0.15	0.39 ± 0.02
V	0.21	0.21	0.10 ± 0.01
AI	-	-	0.04 ± 0.01
Cu	-	-	0.03 ± 0.01
Co	-	-	0.01 ± 0.01
Fe	Bal.	Bal.	89.25 ± 0.34

**Table 1.** T91 Bulk Chemical and APT Composition Measurement (averaged across multiple datasets)

The neutron irradiated alloys were irradiated in the Advanced Test Reactor (ATR): a) as part of the University of California Santa Barbara (UCSB) ATR-1 experiment and are included in the Nuclear Science User Facilities (NSUF) Library irradiation [61]; and, b) as part of the University of Illinois Urbana Champagne (UIUC)) experiment [62]. Both irradiations were drop-in experiments, which did not include thermocouples to directly monitor temperatures. Rather, the temperatures were regulated by a combination of insulating helium/argon mixture gas gap and nuclear heating The temperatures were estimated based on the Abaqus thermal heat transfer and MCNP codes [63] for nuclear heating analysis and the reactor lobe power history [61]. Specimen 0020-2008-139 from the UCSB-1 library and specimen 2008-92-387 from the UIUC library, both have similar compositions and are believed to be from the same heat provided by Los Alamos National Laboratory (see composition in Table 1).

**Table 2.** Irradiation Conditions for the T91 specimens in the ATR reactor [61]

Specimen ID	Steel	Temp. (°C)	Neutron flux (n/cm²/s, E > 1Mev)	Neutron fluence (n/cm² E > 1 MeV)	Dose (dpa)
UCSB 0020-2008-139	T91	327	1.21×10 <sup>14</sup>	1.57×10 <sup>21</sup>	2.14
UIUC 2008-92-387	T91	377	2.30×10 <sup>14</sup>	~7.80×10 <sup>21</sup>	8.81

As-received T91 steel (the same steel batch as 0020-2008-139 and 2008-92-387 sample ID) was analysed using the APT technique [64]. APT analysis on the as-received T91 steel was conducted with a CAMECA LEAP® 5000XR at the Department of Materials, University of Oxford. APT specimens were prepared by the lift-out technique [65] using a Zeiss Crossbeam 540 Analytical Focused-Ion Beam (FIB)-Scanning Electron Microscope (SEM).

Polished and mounted T91 TEM discs were provided by UCSB via the Nuclear Science User Facility (NSUF) of the US Department of Energy. The post neutron irradiation examination was conducted at the Microscopy and Characterization Suite located at the Center for Advanced Energy Studies (CAES)

with the support from the NSUF. APT analysis was conducted with a CAMECA LEAP<sup>®</sup> 4000X HR. The APT specimens were prepared by the lift-out technique using a FEI Quanta 3D FEG FIB Scanning Electron Microscope (SEM). A final FIB cleaning process was performed by using 2 kV Ga ions, in order to minimise FIB-induced damage. The final milled specimen diameters were between ~50 - 100 nm.

In both cases, the APT specimens were analysed at a stage temperature of 55 K, a voltage pulse fraction of 20%, a pulse rate of 200 kHz and the average detection rate was set to 1.0 %. The detection efficiency of the LEAP® 4000X HR and LEAP® 5000 XR were 37% and 52%, respectively. CAMECA IVAS® version 3.8.4 was used to reconstruct all atom probe datasets. Calibration of the final reconstructed APT maps used SEM micrographs of the final tip shape and crystallographic pole indexing.

The search for MNSP was conducted by using both the maximum separation method [66] and the corelink method [67] with the following parameters (averaged):  $D_{MAX} = 0.85$  nm, Order = 2,  $N_{MIN} = 35$  and  $D_{erosion} = 0.425$  nm. These parameters were optimised following the method outlined by Williams, C.A. et al [68]. After the cluster search in IVAS was complete for all datasets (8 datasets with >5M ions) for 2.14 dpa and (7 datasets with >5M ions for 8.82 dpa), the sizes, number densities, compositions, and volume fractions of the precipitates were calculated, where the latter is based on the fraction of solute ions in the clusters. Partial edge clusters (defined as a cluster from the original material whose true extent is not completely contained within the reconstructed APT volume) were removed from the cluster search to avoid underestimation of the sizes. The algorithm used to detect and remove the edge clusters was developed by Jenkins et al. (2020) [58,69]. The number density of clusters, N<sub>d</sub>, was calculated by the following:

$$N_{d} = \frac{N_{ClustersDetected} - \frac{1}{2}N_{EdgeClusters}}{V_{Dataset}}$$
(1)

where  $N_{ClustersDetected}$ , is the number of clusters within the analysed reconstruction and  $N_{EdgeClusters}$  is the number of clusters at the edge of the reconstruction, and  $V_{Dataset}$  is the volume of the reconstruction dataset (in m<sup>3</sup>). The volume was determined by:

$$V_{\text{Dataset}} = \frac{N_{\text{Ranged}}\Omega}{\eta}$$
(2)

Here  $\Omega$  is taken as the volume of one Fe atom (1.178 ×10<sup>-2</sup> nm<sup>3</sup>), N<sub>Ranged</sub> is the ranged atoms within the APT dataset, and  $\eta$  is the detection efficiency of the atom probe instrument used. The volume fraction, f, of the MNSP were calculated by:

$$f = \frac{N_{\text{Ranged}}^{\text{Cluster}} - N_{\text{Fe}}^{\text{Ranged}}}{N_{\text{Total}}},$$
(3)

where  $N_{Ranged}^{Cluster}$  is the number of ranged atoms within all clusters,  $N_{Fe}^{Ranged}$  is the number of ranged Fe in all clusters and  $N_{Total}$  is the total number of ranged atoms within the dataset. The volume of each cluster was assumed to be spherical and with the atomic density of bcc-Fe.

The atom probe mass-to-charge-state spectrum must be ranged by user assigned chemical identities to each peak. With steels that have Ni and Si alloying addition, overlapping mass-to-charge-state peaks occur at 29 Da with <sup>58</sup>Fe<sup>2+</sup>, <sup>58</sup>Ni<sup>2+</sup> and <sup>29</sup>Si<sup>1+</sup> with all three ion species potentially incorporated into the MNSPs. The contribution of <sup>58</sup>Fe<sup>2+</sup> to the 29 Da peak with the clusters has previously been claimed to be limited in other irradiated steels [70]. Some authors have chosen not to include any ions originating from the 29 Da peak in their solute cluster definitions [49]. Other researchers have utilised Scanning TEM (STEM)-Energy-dispersive X-ray spectroscopy (EDS) to claim that the exclusion of Fe from the defined MNSP precipitates in the APT data was reasonable [71]. The situation in APT is further complicated by trajectory aberrations that affect the spatial resolution of the reconstructed atom maps, as discussed by Larson et al. [72], which can erroneously introduce Fe from the surrounding matrix into the defined MNSP cluster. Therefore, in this study, all cluster compositions did include the peak at 29, identifying this as <sup>58</sup>Ni<sup>2+</sup> (not <sup>29</sup>Si<sup>1+</sup> as it did not match the expected natural isotope ratios) and the Fe ions will be removed from the cluster calculation, which is similar to previous studies [53,58,71]. For an

additional check, the spatial distribution of ions within the reconstructed data associated to the 29 Da was visually inspected and observed to correspond to the locations of MNSPs, further indicating that the majority of 29 Da peak was attributed to <sup>58</sup>Ni<sup>2+</sup>.

Following the procedure by N. Almirall et al. [73] solute segregation to dislocations, 2.0 at% Si isoconcentration surface was created and a region of interest (ROI) was placed through the dislocation's core in both transverse and longitude direction to generate composition line profiles.

## Results

A typical reconstruction of the as-received T91 steel is shown in Figure 1a. The microstructure was homogeneous and presented no evidence of nanometric sized ppts or solute segregation.

The typical APT reconstruction in Figure 1(b) of the neutron irradiation T91 steel at 2.14 dpa at 327 °C, shows the formation of Cu rich clusters (CRPs) as well as, segregation of Si, P and Ni to dislocations. The corresponding MNSPs on the dislocations were found to be appendages to CRPs (shown later in Figures 4 and 6). No clustering of Mo, V, Co, Al, Fe or Cr was detected. The average composition of MNSPs was calculated for each dataset and is shown on a ternary projection of the Fe-Mn-Ni-Si phase diagram in Figure 2. The average of 8 APT datasets of MNSP-CRP volume fraction, average radius, volume, composition and number density are summarized in Table 3. Region of Interest (ROI) solute segregation profiles, both transverse and longitudinal (along) dislocations, are shown in Figure 4. The longitude solute profile in Figure 4(c), clearly shows the periodic formation of MNSPs-CRPs along the dislocation line. Enrichment of Ni, Si and P at a carbide interface is shown in Figure 5.

A typical APT reconstruction of T91 neutron irradiated to 8.8 dpa is shown in Figure 1(c). As seen in the close-up atom map, the MNSPs are appendages to CRPs, as frequently observed in RPV steels [53,59] and proton irradiated T91 [34]. No clustering of Mo, V, Co, AI, Fe or Cr was detected. The average compositions of the MNSPs were calculated for each tip dataset and are shown on a ternary phase diagram projection in Figure 2. The average MNSP volume fraction, radius, volume, composition and number density measured for all 7 APT datasets for this irradiation condition of MNSP volume fraction, average radius, volume, composition and number density are summarized in Table 3. The APT reconstruction in Figure 1(c) suggests that the MNSP-CRP features have slightly larger and better defined volumes in the T91 steel neutron irradiated to 8.82 dpa at 377 °C than in the 2.14 dpa at 327 °C condition, along with less apparent segregation of Si, P and Ni to dislocations. Solute segregation to dislocation loops in Figure 6 is shown as transverse concentration profiles. The profile in Figure 6(b) is a 1.0 at.% Cu isoconcentration surface marking a CRP. The longitudinal solute segregation profile, shown in Figure 6(d), indicates the formation of MNSPs-CRPs at the edge of a dislocation loop.



**Figure 1.** a) APT reconstruction of the as-received T91 steel, showing a homogeneous microstructure; b) APT reconstruction of the T91 steel neutron irradiated to 2.14 dpa at 327°C showing MNSPs and CRPs, as well as Ni/Si/P segregating to dislocations; c) APT reconstruction of the T91 steel neutron irradiated to 8.82 dpa at 377°C, showing better defined MNSPs and P/Cu precipitates, perhaps with somewhat less Ni/Si/P segregation to dislocations (but visible in Si). Cr appeared homogeneously distributed in all conditions.



**Figure 2.** The averaged MNSP composition (in at%) of each APT dataset (over >5 million ions) for both 2.14 dpa and 8.82 dpa T91 irradiation conditions displayed on a 277°C isothermal section of the Mn-Ni-Si ternary system projection of a Fe based phase diagram [41,48,74]. The size of the data point is scaled to the MNSP average APT dataset volume (nm<sup>3</sup>). Phase T<sub>1</sub> (800°C) Mn<sub>15</sub>Ni<sub>45</sub>Si<sub>40</sub> from [75] for comparison. The stoichiometric 'G-phase' phase, Mn<sub>6</sub>Ni<sub>16</sub>Si<sub>7</sub>, is marked as T3. Low Ni containing RPV steel neutron irradiated to 0.17 dpa at 290°C is provided from [53] for comparison.



**Figure 3.** An APT reconstruction closeup view of MNSPs and CRPs in T91 neutron irradiated to 2.14 dpa at 327 °C as shown in Figure 1 (b). The right-hand reconstruction is a 180° rotation of the left-hand reconstruction to provide both views.


**Figure 4.** Solute segregation to a line dislocation in a T91 steel irradiated to 2.14 dpa at 327°C. (a) displays a 2.0 at% Si isoconcentration surface; (b) is a 1D transverse ROI concentration profile at a random section of the dislocation and (c) is a 1D longitude ROI concentration profile inside the dislocation displaying peaks in Si, Ni, Mn, P, and Cu precipitation (and Cu is shifted to the right indicating MNSP appendage to CRPs).



**Figure 5.** An APT reconstruction of T91 neutron irradiated to 2.14 dpa at 327 °C. A chromium-based carbide can be seen with a grain boundary/interface that is decorated with Ni, Si and P. The concentration profile was produced using a proxigram from a 5 at% C isoconcentration surface.



**Figure 6.** Solute segregation to a dislocation loop in a T91 steel irradiated to 8.82 dpa at 377 °C; (a) displays a 2.0 at% Si loop isoconcentration surface; (b) is a 1D concentration profile through the 1.0 at% Cu isoconcentration surface; (c) is a 1D transverse ROI concentration profile centered on a random section of the dislocation loop and (d) is a 1D longitude ROI concentration profile inside the randomly selected segment of the dislocation loop.

 Table 3. The volume fraction, average diameter, average volume, volume fraction and solute composition of MNSP in both neutron irradiation conditions using the cluster search, as outlined in Section 2.3

Irradiation Conditions						
	2.14 dpa at 327 °C	8.82 dpa at 377 °C				
MNSP (only solute ions, excluding Fe)						
Number Density (#/cm <sup>3</sup> )	(3.1 ± 0.7) 10 <sup>23</sup>	$(1.5 \pm 0.7) \ 10^{23}$				
Average Radii (nm)	1.1± 0.1	$1.45 \pm 0.2$				
Average Volume (nm <sup>3</sup> )	5.8 ± 1.3	15.6 ± 5.4				
Volume fraction (%)	$0.26 \pm 0.06$	$0.33 \pm 0.14$				
MNSP	solute compositions (F	ig. 6)				
Mn (%)	16.49 ± 4.7	16.47 ± 4.4				
Ni (%)	37.87 ± 6.33	36.80 ± 10.61				
Si (%)	45.64 ± 7.62	46.73 ± 11.59				

# DISCUSSION

The defining microstructural features of T91 steel are the martensitic lath microstructure, high network dislocation densities, M<sub>23</sub>C<sub>6</sub> carbides, as well as somewhat finer scale vanadium nitrides and molybdenum/niobium carbides [60]. The latter features provide the high creep strength [76] needed for elevated temperature boiler and nuclear applications [9]. Note these performance-enabling microstructures are unstable in T91 under irradiation at temperatures more than 450 to 500°C, as indicated by irradiation softening and non-hardening embrittlement [77]. At lower temperatures, the main effects of irradiation are hardening and embrittlement due to segregation and precipitation of solutes, as described in the previous Section. It is well known, and the topic of a large amount of literature, that a smaller amount of hardening is contributed by dislocation loops, as illustrated in [24] for Fe-Cr binary alloys. Potential contributions from the evolution of network dislocations is rapidly emerging as an issue, but is not close to being well quantified [26,27,40,43,78]. However, discussion evolved dislocation loop and line hardening, including the effects of segregation and precipitation, is beyond the scope of this paper. Here we focus on high mass and spatial resolution APT to investigate segregation and nm-scale precipitates, which are absent prior to neutron irradiation.

Precipitate evolution under neutron irradiation was illustrated in Figure 1 (a) – (c). Cr remains homogeneously distributed in all conditions. The high number density nanosized MNSPs act as dispersed barrier obstacles dislocation glide, which results in the hardening and shifts in the ductile-to-brittle transition temperature [5,9,60,79]. The decrease in number density and increase in size (and individual precipitate volume) in the higher dpa and temperature irradiation condition is expected based on the thermo-kinetics of segregation and precipitation; the slightly larger volume fraction at higher fluence and temperature (from  $0.26 \pm 0.06$  to  $0.33 \pm 0.1$  %) is probably within the uncertainties in the APT measurements. Note, RPV studies show that dispersed barrier hardening and embrittlement are primarily controlled by the square root of the precipitate volume fraction [50,53,55,57]. The T91 volume fractions correspond to estimated hardening contributions of ≈168 to 186 MPa.

The average composition of MNSP in both irradiated conditions, shown in Figure 2 and Table 3, is significantly different that the most often cited 'G-phase'. Rather, the MNSP compositions are closer to the Si(Mn,Ni) phase field in the MnNiSi ternary projection of the Fe matrix-based quaternary phase diagram. This phase field, calculated by Xiong et al., is  $Si_{0.5}Mn_xNi_{(1-x)}$  where x varies from ~0.1 to 0.25 [48]. Note, the crystallographic structure of the precipitates in this study has not been characterized. Similar Si(Mn,Ni) phase compositions have been observed on dislocations in a low Ni (0.07 at.%) VVER-440 RPV steel [80]; and more recently in another low Ni RPV steel [57].

The T91 2.14 dpa at 327 °C carbide shown in Figure 3 is likely a  $M_{23}C_6$  phase with a composition of ~ 48.2 ± 0.5 Cr, 16.7 ± 0.4 C, 4.3 ± 0.3 Mo and 29.0 ± 0.5 Fe (in at.%); however the crystallography has not been determined. The composition line profile across the carbide/matrix interface in Figure 3 shows enrichment of Ni, Si and P, which correlates well with previously analysed irradiated carbide interfaces [31,32,37].

Co-precipitation of CRPs and MNSPs, clearly seen in Figure 4, is widely observed in RPV steels at high fluence, and has been extensively characterized [47–50] and modelled [43,45,46,59]. CRPs have been observed in neutron and ion irradiated T91 [39,40] and HT9 [19,31]. Indeed, Cu driven co-precipitation has also been exploited by high strength steels to promote the formation of various intermetallic phases [81]. The corresponding sequence-of-events begins with the rapid precipitation of highly supersaturated Cu, with shells composed of the other solutes. After Cu is depleted from the matrix, Mn, Ni and Si continue to accumulate, so as to eventually form a separate appendage phase [42,43,46,53,59,82]. Even trace amounts of Cu act as a powerful catalyst for MNSP formation [53]. In the case of T91 co-precipitation takes place in highly solute segregated regions at dislocations, as previously observed by APT in irradiated T91 steel [19,39,40].

The nominal transverse solute concentrations profiles at line dislocations in Figure 5(a,b) reaches 4-5% for Si and Ni, and 1 to 2% for Mn, P and Cu. Figure 5(c) presents longitudinal profiles that show periodic peaks of Mn, Ni, Si, Cu and P, indicating the formation of precipitates. Note, the Cu peaks are slightly displaced from those for Ni, and especially Mn, which is consistent with co-precipitation [46]. The Si enrichment is very high and more uniformly distributed along the dislocation lines. This may rationalize the SiMn<sub>x</sub>Ni<sub>(1-x)</sub> precipitate compositions, which are near the Si(Mn,Ni) phase field, as shown in Figure 2. As seen in Figure 6, generally similar solute segregation also occurs at dislocation loops. However, P does not appear to segregate to loops. Cu is localized in the precipitate regions of both dislocation features. Note, these solute compositions are nominal, and may be affected by APT artefacts like trajectory aberrations.

Our analyses highlight the parallels that can be drawn between the much more limited database on MNSPs in neutron irradiated for Fe-Cr alloy systems, including model binary alloys and 9-12%Cr steels like T91 and HT9, with the much more extensive literature on precipitate evolution in RPV steels [16,41,52,55–57,59,42,43,46–51]. Notably, precipitates in some very low Ni RPV steels have compositions that fall near the Si(Mn,Ni) phase field. The major difference between these alloy classes is that the typical Cu + Ni + Mn +Si solute contents in RPV steels are much higher ( $\approx$  3%) than in the 9Cr TMS alloys ( $\lesssim$ 1%). Thus, while precipitation at segregated dislocations (loops and line) occurs and is important for some RPV steels and irradiation conditions, local solute enrichment is probably necessary in alloys like T91. Note, segregation may be either thermally driven, or induced by irradiation (RIS), or both. The main thermodynamic driver for co-segregation is the local bonding interactions between the solutes, lowering their free energies near the dislocations. The other difference between RPV and 9Cr TMS, is that service conditions for the latter involves much higher temperatures and dose.

A combined solute segregation and cluster dynamics (CD) model has been used to predict the nucleation and growth of MNSPs in a sub saturated T91 steel as a function of irradiation dose in dpa [29]. The model, which predicts the MNSP number density, volume fraction and mean radius (and radius distribution), was previously calibrated using the results of a single proton irradiation at 400 °C to 7 dpa [37]. Figure 7 compares these predictions to the 8.8 dpa at 377°C APT data in this study, showing that the model predictions agree with the neutron results. The number density and radius are in almost exact agreement, while the volume fraction is slightly under predicted, perhaps partly due to the lower neutron irradiation temperature. Figure 8 compares the predictions of solute segregation to the observed values; the agreement is reasonable in the case of Si, but Ni segregation is under predicted. It is likely that this is since the model does not treat co-segregation of solutes. That is, solute-so lute interactions in the semi-dilute local micro-alloy regions at dislocations lower free energies in the segregated regions at dislocations. The Cu, Mn and P segregation that is observed in the T91 data is also shown but has not been modelled.



**Figure 7.** The comparison between the T91 MNSP (a) number density, (b) radius, and (c) volume fraction with the full calculation (segregation plus CD) model developed by J. H. Ke et al. [29]. The absence of precipitation without RIS segregation is also shown along with the sluggish kinetics without RED. Permission for reproducing J. H. Ke et al. [29] data has been granted.

Notably, distinct  $\Box$ ' precipitates were not observed in either irradiation condition. The Cr solubility limit is  $\approx 8.8 \pm 0.5$  at% [22,83,84] at 300°C. Thermal  $\alpha$ ' precipitation can occur but is sluggish. However, Cr precipitation is greatly accelerated by radiation-enhanced diffusion [85]. The absence of  $\Box$ ' in T91 is due likely to the low, or absent, Cr supersaturation, depending on the temperature. Such low supersaturations are insufficient to form significant populations of small, discrete  $\Box$ ' precipitates. Results in the literature on  $\Box$ ' vary [22,23,84,86]; for example, SANS [87] showed that a T91 alloy neutron irradiated to 0.7 dpa at 325 °C in the OSIRIS reactor contained a small volume fraction ( $\approx 0.1\%$ ) of high number density (9.0  $\times 10^{23}$  m<sup>-3</sup>)  $\alpha$ ' precipitates with an average radius of 1.3 nm [87]. Conversely, SANS and TEM did not observe  $\alpha$ ' in a T91 steel irradiated to 184 dpa since it was irradiated

at a higher temperature of 413 °C in the Fast Flux Test Reactor [14]. Further discussion of this widely studied topic is beyond the scope of this paper.

While not the primary focus of this work, it is useful to briefly discuss the thermodynamics that appear to be at work here. As noted previously, we have not measured the structure of the MNSPs. However, our results show that the compositions fall near the Si(Mn,Ni) phase field (as calculated by Xiong et al. [48]), and as seen in Figure 2. Further, Hu et al. [75] reported the existence of a  $Mn_{15}Ni_{45}Si_{40}$  compound  $T_1$  phase in the 800°C Mn-Ni-Si isotherm, also shown in Figure 2. These compositions bracket those found in this study, and at least one other on a similar T91 at 500°C and 3 dpa [33].



**Figure 8.** A comparison between T91 Si and Ni segregation to dislocations observed with predictions by J. H. Ke et al. [29]. The observed segregation of Cu, Mn and P is also show but was not modelled in the original study. Permission for reproducing the figure has been granted.

A full thermodynamic assessment of these phases is not yet available. However, the bulk and segregated alloy compositions can be compared to the thermodynamic solute product requirements for G-phase formation by the reaction the reaction:

$$16Ni_{s} + 6Mn_{s} + 7Si_{s} \rightleftharpoons Ni_{16}Mn_{6}Si_{7}$$
(1)

where the subscript s denotes that the solutes are in solution. Thus, the reaction solute product is SP =  $\{[X_{Ni}]^{16}[X_{Si}]^7\}^{1/29}$ , where X<sub>i</sub> are the mole fractions of the dissolved Ni, Mn and Si. The equilibrium solute product (SP<sub>e</sub>), or phase boundary, at 377°C is  $\approx 5x10^{-3}$  [41]. The APT composition X<sub>i</sub> values in Table 1 yield an alloy solute product of  $\approx 4.3x10^{-3}$ ; thus, the bulk system is nominally slightly undersaturated. In contrast, the local peak segregated X<sub>i</sub> for Mn  $\approx 0.01$ , Si  $\approx 0.05$  and Ni  $\approx 0.02$ , in Figure 6(c), produces a local alloy SP of  $\approx 0.044$ , which is highly supersaturated. The difference between the composition of G-phase, and that found in this work, is almost certainly due to the unusually high Si concentration in the segregated region. As shown by J. Ke et al. (2018) [29], RIS results in Ni and Si segregation, which is sufficient to drive precipitation. However, it should be noted that thermal segregation and precipitation, which is greatly accelerated by RED, could also be significant [88–90].

# CONCLUSIONS

APT was used to quantify and understand the effect of neutron irradiation on solute segregation and CRP and MNSP co-precipitation in T91 steel. Two ATR irradiation conditions were investigated: 2.14 dpa at 327 °C and 8.82 dpa at 377 °C. Key observations are as follows:

- The compositions of all the MNSPs were similar and fell near the Si(Mn,Ni) phase field. While the structure of the precipitates has not been characterized, this composition range is distinctly different than for that for the typically cited G-phase and is consistent to the observations of Si(Mn,Ni) precipitates in neutron irradiated low Ni % RPV steels.
- Co-precipitation of MNSP and CRP is observed, where the MNSPs appear as an appendage to the CRPs.
- Significant solute segregation (P, Si, Ni and Mn) to dislocation lines and loops is observed, with large enrichment factors for Si and Ni ≈ 10.
- MNSP and CRP form on the micro alloyed regions at dislocation lines and loops.
- The T91 bulk Ni, Mn and Si composition is undersaturated and insufficient to cause precipitation. However, the corresponding composition in micro alloy regions of segregated dislocations is highly supersaturated.
- CRP-MNSP number densities, sizes, volume fractions, and Si enrichment at dislocations are in good agreement with predictions of a previously reported model, combining solute segregation and CD sub models. Ni solute segregation to dislocations is significant but under predicted in the J. Ke model.
- α' formation was not observed in any atom probe data sets.

This study has provided an insight into the MNSP compositions, volume fractions and sizes, which may contribute to a better understanding of the embrittlement of T91 steel. Moreover, this study builds upon the extensive understanding of precipitation in RPV steels and corresponding much more limited Fe-Cr alloy systems.

# ACKNOWLEDGEMENTS

T. P. Davis is funded by the Clarendon Scholarship from the University of Oxford and Engineering and Physical Sciences Research Council Fusion Centre for Doctorial Training [EP/L01663X/1]. Other who contributed to this work includes M. A. Auger (Oxford, Universidad Carlos III de Madrid), P. A. J. Bagot (Oxford) and P. Hosemann (UC Berkeley). APT was supported by EPSRC grant EP/M022803/1 "A LEAP 5000XR for the UK National Atom Probe Facility." The authors acknowledge use of characterisation facilities within the David Cockayne Centre for Electron Microscopy, Department of Materials, University of Oxford, along with financial support provided by the Henry Royce Institute (Grant ref EP/R010145/1). This work was supported by the U.S. Department of Energy, Office of Nuclear Energy under DOE Idaho Operations Office Contract DE-AC07- 051D14517 as part of a Nuclear Science User Facilities (NSUF) experiment. Post irradiation experiments on neutron irradiated samples were conducted at the Microscopy and Characterization Suite (MaCS), Center for Advanced Energy Studies using the LEAP 4000X HR under the NSUF Rapid Turnaround Experiment No 19-1721. The deep, long-term involvement of UCSB in this work was supported by the DOE National Scientific Users Facility, who sponsored the ATR-1 irradiation; and more recently in the analysis, evaluation and interpretation of the data, which was supported by the DOE Office of Fusion Energy Sciences. Finally, we thank Dr. Jia Hong Ke for his assistance in including the modelling comparison.

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**1.6 PRIMARY CREEP MODELS FOR 9CrW TEMPERED MARTENSITIC STEELS: EFFECTS ON THE HIGH TEMPERATURE DIMENSIONAL STABILITY OF FUSION STRUCTURES**—M.E. Alam, T. Yamamoto, G.R. Odette (University of California, Santa Barbara)

# OBJECTIVE

The objective of this study is to develop primary creep models for assessing the dimensional stability of reduced activation tempered martensitic steels used in large fusion structures.

### SUMMARY

Thermal creep models typically treat minimum creep rates and rupture times. However, primary creep cannot be ignored in assessing the dimensional stability of large fusion structures. Therefore, three new engineering primary creep models have been developed, for reduced activation variants of 9Cr tempered martensitic steels in the Grade 91 class. The applied creep stress ( $\sigma$ ) was taken as the independent variable to be optimized. The models included: 1) the Larson-Miller parameter (LMP); 2) the applied stress ( $\sigma$ ) normalized to the temperature dependent 0.2% tensile yield stress, [ $\sigma/\sigma_y(T)$ ]; and 3) a threshold stress that scales with  $\sigma_y$ , ( $\sigma$ -C $\sigma_y$ ). The models were calibrated to a database reported by Reith et al. [1] for 8 heats of Eurofer97. The primary creep predictions are for 0.2 to 2% strains at 450 to 550°C. All three models predict the primary creep stress standard deviations (SD) of  $\approx$  12 MPa, and mean error (ME)  $\approx$  -0.161 to 2.9 MPa. Further optimization on a smaller set of the most pertinent data, minimized systematic bias, while reducing the SD and ME to  $\leq$  8 MPa and 0.1 MPa, respectively.

### PROGRESS AND STATUS

### Background

Creep testing of structural alloys and design of metallic structures are often limited to the consideration of secondary, or minimum creep rates ( $\varepsilon'_m$ ), based on a simple Norton's power law model. However, the accumulation of strain during the primary creep cannot be neglected, especially for the large structures, like fusion first wall and blankets energy conversion systems, which must maintain precise dimensional tolerances. Primary creep is also important for long time service environments manifesting cyclic stresses and temperatures; this is even true for much more benign environments, like pressure boundaries in fossil energy systems [2-3]. A number of empirical models treating primary creep strains ( $\varepsilon_r$ , where x is the primary creep strain) have been proposed, including: (i) the theta-projection method [3-4], (ii) power law model [5-6], (iii) logarithmic law [7], exponential law [8], and the Wilshire normalized stress equations [3,9], just to name some examples. These models have various individual advantages and disadvantages [3]. Here, we develop three new primary creep models, namely: 1) a Larson-Miller Parameter (LMP) based model; 2) a normalized stress model; and, (3) a threshold stress model. In the latter two cases, the normalization and threshold stresses are related to quasi-static tensile properties. This approach has the potential advantage of allowing a model to be applied to a range alloys, at least within a given class. These models are intended to provide design engineers a convenient tool to predict the stress ( $\sigma$ ) for primary creep at  $\varepsilon_x$  at specified t and T.

Here we focus on normalized and tempered martensitic Grade 91 class of 9Cr steels. Table 1 shows the typical solute contents of Grade 91 steels are  $\approx 0.1$ C, 9 Cr, 1 Mo, 0.23 V, 0.08 Nb (wt.%) [4, 9,10]. These steels are characterized by a tempered lath packet microstructure, within larger prior austenite grains. Grade 91 steels are typically austenitized at  $\approx 1040^{\circ}$ C for 4h, air-cooled (normalized) and tempered at  $\approx 750^{\circ}$ C for 1h, leading too tensile yield strength ( $\sigma_y$ ) of  $\approx 450$  MPa. Grade 91 steels contain a variety of carbides, including secondary hardening Mo<sub>2</sub>C precipitates. At high temperatures and service stresses, these microstructures evolve over time in association with things like general lath scale instabilities, precipitate coarsening and the formation of detrimental intermetallic phases. These evolutions occur at lower temperatures and shorter times under neutron irradiation conditions. Higher strength variants of 9Cr TMS are based on the formation of very fine scale alloy (M) carbide, nitride and oxide phases (and

engineered grain boundary phases). However, here we focus on a variant of Grade 91 specifically targeting fusion applications, which are most often referred to as reduced activation ferritic-martensitic (RAFM) steels. Substituting W for Mo and controlling the contents of various alloying elements and impurities reduces the inventory long-lived radioactive isotopes. The close relationship between fusion relevant RAFM and Grade 91 steels is a great benefit, since the latter has been used since the early 1980s, are code qualified and are resistant to void swelling [11]. The models developed here are specifically based on a creep database on eight different heats of Eurofer97 reported by Reith et al. [1].

Comp	С	Cr	Мо	V	Nb	Mn	Ni	Si	W	Та	Cu	Ν	S	Ti
Gr91	0.1	9	1	0.3	0.8	0.4	0.13	0.23	-	-	0.06	0.04	0.002	0.002
Eu97	0.09- 0.12	8.1- 9.5	-	0.19- 0.28	-	0.3- 0.6	0.1	-	1- 1.5	0.1- 1.6	-	-	-	-

Table 1. Nominal compositions (wt.%) of Grade91 steel [4,9,10] and Eurofer97 [1]

Reith's Eurofer database covers a wide range of  $\sigma$  and T for primary strain and other creep properties. The new models developed here are for primary creep strains ( $\varepsilon_x$ ) from x = 0.2 to 2% at T = 450 to 550°C and  $\sigma$  from 160 to 360 MPa (depending on the T). Note, the database does not include the full creep curves, so the  $\sigma$ , T,  $\varepsilon_x$  and  $t_x$  data were used for least square fitting (LSF) optimization of the models. The primary least square fit parameter is the predicted minus measured standard deviation (SD) of  $\sigma$ . The results show that all three models predict reasonably similar  $\sigma$ , with SD  $\approx$  12 MPa. The secondary best-fit criteria are discussed below. It is important to emphasize that many alternative models were examined that are not described here. For example, models that normalized  $\sigma$ , or based the threshold stress, with the ultimate tensile stress ( $\sigma_u$ ), rather than  $\sigma_v$ , were also examined. We first developed models with fixed values of C<sub>LM</sub> = 30 and Q = 300 kJ/mole, since these choices are physically motivated and/or are consistent with other sources of information. The main fitting was to parameterize functions that allowed application of the model over the entire range of  $\varepsilon_{x}$ . However, the LSF values for other parameters resulted in systematic bias in some variable residual trends. Therefore, unconstrained, more highly optimized models, were also developed for a more limited set of the most pertinent data. The further optimization minimized bias, while reducing the SD and ME to  $\leq$  8 MPa and 0.1 MPa, respectively. Finally, this analysis was useful in identifying gaps in high temperature creep data and in limiting the design window.

### Creep in 9Cr TMS: Basic characteristics and primary creep mechanisms

Reduced activation fusion alloys, like Eurofer97, are a subclass of Grade 91 9Cr TMS. They share a similar set of mechanical properties, including those characterizing creep and primary creep [1,4,11]. For example, Figure 1a shows that the  $\sigma$  dependence of the time to  $\varepsilon = 1\%$  can be described by a simple Norton power law model ( $\varepsilon' = A\sigma^n \exp(-Q/RT)$ ) with a large exponent (n  $\approx 16$ ), that is typical of Grade 91 steels at relatively high  $\sigma$  [9]. Figure 1b, plotting a T compensated time to 1% strain against  $\sigma$  normalized by the ultimate tensile stress ( $\sigma_u$ ), is also approximately consistent with an activation energy (Q = 300 kJ/mole), associated with self-diffusion in ferrite. Plots of creep rupture time and associated temperature compensated  $\sigma/\sigma_u$  (the ultimate tensile stress) for a wide range of Grade 91 steels look very similar [9]. Grade 91 steels typically exhibit primary creep behavior up to  $\varepsilon$  of  $\approx 1$  to 2%, while rupturing or beginning tertiary creep by  $\approx 5\%$ , or less [10,11]. As a result, estimated creep lifetimes of structures based on  $\varepsilon'_m$  may be non-conservative.

Typical primary creep behavior is schematically illustrated in Figure 2 [1]. Detailed discussion of the mechanisms controlling primary creep is beyond the scope of this report. However, briefly the primary creep rate ( $\varepsilon'_p$ ) up to  $\varepsilon'_m$  can be represented by

$$\varepsilon'(\varepsilon) = \varepsilon'_m + (\varepsilon'_o - \varepsilon'_m) \exp\left(-\frac{\varepsilon}{\varepsilon_{pr}}\right)$$
(1)

Here,  $\varepsilon'_o$  is the initial creep rate (t -> 0) and  $\varepsilon_{pr}$  is the primary creep relaxation strain, which are phenomenological fit parameters. The initial decrease in  $(\varepsilon'_o - \varepsilon'_m)$  is due to hardening most likely

associated with the build up dislocation structures, in a manner analogous to strain hardening in static tensile tests. This buildup reaches a steady state condition at  $\varepsilon' = \varepsilon'_m$ . Note this phenomenological description is sometimes couched in terms of a decaying internal back stress. The major significance of this behavior is that the creep rates are initially mediated by an evolving alloy microstructure, which is also, to some extent, reflected in the initial strength and strain hardening rates observed in static tensile properties. Although quantitative details certainly differ, and are a function of both T and t, normalizing  $\sigma$  to tensile yield ( $\sigma_y$ ) or ultimate ( $\sigma_u$ ) stresses captures some of this physics. Another advantage of using normalized  $\sigma$  values is that it permits the use of the same model, perhaps with some fine-tune fitting, for a range of 9Cr TMS steels and corresponding tensile properties.



**Figure 1.** (a) The stress dependences of primary creep  $t_{1\%}$ ; and, b) temperature compensated  $t_{1\%}$  against  $\sigma/\sigma_u$  for Q = 300kJ/mol.



Figure 2. Schematic illustration of primary creep behavior taken from the Reith report [1].

### Baseline primary creep models for 450 to 550°C with some constrained parameters

The tensile properties ( $\sigma_y$  and  $\sigma_u$ ) used in this study are plotted in Figure 3 [1]. Here we focus on T between 450 and 550°C marking the likely limit of standard Grade 91 type Eurofer97 steels for extended irradiation service. The tensile properties for 450 and 550°C are the average between 400 and 500°C; and 500 and 600°C, respectively.



**Figure 3.** a)  $\sigma_y(T)$ ; and, b)  $\sigma_u(T)$  of different Eurofer97 heats [1].

### Primary Creep Models for 0.2 to 2% Strains from 450 to 550°C

### (1) Larson-Miller parameter (LMP) model

The Larson-Miller parameter (LMP) is one of the most commonly used creep data correlation and extrapolation procedures, for using short time laboratory test results to estimate longer in service life rupture times and various  $\varepsilon$ . The procedure plots the t-T dependent LMP parameter versus the  $\sigma$ , as  $\sigma = f(LMP)$ . The LMP for various t and T is given by

$$LMP = T(C_{LM} + \log t_x)$$
<sup>(2)</sup>

 $C_{LM}$  is the Larson-Miller constant with different values for various alloys and alloy conditions [3,9,10]. LMP plots are also applied to correlating minimum creep rate ( $\varepsilon'_m$ ) data in terms of  $1/\varepsilon'_m$ . Here we have adopted the same LMP procedure to estimate the primary creep  $\sigma$  as a function of  $t_x$  and T, where  $t_x$  is the time to reach  $\varepsilon_x$ . As shown in Figure 4a the primary creep data can be approximately represented by a simple linear fit:

$$\sigma(\varepsilon_x, T) = M_0(\varepsilon_x) + M_1(\varepsilon_x, \mathsf{LMP})$$
(3)

The fit parameters  $M_0(\varepsilon_x)$  and  $M_1(\varepsilon_x)$  are used to predict the  $\sigma$  needed to reach various  $\varepsilon_x$  as a function of the corresponding  $t_x$  and T. Specifically,  $M_0$  and  $M_1$  are the LMP = 0 intercepts and slopes of  $\sigma$  vs. LMP fitted line, respectively. Figure 4a shows  $\sigma$  versus LMP (t in h) for  $C_{LM}$  = 30 for  $\varepsilon_x$  from 0.2 to 2% for all eight heats of Eurofer97 in the Reith et al. database [1].



**Figure 4.** a) the measured  $\sigma$  versus the LMP for various  $\varepsilon_x$  and fit lines; b) LSF for M<sub>0</sub> and M<sub>1</sub> as a function  $\varepsilon_x$ ; c) M versus P  $\sigma$  for the LMP model; and, d) M (points) and P (lines)  $\sigma$  for t<sub>1%</sub>.

Note a slightly better fit over the entire range of  $\sigma$ -LMP data is provided by a second order polynomial; however, the linear fit is adequate for the baseline model. Figure 4b shows the M<sub>0</sub> and M<sub>1</sub>, as a function of  $\varepsilon_{x}$ , fitted with a second order polynomial for C<sub>LM</sub> = 30 from Fig. 4a, where  $\sigma$  is

$$\sigma = (C_{00} + C_{01}\varepsilon + C_{02}\varepsilon^2) + (C_{10} + C_{11}\varepsilon + C_{12}\varepsilon^2)LMP$$
(4)

The Excel equation solver was used to determine the LSF  $C_{ij}$  parameters. The fits minimized the standard deviation (SD) between measured (M) and predicted (P)  $\sigma$ :

$$SD = \sqrt{\left(\frac{\Sigma(P-M)^2}{N}\right)}$$
(5)

N is the number of data points. A secondary fitting requirement is that the P-M data are well centered on a 1:1 line with a SD,  $\sigma$  versus LMP intercept mean error (ME) that are all small, where the ME = [ $\Sigma(M - P)$ ]/N). Figure 4c plots the corresponding measured (M) versus predicted (P)  $\sigma_a$ , yielding a SD  $\approx$  11.5 MPa, a ME = 0.046 MPa, a fit line slope of 1 and intercept of 0.05 MPa. The corresponding LMP model parameters are summarized in Table 2.

Fit Parameters	LMP Model M <sub>0</sub> , M <sub>1</sub> 2 <sup>nd</sup> order poly	$\sigma/\sigma_y$ Model M <sub>0</sub> , M <sub>1</sub> 2 <sup>nd</sup> order poly	$\sigma - C\sigma_y$ Model,
C00	1339	-1.07	0.7046
C01	-0.001	17	
C02	-1.518	-0.3	
C10	-0.046173	-0.037555	0.148
C11	0.004282	-0.21	
C12	-0.00118	19	
A			0.15447
n			6.526
Сьм	30		
Q (kJ/mol)	-	300	300
Slope	1	1	1
Intercept (MPa)	0.05	2.9	-0.15
R <sup>2</sup>	0.9604	0.9569	0.9671
SD (MPa)	11.45	12.33	10.45
ME (MPa)	0.046	2.9	-0.161

<b>able 2.</b> Least square fit	(LSF) parameters	and SD for various	primary creep models
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### (2) Tensile $\sigma_y$ Normalized Stress Model

The most common approach to fitting data at higher  $\sigma$  and lower T, in the dislocation creep (climb-glide) regime, is the use of the simple Norton power law model as:

$$\varepsilon' = A\sigma^n \exp(-Q/RT)$$

(6)

While the parameters A, the stress exponent n and the activation energy Q are often assumed to be constant, they actually depend on the combination of  $\sigma$  and T; and fitted values tend to be non-physical, for example with high values of Q and n. Q and n also tend to be highly covariant [9]. Some improvement in the model parameterization is possible by using ratio  $\sigma$  to the shear modulus (G) as a normalized dimensionless  $\sigma/G$ .

The Norton model is usually used for  $t_r$  and  $\varepsilon_m$  data correlations. Here we normalized  $\sigma$ , by dividing it by tensile strength properties. The potential advantages of this approach include achieving a more physical parameterization for n and Q, and exploiting the relation to microstructures and their general, static and creep, strengthening contributions. Further, once calibrated, such models could be applied to some range of alloy conditions, encompassing different strengths, albeit with some fine tuning. Wilshire et al [9] proposed dividing  $\sigma$  by the ultimate tensile stress,  $\sigma_u$ :

$$\varepsilon' = A^* (\sigma/\sigma_u)^n \exp(-Q/RT) \tag{7}$$

He further modified the Equation (7) for  $\sigma/\sigma_u$  over the entire stress range from  $\sigma/\sigma_u = 1$  to 0, where  $\varepsilon' \to \infty$  and  $t_f \to 0$  as  $\sigma/\sigma_u \to 0$ , and where  $\varepsilon' \to 0$  and  $t_f \to \infty$  as  $\sigma/\sigma_u \to 0$ , as:

$$\frac{\sigma}{\sigma_u} = \exp\left\{-k\left[t_x \exp\left(-\frac{Q}{RT}\right)\right]^n\right\}$$
(8)

The k and n are fit parameters, and  $t_x$  is the time to reach for strain  $\varepsilon_x$ .

We applied a modified Equation 8 to four primary  $\varepsilon_x$  at the three different T for all eight heats of Eurofer97. Since the primary  $\varepsilon_x$  are low, we use  $\sigma_y$  rather than  $\sigma_u$  for the normalization. The procedure involves fitting  $\sigma/\sigma_y$  data as a function of a temperature-compensated primary creep time  $t_x \exp\left(-\frac{Q}{RT}\right)$  as shown in Fig. 5a. Once again, these four linear curves have different intercepts (M<sub>0</sub>) and slopes (M<sub>1</sub>) for the various  $\varepsilon_x$ . Figure 5b shows the M<sub>0</sub> and M<sub>1</sub> cross fit to a second order polynomial as a function of  $\varepsilon_x$ . Thus the predicted stress for all primary creep strains is:

$$\sigma(\varepsilon_x, T)(MPa) = \sigma_y\{(C_{00} + C_{01}\varepsilon + C_{02}\varepsilon^2) + (C_{10} + C_{11}\varepsilon + C_{12}\varepsilon^2)\ln\left[t_x \exp\left(-\frac{Q}{RT}\right)\right]\}$$
(9)

Here,  $C_{ii}$ 's are again the intercept and slope fit parameters and Q is the effective activation energy.



**Figure 5.** a) Temperature-compensated  $t_x$  versus  $\sigma/\sigma_y$  and fit lines; b) LSF for  $M_0$  and  $M_1$  as a function of  $\varepsilon_x$ ; (c) P versus M  $\sigma$  for the normalized  $\sigma/\sigma_y$  model; and, d) the M (points) and P (lines)  $\sigma$  for  $t_{1\%}$ .

The LSF using the Excel solver for C<sub>i,j</sub> and n yields a SD = 12.3 MPa, ME = 2.9 MPa, a slope = 1 and intercepts at 2.9 MPa for Q = 300 kJ/mol (see Fig. 5c). The corresponding normalized  $\sigma/\sigma_u$  model slope of 1 yielded a SD = 13.8, a ME = 6.44, and an intercept = 6.4 MPa. Table 2 also summarizes the corresponding  $\sigma_y$  normalized stress model parameters. Figure 5d plots the predicted (lines) and measured (points) stresses versus time to  $\varepsilon_x = 1\%$  at the 3 temperatures.

### (3) Threshold stress model

In many engineering alloys creep occurs under the reduced threshold stress  $(\sigma - \sigma_t)$ , such that  $\varepsilon' \propto (\sigma - \sigma_t)^n$ , where  $\sigma_t$  often viewed as a threshold stress [9,12]. A variety of models exist for dispersionstrengthened alloys, which relate  $\sigma_t$  to a fraction of the particle strengthening in static tensile tests [13]. A model that treats  $\sigma_t$  as a function of strain is expected to be especially pertinent to primary creep. Here in our study, we have defined threshold stress as  $C(\varepsilon)\sigma_y(T)$ , where C is the function of primary strains as  $C = C_0\varepsilon^{C_1}$  and  $C_0$  and  $C_1$  are fit parameters. Thus

$$\varepsilon' = A(\sigma - C\sigma_y)^n \exp(-Q/RT)$$
(10)

The corresponding required applied creep stress is

$$\sigma = \left\{ \frac{\varepsilon' \exp\left(\frac{Q}{RT}\right)}{A} \right\}^{1/n} + C\sigma_y \tag{11}$$

The dependent (measured) variable  $\varepsilon'$ , is defined as the specified  $\varepsilon_x$  divided by the time to reach this primary strain,  $\varepsilon_x/t_x$ , from the Reith database. The LSF parameters are A, n, C<sub>0</sub> and C<sub>1</sub> are also summarized in Table 2. Figure 6a shows the  $C = C_0 \varepsilon^{C_1}$  fit to the fitted  $C(\varepsilon)$  data. The threshold  $\sigma - C\sigma_y$  model predicts the lowest SD and ME (≈10.35 and -0.283 MPa, respectively) among all the primary creep models for the 450 – 550°C dataset. Fit parameters were adjusted for a 1/1 M/P slope and ≈ 0 MPa, that increases the SD to 10.45 MPa and reduces ME to -0.161 MPa (see Table 2 and Fig. 6b), still the best among all models. The M (points) and P (lines)  $\sigma$  for t<sub>1%</sub> from 450 to 550°C in Figure 6c shows the threshold model systematically under predicts stress at lower T, while providing reasonably good fits at 500 and 550°C temperature test. The color-coded data points in Figure 6d show that at 450°C there is also a systematic bias (red dashed lines) in the threshold model predictions as a function of  $\varepsilon_x$ .

### An Unconstrained Model for a Constrained Database

Although on average the baseline models described above all give reasonably good overall global fits, there are troubling residual biases in parts of independent variable space. This is not entirely surprising, since the temperature range covered lies in the transition between dislocation glide dominated deformation and dislocation climb controlled viscoplastic creep. Conditions that cross such mechanism boundaries are difficult to treat with simple global creep models. Given complex microstructural evolutions this may especially be the case for primary creep. One manifestation of this complex behavior is that the activation energy Q varies between the 450 and 500°C versus 500 to 550°C are not the same.



**Figure 6.** a)  $C = C_0 \varepsilon^{C_1}$  LSF to the  $C(\varepsilon)$  data; b) M versus P for the threshold  $\sigma$  model, (c) M (points) and P (lines)  $\sigma$  for  $\varepsilon_{1\%}$ ; and d) M versus P  $\sigma$  with systematic bias (red dashed lines) for various  $\varepsilon_x$  at 450°C.

In order to fine tune the models, we refit the data to the 400 and 500°C and t > 10 h, while leaving C<sub>LM</sub> or Q unconstrained. The rationale for restricting the database conditions is that shorter times are irrelevant, and T > 500°C is likely beyond the use limit for the 9CrW steels, since under irradiation these steels soften significantly [14]. The relaxed constraint on C<sub>LM</sub> is not unusual, although this is typically associated with best fit values < 30. The unconstrained Q is an effective activation energy, which is typically > 300 kJ/mole in power law creep models. Figure 7a-c plots the M versus P  $\sigma$  for the t<sub>x</sub> > 10h, T = 450 and 500°C data. The color-coding shows the corresponding M (points) and P (lines) for  $\sigma$  as a function of t<sub>x</sub>, that are also all well centered (solid line) and absent significant bias (black dashed lines from the center line with ± 10 MPa, also see Fig. 6d and 7c for the threshold model for comparison) with a SD ≈ 7.1 to 8.4 MPa and ME ≈ 0 to 0.1 MPa. Fig. 7(d-f) shows the M and P stresses for times to 1% strain,  $t(\varepsilon_x) = 1\%$ ), for the respective models. Table 3 summarizes the parameters and statistic for these models.



**Figure 7.** P versus M  $\sigma$  plots for all three models for t<sub>x</sub>>10h and 450 and 500°C for (a) LMP, (b)  $\sigma/\sigma_y$ , and (c)  $\sigma - C\sigma_y$ , respectively, and are color coded for temperature and strains with bias lines. Figure 7(d-f) shows the M and P stresses for times to 1% strain for the respective models.

	100 000		
Fit Parameters	LMP Model	$\sigma/\sigma_y$ Model	σ – Cσ Model
	M <sub>0</sub> , M <sub>1</sub> 2 <sup>nd</sup> order poly	$M_0$ , $M_1$ 2 <sup>nd</sup> order poly	
C00	1504.482162	-1.45348262	0.55736768
C01	-0.0010005	0.00001114	
C02	-8.29819663	-0.3018195	
C10	-0.04834039	-0.03515393	0.131671433
C11	0.003824127	-0.42888656	
C12	-0.00079287	12.1124783	
A			0.155198
n			10.704
Сьм	33.08		
Q (kJ/mol)	-	387.17	439.64
Slope	1	0.9846	1
Intercept (MPa)	-0.346	4.506	-0.045
R <sup>2</sup>	0.973	0.962	0.971
SD (MPa)	7.08	8.40	7.31
ME (MPa)	0.0001	0.101	0.005

Table 3. Least square fit (LSF) parameters and results for various primary creep models for tx>10 and
450 -500°C data sets

# **Conclusions and Future Work**

Time does not allow full discussion of the limitations primary creep models reported here, since they remain work in progress. Briefly one major issue is the absence of long  $t_x$  data, say up to at least 20,000 h. A second issue is whether or not the primary creep data can be scaled with tensile data, like  $\sigma_y$ , in terms of the normalized or threshold stress approaches, since the 8 heats of Eurofer97 here had very similar static strength properties. Note, it would even be useful to see if the LMP model  $\sigma$  could also be ratioed based on relative tensile properties for heats with different  $\sigma_y$  and  $\sigma_u$ . To address these issues, and to fine tune the models, we will compare the results on Eurofer97 with other 9CrW TMS steels, and more importantly to the enormously larger database on Grade 91 9CrMo steels including modified variants (e.g., Grade 92 NF616) and heat treatments with higher and lower strength levels.

Another huge issue is the softening experienced by 9CrW and 9CrMo steels in irradiation service at temperatures as low as 400 to 450°C.

In the interim, we recommend fusion designers use the unconstrained  $\sigma/\sigma_y$  model fit to the constrained database to predict the nominal  $\sigma(\varepsilon_x, t_x, T)$  for *unirradiated* 9CrW steels, using the parameters in Table 3. Notably, Wilshire has championed a  $\sigma/\sigma_u$  normalization for 9CrMo alloys [9]; he argues that this approach has been a great success for standard creep properties, like minimum rates and rupture times (to our knowledge he did not treat primary creep properties). The  $\sigma/\sigma_y$  model results can be checked against those for other models, as shown in Table 4. Alternatively, the designer might choose the lowest value of the 3 predicted  $\sigma$ . Finally, design assessments should include at least -20 MPa margin in determining  $\sigma$  allowables, which are included in Table 4.

Temperature, ºC	LMP Model (MPa)	σ/σ <sub>y</sub> Model (MPa)	σ – Cσ <sub>y</sub> Model (MPa)
450	252	248	230
500	167	169	179

Table 4. Predicted allowable stress (MPa) for 1% strain at 20,000h at 450 and 500°C

Finally, we note that irradiation creep and void swelling also will contribute to dimensional instabilities. The combination of these instability mechanisms, including potential stress effects on swelling, will be addressed in future research.

### Acknowledgments

We gratefully acknowledge the support provided by U.S. Department of Energy through the Office of Fusion Energy Sciences (8-442520-22419-3).

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# **1.7 CONSTITUTIVE MODELS FOR HARDENING OF TEMPERED MARTENSITIC STEELS IRRADIATED AT 300 TO 500°C UP TO HIGH DPA AND He**—T. Yamamoto, G.R. Odette (University of California, Santa Barbara)

### OBJECTIVE

The objective of this work is to develop models of irradiation effects on the constitutive properties of 9Cr tempered martensitic steels, including the effects of He and nanoscale precipitation at high dpa.

### SUMMARY

We update irradiation hardening models for 9Cr tempered martensitic steels (TMS), based largely on the UCSB database, which currently contains 2334 tensile and 353 hardness data and 382 microstructural data points. This database mainly includes results from neutron (NI) and spallation proton (SPI) irradiations. The expanded database is used to fit phenomenological models of vield stress changes ( $\Delta \sigma_v$ ) as a function of the NI and SPI dose (in displacement-per-atom, dpa), irradiation (Ti), test temperatures (Tt) and He concentration (He). Notable advances include: a) update of predictive dpa damage dominated  $\Delta \sigma_v$ (dpa, T<sub>i</sub>, Tt) models, including demonstration and quantification that 9Cr TMS continue to harden, after an intermediate dpa plateau, at rates that are likely linked to minor alloy solute contents; this is likely in association with increasing segregation driven nanoscale precipitation of MnNiSi phases on dislocations; b) refinement of high T<sub>i</sub> softening rates in dpa dominated irradiations; c) quantification of high He contributions to hardening, above an  $\approx$  500 appm threshold, as a function of a wide range of T<sub>i</sub>, dpa and He (appm/dpa); d) quantification of the effect of high He on the post yield flow stress ( $\sigma_{\rm fl}$ ) in reducing the irradiation induced loss of strain hardening; e) refinement of the He bubble hardening factor ( $\alpha_{b}$ ) and comparison of  $\alpha_b$  to atomistic models; e) dispersed barrier modeling of in situ helium injection microstructure hardening, including high He effects on enhancing loops and loop strengthening factors, which, along with bubble contributions, result in predictions that are consistent with observed  $\Delta \sigma_{v}$ .

### PROGRESS AND STATUS

### Introduction

An important objective for the fusion materials research is to develop quantitatively predictive models for irradiation induced changes in 9Cr TMS constitutive properties as a function of the combination of all significant metallurgical and irradiation variables. The metallurgical variables include the start-of-life alloy composition, microchemistry and microstructure, including the effects of product form (weld and base metal) and thermo-mechanical processing treatment (TMT) history. The primary irradiation variables include irradiation temperature (T<sub>i</sub>), stress and the total and rates of production of damaging species, including for displacements-per-atom (dpa), helium (He), hydrogen (H) and a range of solid transmutation products (appm). Post-irradiation testing and data analysis variables are also significant. For example,  $\Delta \sigma_v$  depends on the test temperature ( $T_t$ ) and strain rate ( $\epsilon$ ) [1,2]. Ultimately linked multiscale models will sequentially relate: a) the primary variables to microstructural evolutions; b) the effects of these evolutions on fundamental structure-sensitive constitutive and local fracture properties; c) and the consequences of changes in these fundamental properties to more complex engineering properties, like shifts in fracture toughness Master Curve reference temperatures,  $\Delta T_o$ , or corresponding Charpy shifts,  $\Delta T_c$ . [1,2]. We have continued to accumulate tensile and other mechanical property as well as microstructure data, with a special emphasis of the hardening and embrittlement effects of high concentration of He that persists even at high temperature. High He also reduces the loss of strain hardening generally observed in neutron-only (dpa dominated) irradiated TMS [3]. This is significant since, for example, engineering tensile ductility is enhanced and changes in the average flow stress between 0 to 10% plastic strain are more directly correlated to hardening induced  $\Delta T$  then  $\Delta \sigma_v$  [4]. Thus, true stress-strain curves are also analyzed to quantify He effects on  $\Delta \sigma_{fl}$ . Another focus is the re-initiation of hardening, following an intermediate dpa plateau, that is now being observed at higher dpa, likely in association with the nm-scale MnNiSi precipitates (MNSP) that form and grow on dislocations.

### Approach to developing hardening $\Delta \sigma_y$ (dpa, He, T<sub>i</sub>, T<sub>t</sub>, material) models

The low He dominated  $\Delta \sigma_y$ -dpa trends are separated by irradiation type and temperature. The alloys are divided into four broad categories: a) F82H; b) Eurofer97; c) other 9CrW steels containing 1-2%W; and d) 9CrMo steels containing 0.5 to 1.5%Mo. The following approach was taken to derive the hardening models:

1) The displacement damage (dpa) induced hardening models,  $\Delta \sigma_{yn}$ (dpa, T<sub>i</sub>, T<sub>t</sub>, material), were refit to the updated NI (low He) data for the various alloy subsets, distinguished by the alloy class, as well as the irradiation and test temperatures T<sub>i</sub> and T<sub>t</sub>. The new model is a combination of simple saturating Makin and Minter model [5,6] and a Mn-Ni-Si precipitation (MNSP) hardening model at high dose as:

$$\Delta \sigma_{yn} = \Delta \sigma_{ys} \left[ 1 - \exp(-dpa/dpa_o) \right]^{1/2} + C_{yp} \left( \sqrt{dpa} - \sqrt{dpa_p} \right)$$
(1)

Here  $\Delta \sigma_{ys}$  is initial saturation hardening, dpa<sub>o</sub> is the dpa to reach 80% of  $\Delta \sigma_{ys}$ ,  $C_{yp}$  is precipitate hardening coefficient (MPa/√dpa) in the √dpa dependent term, and dpa<sub>p</sub> is the onset dose for precipitation hardening. Simpler form without the MNSP term or simple linear C√dpa type fits were adopted in some cases that were indicated by the data, like at high Ti, or with limited number of data points at lower dpa. Figure 1 shows an example of  $\Delta \sigma_y$  versus √dpa for NI of Eurofer97 irradiated at ≈ 300°C up to ≈ 80 dpa. There, stages of  $\Delta \sigma_y$ (dpa) are observed: an initial rapid increase up to a plateau; b) an intermediate dpa  $\Delta \sigma_y$  plateau; and, c) re-initiation of linear increase of  $\Delta \sigma_y$  with dpa above ≈ 16 dpa.



**Figure 1.** An example of  $\Delta \sigma_y$  versus  $\sqrt{dpa}$  for NI of Eurofer97 irradiated at  $\approx 300^{\circ}$ C up to  $\approx 80$  dpa for room temperature (RT) tests.

2) The effect of high He was estimated from the SPI data,  $\Delta \sigma_y$ (dpa, He, T<sub>i</sub>, T<sub>t</sub>, material), by simply decomposing the dpa induced and He induced dispersed barrier hardenings,  $\sigma_n$  and  $\sigma_{He}$ , as:

$$\Delta \sigma_y$$
(dpa, He, T<sub>i</sub>, T<sub>t</sub>, material) = S ( $\sqrt{\sigma_N^2 + \sigma_{He}^2}$ ) + (1-S)( $\sqrt{(\sigma_N^2 + \sigma_{He}^2 + \sigma_U^2)} - \sigma_U$ ) (2)

Here, S controls mixture of linear-sum (LS) and root-sum-squares (RSS) super-positioning as described in more details below,  $\sigma_U$  is pre-existing feature hardening of  $\approx$  203MPa. S = 0.2, typically found in microstructure based hardening models also described below is used for simplicity.

3)  $\sigma_{He}(He, ...)$  is estimated as the difference between SPI and NI data points for a range of He and  $T_i \approx T_t$ .

4) dpa induced  $\Delta \sigma_y$ (dpa, T<sub>i</sub>, T<sub>t</sub>, material) and He hardening  $\sigma_{He}$ (He, ...) models are super imposed to constitute a model  $\Delta \sigma_y$ (dpa, He, T<sub>i</sub>, T<sub>t</sub>, material) describing hardening for various dpa and He conditions.

### He effects on flow stress hardening $\Delta\sigma_{\rm fl}$

The flow stress  $\sigma_{fl}$  is taken as the average of the true stress – strain,  $\sigma(\epsilon)$ , from  $\epsilon = 0$  to 10% plastic strain. Deformation in tensile tests takes place under necking conditions since the uniform elongation for NI steels

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is typically < 1%. We previously developed an iterative finite element (FE) inverse method to derive  $\sigma(\varepsilon)$ beyond the necking [3,7]; multiple iterations require a large number of FE runs. Here new simplified method was used to derive  $\sigma_{fl}$ , which works well, at least for 0 to 10%  $\sigma_{fl}$  strain range, as shown by comparisons with cases where the iterative FE was applied previously. Details of the new method will be described in a future report. Here the derived true  $\sigma(\varepsilon)$  were used to estimate  $\Delta \sigma_{fl}$  in comparison to  $\Delta \sigma_{v}$ . It was found that  $\Delta \sigma_{\rm fl} / \Delta \sigma_{\rm v}$  depends on He.

### Microstructure based hardening models

Hardening Contributions of Individual Features: As has been reported previously simple dispersed obstacle individual hardenings were super-positioned appropriately considering the dislocation bowing limits of multiple features, like various precipitates, dislocation loops, bubbles and voids. The individual models for isolated obstacle hardening, based on single dislocation obstacle interactions, can be expressed in various ways but the most frequent and simplest formulation is [8.9]

$$\sigma_{j} = M\alpha_{j}(r_{j})Gb/(L - 2r_{j})$$
(3a)

Here, the spacing between the centers of the obstacles is

$$L \approx 1/\sqrt{(2N_jr_j)}$$
(3b)

Here N<sub>i</sub> and r<sub>i</sub> are the feature number density and radius, respectively. The  $\alpha_i$  is the obstacle-dislocation interaction strength parameter, M ≈ 3.06 term is the polycrystalline Taylor factor for bcc lattices, G is the shear modulus ( $\approx$  82000 MPa at 25°C) and b = 0.248 nm is the dislocation Burgers vector. Here we focus on refining the bubble  $\alpha_b$ .

Strength Superposition Models: Earlier computer simulations showed that the net  $\Delta \sigma_y$  based on the individual yield stress contributions from combinations of weak ( $\alpha_w < 0.05$ ,  $\sigma_w$ ), medium (0.05 <  $\alpha_m < 0.6$ ,  $\sigma_m$ ) and high ( $\alpha_s > 0.6$ ,  $\sigma_s$ ) strength obstacles can be described by a simple fitted analytical expression interpolating between root sum square (RSS) and linear sum (LS) rules [7]:

$$\Delta \sigma_{y} = \sigma_{w} + (1-S)(\sigma_{m}^{2} + \sigma_{s}^{2})^{1/2} + S(\sigma_{m} + \sigma_{s}) - \sigma_{s}$$
(4)

Here the superposition factor S is [9-11]

$$S \approx \alpha_{so} - \alpha_{mo} (5.0 - 3.3\alpha_{so})$$
<sup>(5)</sup>

Here the  $\alpha_{io}$  are for an isolate single obstacle based on the critical angle when dislocations bypass the obstacle. The strength factors  $\alpha_i$  used in Equation 1 are for randomly distributed obstacles, which is related to α<sub>io</sub> by [6,12].

$$\alpha_{i} = \alpha_{io}^{3/2} (\alpha_{io} < 0.64) \text{ or } 0.8 \alpha_{io} (\alpha_{io} \ge 0.64)$$
 (6)

Thus, obstacles with similar strengths can approximately be described by an RSS superposition model, while those with very different strengths (very low and high) come closer to a LS law. The superposition of the strengthening contributions of medium strength and strong obstacles falls in between.

The model has been calibrated to neutron irradiated Fe-Cr alloys and TMS, to determine the  $\alpha_j$ , for dislocation loops (DL), solute clusters and G-phase precipitates (SC and P), α' Cr-rich phases and preexisting strong obstacles (Mo<sub>2</sub>C and network forest dislocations), as shown in Table 1. G-phase like MnNiSi precipitates hardening is based on Russel-Brown model calibrated by database for reactor pressure vessel (RPV) steels. The models were also calibrated to hardening in SPI and post-irradiation annealed (PIA) SPI microstructures to determine the  $\alpha_b$  for He bubbles and small defect clusters. Here, refined  $\alpha_b$  were used

to model  $\Delta \sigma_y$  from the observed microstructure formed by in-situ He injected (ISHI) at high T<sub>i</sub>, where NI (low He) would lead softening.

Obstacle	Strength, $\alpha_j$	Value
Dislocation loop	α <sub>DL</sub>	0.224
Small solute cluster	αsc	0.224
α' precipitate	$\alpha_{\alpha'}$	0.040
G-phase precipitate	α <sub>p</sub>	≈ 0.26
Pre-existing (like from	αυ	0.8
Mo <sub>2</sub> C)	σu	203 MPa

**Table 1.** Previously determined  $\alpha_j$  values and pre-existing obstacle hardening ( $\sigma_u$ )

The calculated ISHI  $\Delta \sigma_y$  was used to help estimate the T<sub>i</sub> dependence of He contributions to hardening. The  $\alpha_b$  was compared to values independently reported elsewhere, and to the predictions of MD atomistic models.

# Results

# Hardening models for dpa dominated neutron irradiation data

Figure 2 summarizes the neutron dpa induced  $\Delta \sigma_{y,N}$  versus  $\sqrt{dpa}$  trends for the material groups: a) F82H; b) Eurofer 97; c) 9Cr-1-2W steels; d) 9Cr-1Mo steels; and temperature bins 1) T<sub>i</sub> < 225°C; 2) 250 ± 25°C; 3) 310 ± 35°C; 4) 360 ± 15°C; 5) 400 ± 25°C; 6) 450 ± 25°C; 7) 500 ± 25°C; and 8) > 525°C. Fitting to Eq.(1) was carried out when the data subset is large enough to derive a pertinent saturating trend. A simple linear fit was used for high temperature cases where softening takes place, and saturation behavior is not observed.

The  $T_i = 310 \pm 35^{\circ}C$  F82H and Eurofer 97 result in good fits to the saturating-rehardening trend is seen in Figure 2. In other cases, the  $\Delta\sigma_y$  data are generally fewer and more scattered. Table 2 summarizes the best-fit parameters for the temperature bins for all the alloy groups. The F82H (2a), Euofer97 (2b) and 9CrW (2c) alloys have a similar saturation  $\Delta\sigma_{ys} \approx 433 \pm 10$  MPa and is highest in the 9CrMo (2d) alloys. However, the dpa<sub>o</sub> is significantly lower for Eurofer 97 (the initial hardening rate is faster). The MNSP hardening is larger in Eurofer 97 than in F82H, with both a lower dpa<sub>p</sub> and a higher  $\Delta\sigma_{yp}$ -hardening rate. The  $\Delta\sigma_{yp}$ -hardening rate is even higher in the 9Cr2W steels, and highest in the 9CrMo alloys. Typical *nominal* Mn, Ni and Si contents in F82H are 0.12%, 0.02% and 0.1%, while those in Eurofer 97 are 0.5%, 0.02, and 0.05%, respectively. The difference in Mn content is considered to be the main reason for the larger MNSP  $\Delta\sigma_{yp}$  in Eurorer97. The MNSP hardening is even larger in the 9CrW and 9CrMo steels. The key 9CrW alloy contains 0.5% Mn, 0.02% Ni and 0.2% Si, while the 9Cr-1Mo alloys contain more Ni  $\approx 0.2$  and Si  $\approx 0.3$ , leading to the highest  $\Delta\sigma_{yp}$  hardening rate. Note these compositions, in wt.%, are nominal and vary considerably, in the range of several tenths of a percent. More detailed analyses of the MNSP hardening including alloy chemistry dependence will be carried out in the future research.

There are a significant number of F82H  $\Delta\sigma_y$  data points at higher T<sub>i</sub> up to  $\approx 600^{\circ}$ C. While highly scattered, the average trend indicates that  $\Delta\sigma_y$  approaches 0, or slightly softens, at T<sub>i</sub> = 400 ± 25°C; and softening is dominant at higher T<sub>i</sub>. While Eurofer 97 has very limited number of data in the other T<sub>i</sub> bins, the  $\Delta\sigma_y$  are generally consistent with those in the F82H and 9CrW steels. The  $\Delta\sigma_y$  trends for all 9CrW steels in Figure 2c shows: a) the initial  $\Delta\sigma_y$  versus  $\sqrt{d}$  aloge decreases with increasing T<sub>i</sub>; b) the saturation  $\Delta\sigma_{ys}$  increases with temperature at low T<sub>i</sub>, peaks at T<sub>i</sub> = 310 ± 35°C bin, then decreases, transitioning to softening around T<sub>i</sub> = 450 ± 25°C. Trends in 9CrMo steels in Figure 2d also show that the systematic T<sub>i</sub> dependence is similar to that in 9CrW steels, including a hardening to softening transition around T<sub>i</sub> = 450 ± 25°C.

Figure 3 shows guidelines summarizing the temperature dependence of the model parameters: a)  $\Delta\sigma_{ys}$ ; b) dpa<sub>o</sub>; c) the  $\Delta\sigma_{y}$ -hardening slope (initial slope for the saturating curve or the linear fits). The T<sub>i</sub> dependence for  $\Delta\sigma_{ys}$  and dpa<sub>o</sub> were drawn for 9Cr-1-2W and partially for F82H, but the other alloy groups also follow the similar T<sub>i</sub> trends. The T<sub>i</sub> dependence of hardening slope is also general similarity in all the alloy groups, while softening may start at a lower T<sub>i</sub> in F82H and a higher T<sub>i</sub> in 9Cr1Mo as indicted by the  $\Delta\sigma_y$  at T<sub>i</sub>=400°C. Softening rates ( $\Delta\sigma_{y,N}/\sqrt{dpa}$ ) do not systematically change for T in individual alloy datasets, but the linear fitting gives the following T<sub>i</sub> dependence:

 $\Delta \sigma_{y,N} / \sqrt{dpa} = 26.18 - 0.0800 T_i \text{ (for F82H)}$  (7a)

 $\Delta \sigma_{y,N} / \sqrt{dpa} \approx 18.0 - 0.0525 T_i$  (for all alloys combined) (7b)

Alloy group	dpa₀	$\Delta\sigma_{ys}$	dpap	$\Delta\sigma_{yp}$	Std. dev.
Euroer97	4.5	437.0	10.1	19.4	32.9
F82H	8.1	424.1	25.1	8.5	43.0
All 9CrW	6.8	436.7	12.0	32.4	61.0
9Cr-Mo	7.7	539.8	4.3	38.1	47.1

**Table 2.**  $\Delta \sigma_{y,N}$ (dpa) model parameters for 310±35°C data sets



**Figure 3.** the temperature dependence of  $\Delta \sigma_{y,N}$ (dpa) model parameters: a)  $\Delta \sigma_{ys}$  and b) dpa<sub>o</sub>, as well as c) hardening slope (initial slope for the saturating curve or that of linear fits).

### He contributions to the SPI $\Delta \sigma_y$

Figure 4 shows the isolated He hardening  $\sigma_{He}$  decomposed based on Eq.(2) super-positioning for SPI irradiated F82H and Eurofer97 alloys [13-19] as a function of  $\sqrt{He}$  (appm<sup>1/2</sup>) for T<sub>i</sub> 100°C groups. Due to large uncertainties and lack of relevance, the data for T<sub>i</sub> <  $\approx$  100°C and 9Cr1Mo alloys were excluded. The general softening trends shown in Figure 3c is used for  $\Delta\sigma_{y,N}$ (dpa, T<sub>i</sub>, T<sub>t</sub>) for T<sub>i</sub> = T<sub>t</sub> > 450°C. Note, high He SPI  $\Delta\sigma_y$  data are also limited by linear elastic fracture. The elastic tensile fracture data indicate a large reduction of intergranular fracture stress, which will be used in fracture models to be reported in the future. Figure 4 also includes an isolated He hardening decomposed for microstructure observed in ISHI irradiated Eurofer97 at 500°C to 21.2 dpa and 1230 appm He [20]. Obtained  $\sigma_{He} - \sqrt{He}$  trends are similar for F82H and Eurofer97, so the combined trends are that  $\sigma_{He} \approx 0$  at He <  $\approx$  433 appm, then increase  $\approx$  linearly with  $\sqrt{He}$  as:



**Figure 4.** a) Isolated He hardening  $\sigma_{He}$  for SPI irradiated F82H and Eurofer97 alloys shown for T<sub>i</sub> groups with overall fitting for He > 500. Open triangle is for a hardening estimated for the microstructure observed in ISHI irradiated Eurofer97 at 500°C to 21.2 dpa and 1230 appm He; b) examples of decomposed  $\sigma_{He}$  from SPI  $\Delta \sigma_y$  at various T<sub>i</sub> in relation to low He  $\Delta \sigma_y$ (T) trend.

Combining  $\sigma_{\text{He}}(\text{He})$  in Eq(8) with the neutron only  $\Delta \sigma_{y,N}(\text{dpa, T}_i, \text{T}_i)$  models can generate  $\Delta \sigma_y$  prediction models for various He/dpa cases. For example, Figure 5 shows a model for F82H at He/dpa = 80, corresponding to a typical SPI condition at Ti = 300 to 500°C. SPI measured  $\Delta \sigma_y$ , plotted along are in good agreement with the models.

### High He effects on flow stress changes

The uniform engineering strains in tensile tests on neutron irradiated TMS (and other metals and alloys) are typically < 1%, due to plastic instabilities and immediate necking. However, in SPI steels, with high He, uniform-engineering strains are typically several percent (necking is delayed). Figure 6a shows true stress-strain curves [3,14-15],  $\sigma(\epsilon)$ , used to estimate true flow stress changes. The unirradiated  $\sigma(\epsilon)$  shows typical strain hardening. The NI  $\sigma(\epsilon)$  shows slight initial softening. The  $\sigma(\epsilon)$  with high He concentration do not show immediate drop after yielding suppressing loss of strain hardening, which is generally observed after neutron only irradiation. The effects result in gradual but continuous increase in  $\Delta\sigma_{\rm fl}$  to  $\Delta\sigma_{\rm y}$  ratio as shown in Figure 6b. This will lead a larger transition temperature shift in fracture toughness, since  $\Delta\sigma_{\rm fl}$  is more directly correlated to  $\Delta T_0$ [4]. It is notable that the total elongation decreases a lot – may be IG fracture occurs after a little strain hardening.







**Figure 6.** a) True stress-strain curves of Eurofer 97 after various neutron or SPI irradiations; b) the average 0 to 10% strain flow stress change ( $\Delta \sigma_{\rm fl}$ ) to  $\Delta \sigma_{\rm y}$  change ratio as a function of the He concentration.

### **Microstructure-Hardening Model**

Our database includes 31 cases where hardening measurements (by hardness or tensile tests) are accompanied by fairly comprehensive microstructural data sets; 15 cases are for post-STIP irradiation annealed microstructure, where only He bubbles are observed. Figure 7 shows the corresponding derived bubble obstacle strength,  $\alpha_b$ , compared to the values reported by Pen, Vieh and others [19,21-23]. The PSI  $\alpha_b$  are, on average, 27% lower than ours. This is due to different assumptions about strength superposition. The PSI analysis did not consider pre-existing hardening features for the annealed bubble only case and used an RSS superposition law in the case of multiple hardening features. In contrast, we used to mix LS and RSS superposition procedure, accounting for  $\approx$  200 MPa of pre-existing obstacle hardening. Figure 7b shows  $\alpha_b$  as a function of the bubble size compared to the predictions of MD simulations by Osetsky et al. [24]. The MD results for isolated bubbles were converted to randomly distributed bubbles using weak obstacle theory of  $\alpha_b^{3/2}$  [12]. Our results are a factor of 1.29 higher than the MD based values, assuming the Osetsky  $r_b$ -dependence, while the PSI results are lower by factor of 0.87. The heavy dashed curves are simple linear fits of  $\alpha_b$  over the range of  $r_b$ . Given various sources of uncertainty in the data, analysis and model, these results are remarkably consistent, hence, an average  $\alpha_b \approx 0.19$  is appropriate for in modeling He bubble contributions to  $\Delta \sigma_y$ .



**Figure 7.** a) Comparisons of UCSB versus PSI estimates of bubble obstacle strength factors ( $\alpha_b$ ) for individual post-SPI annealed (PSA) conditions, with only bubbles in the microstructure; and, b) Osetsky's MD predictions  $\alpha_b$  as a function of the bubble diameter [21] compared to the UCSB and PSI evaluations along with heavy fitted lines. Note the Figure 7b has one more UCSB data point than in 7a.

The size dependent and average  $\alpha_b$  were applied to the larger dataset, including as-irradiated conditions, with defect clusters (small solute segregated loops) as well as bubbles. Fitting size-independent single values of  $\alpha_b$  and  $\alpha_{dc}$  resulted in better statistics than using the  $\alpha_b(r_b)$  normalized Osetsky relation determined above. The best fit defects cluster  $\alpha_{dc} \approx 0.328$  and bubble  $\alpha_b \approx 0.17$ , only slightly lower than the average of 0.19 in the case of PIA conditions only. In the case of microstructures with dislocation loops,  $\alpha_{dc}$  and  $\alpha_b$  were found to be 0.354 and 0.165, respectively, with a fixed loop  $\alpha_l = 0.22$ , as previously derived from NI (low He) data. A fitted  $\alpha_l$  increases to an arbitrary limit of 0.5, for fixed  $\alpha_b$  and  $\alpha_{dc}$  of 0.17 and 0.35, respectively. The reason for such a large  $\alpha_l$  is not clear, but may be associated with a loop bubble complex, which are often observed, that they are a stronger obstacle than either bubbles or loops alone. Bubble-loop complex mechanical stability may also be signaled strain hardening versus strain softening behavior with and without high He as described above. These results are summarized in Table 3.

5	Strength, a				Datasets us		
Bubble, α <sub>b</sub>	Defect cluster, α <sub>dc</sub>	Disl. Loop, αι	S.D. MPa	PIA	As-irrad. (no DL)	As-irrad. (w/ DL)	Methods
0.19 (avg.)	N/A	N/A	n/a	х			$\alpha_b$ derived from individual $\Delta H$ - microstructure pairs
0.17	0.33	N/A	127	Х	Х		fitted $\alpha_b$ and $\alpha_{dc}$
0.17	0.35	0.22	192	Х	Х	Х	$\alpha_b$ , $\alpha_{dc}$ fitted with $\alpha_l$ fixed.
0.17	0.35	0.5	163	X	Х	Х	$\alpha_{b}, \alpha_{dc}, \alpha_{l}$ ( < 0.5) fitted

Table 3 Sun	mary of strengt	h factor quise	d/determined t	for various	datasets
Table J. Our	innary or subrigu	Tactor uluse	u/uetermineu i		ualasels

A comprehensive microstructural dataset on bubbles, voids and dislocation loops was obtained from an ISHI irradiation carried out in HFIR to 21 dpa and 1230 appm He at 500°C [20]. The ISHI method injects a uniform concentration of He to a depth of  $\approx 6 \ \mu m$ . Thus, the effects of He can be determined by comparing the microstructures in the implanted and un-implanted (NI only) regions. Thus the  $\alpha_i$  for the various features can be used in dispersed barrier hardening models described above to calculate  $\Delta \sigma_y$ . Table 4 summarizes the ISHI data and model predictions for cold worked F82H and Eurofer97. In the most relevant case of Eurofer97 the model predicts 318 MPa hardening, 284MPa more than neutron only case of 34 MPa. As shown in Figure 4a and 5e, this is remarkably consistent with the SPI data and the value predicted by Equation 8.

Table 4. Summary of the microstructure and predicted hardening in F82H-M3 (20%CW) and Eurofer 97
after ISHI and NI in HIFR

	Irradiation				Predic-	Dislocation loop		Void		Bubble	
Alloy	Туре	Ti ℃	Dose dpa	He appm	ted ∆σ <sub>y</sub> MPa	<d> nm</d>	N 10 <sup>21</sup> m <sup>-3</sup>	<d> nm</d>	N 10 <sup>21</sup> m <sup>-3</sup>	<d> nm</d>	N 10 <sup>21</sup> m <sup>-3</sup>
	NI	500	21.2		45.9	10.2	2.4			1.3	21.0
F82H M3 (20% CW)	ISHI	500	21.2	1230	459.1	35.0	7.6			2.7	110
	NI	500	21.2		34.3	9.6	2.4				
Eurofer97	ISHI	500	21.2	1230	318.0	28.0	3.9	6.9	7.5	1.8	2.0

### Hardening model predictions for fusion reactor environment

Equation 8 and neutron induced hardening models were combined to predict  $\Delta \sigma_y$ (dpa, He, T<sub>i</sub>, T<sub>t</sub>) for fusion reactor relevant He/dpa = 10 conditions at temperatures from 300 to 500°C by 50°C step as shown in Figure 8 for T<sub>i</sub> = T<sub>t</sub>. Dashed curves are for neutron only cases while solid curves are for fusion conditions.



**Figure 8.** Hardening model  $\Delta \sigma_y$  predictions for F82H at fusion reactor relevant He/dpa = 10 condition for T<sub>i</sub> = T<sub>t</sub> from 300 to 500°C. The solid curves are for fusion relevant 10 appm He/dpa, while the dashed curves are for neutron only (He/dpa  $\approx$  0) conditions.

# Summary and Future Research

We have developed a new toolbox to predict the effects of fission and fusion neutron irradiations on the constitutive properties of 9CrW TMS. The toolbox predicts changes in both yield  $(\Delta \sigma_y)$  and flow  $(\Delta \sigma_{fl})$  stress as a function of dpa, He/dpa, T<sub>i</sub> and T<sub>t</sub>. While not amenable to being described by simple trend curve equations, the model is conveniently coded in an Excel spreadsheet. The model is based on analysis of a large database on mechanical property changes in NI and SPI. It is shown to be in good agreement with the SPI database on high He effects, that was used to quantify the He hardening contributions. This hardening contribution is fairly independent of T<sub>i</sub>, with a threshold at about 400-500 appm, and subsequently scales with the  $\sqrt{He}$ . The mechanical property data analysis was complemented by a calibrated
microstructure property model applied to a ISHI irradiation experiment; the microstructure based prediction of  $\Delta \sigma_y$  is in excellent agreement with the SPI data trends, The model shows that hardening contributions from He are dominated by enhanced dislocation loop formation, with smaller increases from bubbles. The calibrated model, including all of the hardening contributions, was applied to fusion relevant 10 appm He/dpa  $\approx$  10 conditions for F82H (and Eurofer97 at 300°C).

The database also reveals that high He suppresses loss of strain hardening and low uniform strains, typical of NI conditions. The analysis of NI data also reveals hardening that increases at high dpa due to MNSPs, associated with solute segregation to dislocations. The MNSP hardening varies with the steel's impurity/trace element Mn, Ni, Si, P contents. The NI irradiation database also shows that at high temperature the 9CrW steels soften under irradiation, starting at  $T_i$  as low as 450°C, and increasing with dpa. Any significant softening would have enormous structural integrity implications and could severely limit the upper temperature limit for the use of the 9CrW TMS in irradiation service. For example, even modest reductions on strength would have a very larger effect on creep stress allowable [25]

It is important to acknowledge that the database is highly scattered and the various trends that we extracted are not statistically rigorous. The models are also uncertain due to a number of both known and unknown, and unmodeled/untreated physics (such as dislocation loop obstacle strength in He rich environments). However, further discussion of these complex issues will require additional modeling and experimental research. For example, nanoindentation measurements of hardening in the ISHI specimens would be very useful.

Another focus of future research will be to combine the constitutive model presented here, with a treatment of grain boundary weakening by He leading to intergranular fracture in a fracture toughness embrittlement model accounting for the severe synergistic effects of high He [26].

#### Acknowledgements

The authors explicitly acknowledge the extensive research that produced the data analyzed in this report and thank the large number researchers around the world for their sustained contributions to the development of materials for fusion energy. Particular thanks go to Dr. Michael Reith and his FZK/KIT colleagues for generating the Eurofer97 database. We gratefully acknowledge the support provided by U.S. Department of Energy through the Office of Fusion Energy Sciences (8-442520-22419-3).

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2. ODS AND NANOCOMPOSITED ALLOY DEVELOPMENT **2.1 Fe-Cr-AI ODS ALLOYS FOR FUSION REACTOR APPLICATIONS**—Sebastien Dryepondt, Caleb Massey, K.A. Unocic (Oak Ridge National Laboratory)

# OBJECTIVE

The goal of this task is to develop and characterize new oxide dispersion strengthened (ODS) Fe-10/12Cr-5/6Al-0.3Zr +  $Y_2O_3$  steels containing a high density of nano oxides for superior irradiation and creep performance. The formation of an Al-rich scale will provide great compatibility with Pb-Li at 600-800°C.

# SUMMARY

The dual coolant lead-lithium (DCLL) blanket concept for DEMO-type fusion reactors requires that materials with good Pb-Li compatibility and alumina-forming alloys will likely be required at T>550°C. This is due to the formation of a "semi-protective" LiAIO<sub>2</sub> oxide layer [1,2] leading to better Pb-Li compatibility in comparison with chromia forming alloys. Oxide dispersion strengthened (ODS) FeCrAI are, therefore, prime candidate materials for fusion reactor operating at T >650°C due to their superior irradiation and creep resistance in addition to their good Pb-Li compatibility. The ORNL has developed several advanced ODS Fe-10/12-Cr-5/6AI-0.3Zr + 0.25Y<sub>2</sub>O<sub>3</sub> alloys based on a systematic analysis of the processing parameters-microstructure-properties relationship [3-6]. The ODS FeCrAI steels with high temperature creep strength are also of interest for accident tolerant fuel cladding applications [7], and several studies have shown that the creep deformation mechanisms vary significantly based on the testing conditions [8-11]. For the range of stress and temperature (<800°C) of interest for fusion reactor, grain boundary sliding (GBS) associated with the formation of voids was identified as the key damage mechanism, but dislocation motion to release stress concentration from GBS is thought to be the creep limiting factor [11]. The nano precipitates play a major role in hindering dislocation motion and significant work has been conducted in FY20 to assess the stability of the ODS FeCrAI microstructure after long-term creep exposure.

# PROGRESS AND STATUS

#### Experiments

CM01 or CM08 Zoz Simoloyers were used to ball mill under Ar atmosphere for 40h either gas atomized Fe-10Cr-6.1Al-0.3Zr (wt.%) powder with nanocrystalline  $Y_2O_3$  or Fe-12Cr-5Al (wt%) powder with both  $Y_2O_3$ and ZrO<sub>2</sub>. The first powder was extruded at 900°C after annealing for 1h using a 2" OD mild steel extrusion can (106ZY9C steel) while the second powder was extruded at 950°C after annealing for 1h at the same temperature using a 4" OD extrusion can and a 2"x1.5" rectangular die. Compositions of the two alloys are given in Table 1.

Sample	Mill	Fe	Cr	AI	Zr	Y	0	С	N
125YZ	CM08	77.84	11.62	9.46	0.17	0.1	0.63	0.11	0.06
106ZY9C	CM01	77.48	9.72	11.58	0.16	0.12	0.42	0.07	0.34

Table 1. Chemical compositions of powders (at.%) and alloys provided by DIRATS using ICP-OES

Creep testing was performed at 700 and 800°C on sub size SS3-type dog bone specimens 7.62mm thick for the tensile specimens and 2mm thick for the creep specimens. Characterization of the alloys was mainly conducted using scanning or transmission electron microscopy (SEM/TEM) methods.

# Results

#### Long-term creep tests

Long-term creep results for the 125YZ and 106ZY9C steels are compared in Figure 1a with ODS FeCrAI results from Kimura et al.[12], showing the superior creep resistance of these two ODS FeCrAI steels. All the tests were interrupted before failure for microstructure characterization, so the creep lifetime is potentially significantly longer than the reported data. Jaumier et al. conducted an extensive review of the creep properties of various FeCr ODS steels and they summarized the data in a Larson Miller parameter (LMP) versus applied stress plot shown in Figure 1b [12]. Data for the 700°C, 140MPa, 25-26kh tests and 800°C, 100MPa, 6,000h tests were added to highlight the good creep performance of the ODS FeCrAI alloys when compared to ODS FeCr steels.



**Figure 1.** a) Test duration for ODS FeCrAlYZr specimens creep tested at 700°C or 800°C [12]. b) LMP plot comparing various ODS FeCr steels with the 125YZ and 106ZY9C ODS FeCrAl alloys [13].

#### Microstructure characterization

Previous reports highlighted the presence of voids in the 125YZ and 106ZY9C steels after creep testing at 700°C and 800°C (Figure 2). For both steel these voids were often related to alumina stringers at grain boundaries aligned with the extrusion direction. As can be seen in Fig 2c, for the 106ZY9C steel, larger voids were also associated to the presence of AIN clusters observed in the as fabricated steel due to a high N content. A few large voids were also observed in the 125YZ steel in regions with larger grains elongated along the build direction. All these observations are consistent with Ukai et al. results with creep cavities formed at grain boundaries [11].

Estimates of the grain size after creep testing were obtained using the intercept method on pictures such as the ones showed in Figure 2b and 2d. The data summarized in Table 2 shows no significant change in grain size after exposure for 6,000h at 800°C or 26,000h at 700°C.



**Figure 2.** Specimens creep tested at 700°C, 140MPa, a) and b) Back scattered (BSE) SEM micrographs of the 125YZ after 26,000h, c) optical and d) BSE-SEM images of the 106ZY9C specimen after 25,110h.

Table 2.	. Comparison of the grain size before and after creep testing at 700°C and 800°C for the 125Y	Ζ
	and 106ZY9C specimens	

	As Fab	ricated	800°C, 1	LOOMPa	700°C, 140MPa		
	Parallel to ED	Normal to ED	Parallel to ED	Normal to ED	Parallel to ED	Normal to ED	
125YZ	0.27	0.17	0.34	0.29	0.29	0.18	
106ZY9C	0.47	0.4	0.4	0.32	0.57	0.38	

The high creep strength of the two steels is directly related to the nano precipitates and TEM characterization was conducted on the creep specimens to assess the precipitate stability. Figure 3 highlights a high number density of nano precipitates, identified as (Y,AI)-rich oxides, in the 125YZ specimen tested for 26,000h at 700°C, 140MPa. A few course Zr(C,N) precipitates were also observed. Figure 4 reveals similar precipitates for the 106ZY9C specimen creep tested for 25,000h at 700°C, with slightly smaller Zr(N,C) particles. The Y and Zr maps were combined to highlight the co-nucleation of these Y-rich and Zr-rich precipitate size in ODS FeCrAl steels due to the formation of (Y,Zr)-rich nano oxide instead of (Y,AI)-rich oxides in ODS FeCrAl with no Zr [14]. Our results indicate that (Y,AI)-rich nano oxide can form and be very stable in Zr containing steel, leading to superior creep properties. Recent work has shown that the formation or (AI,Y) oxide and (C,N)Zr precipitates or (Y,Zr) oxide is dependent on the C and N concentration in the alloy [15].

Finally, Figure 4c illustrates the pinning of dislocations by nano precipitates confirming that hindering dislocation motion is key to the ODS FeCrAl high creep strength.



**Figure 3.** 125YZ specimen creep tested at 700°C, 140MPa for 26,000h, a) TEM micrograph, b) Chemical maps.



**Figure 4.** 106ZY9C specimen creep tested at 700°C, 140MPa for 25,110h a) and c) TEM micrographs, b) Chemical maps.

# CONCLUSION AND FUTURE WORK

Advanced characterization of two ODS FeCrAlYZr steels creep tested at 700°C and 800°C for 26,000h and 6,000h, respectively, has shown that the microstructure is very stable in that range of temperature. The high number density of (Y,AI) nano oxides led to superior creep resistance comparable to some ODS FeCr steels. The difficulty in manufacturing these steels and the associated cost remains a barrier to the large-scale use of these alloys and additive manufacturing could be a promising route for the fabrication of complex parts using ODS FeCrAl powders.

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3. CERAMIC COMPOSITE STRUCTURAL MATERIAL DEVELOPMENT **3.1 ELECTRIC CURRENT – ASSISTED DIRECT JOINING OF SILICON CARBIDE**—Huaxin Li (Zhejiang University of Technology, Hefei University of Technology), Takaaki Koyanagi, Yutai Kato (Oak Ridge National Laboratory), Caen Ang (University of Tennessee)

#### Abstract of a manuscript in Journal of the European Ceramic Society (In Press, https://doi.org/10.1016/j.jeurceramsoc.2020.05.072.

Conventional direct joining technologies are difficult to use with silicon carbide (SiC) materials, especially for fiber composite forms of SiC, because of the harsh conditions required. To reduce the temperature and/or process time required for the direct joining process, an electric current–assisted joining (ECAJ) method was studied. Joining of low–resistivity grade, nitrogen doped  $\beta$ -SiC was demonstrated at a relatively low nominal temperature of 1750°C with a 10 min hold by enhancing the passage of current through the material. The joining mechanism is discussed in terms of localized overheating and accelerated self-diffusion at the interface. In the case of joining at 2160°C for 1 min, rapid crystal growth of textured SiC was found at the interface. This study indicates that rapid ECAJ-based direct joining is a practical and appropriate method for joining SiC-based materials.

**3.2 GRAIN SIZE DEPENDENCE OF HARDNESS IN NANOCRYSTALLINE SILICON CARBIDE**—Chenglong Pan, Limin Zhang, Liang Chen, Zhiming Li, Ning Liu, Tieshan Wang (Lanzhou University), Weilin Jiang, Wahyu Setyawan (Pacific Northwest National Laboratory)

# This extended abstract presents some of the major results in a paper recently published in the Journal of the European Ceramic Society 40 (2020) 4396-4402 [1].

Grain refinement may have a great potential to enhance the hardness of SiC, which is important to the nuclear applications. This study reports on the response of nanocrystalline SiC (nc-SiC) to nanoindentation using molecular dynamics (MD) simulation. It is found that the hardness of the nc-SiC decreases with decreasing grain size, showing an inverse Hall-Petch relationship. The behavior is primarily attributed to the reduced number of intact covalent bonds with grain refinement. Dislocation nucleation and growth in nc-SiC are strongly suppressed by the grain boundaries (GBs). In addition to the dislocation region in the grains, the indentation-induced amorphization of nanograins proceeds preferentially from the GBs, which is attributed to the lower threshold energies for atomic displacements at GBs. The results provide an improved understanding of the mechanical properties in nc-SiC and other nanostructured covalent materials.





**Figure 1.** Atomic-scale model of nc-SiC indented with a spherical indenter.

**Figure 2.** Hardness versus average gain size of the nc-SiC from simulations (solid symbols) and experiments (open symbols).

Figure 1 shows an atomic-scale model of nc-SiC indented with a spherical indenter. The atoms are colored based on the crystallographic orientations. Figure 2 shows the calculated and experimental hardness values of various nc-SiC together with those of single-crystal SiC (sc-SiC) and amorphous SiC (am-SiC). Both the calculated and experimental hardness of the nc-SiC increases with increasing grain size, which shows an inverse Hall-Petch relationship. The difference between the calculated and experimental results may be attributed to the native defects in the as-grown SiC nanograins prepared by the experimental methods.

Figure 3 shows the indentation-induced dislocation evolution processes in sc- and 12-nm-sized nc-SiC. For sc-SiC, dislocation lines are emitted from the indenter and their size and number increase with increasing indentation depth. In contrast, for the nc-SiC, only a few dislocation lines are emitted from the indenter. The dislocation lines extend towards the GBs and then they are terminated at the GBs. With further indentation, most of the dislocation lines are absorbed by the GBs and at the same time new dislocation lines are emitted from the neighboring grains.





Figure 3. Indentation-induced dislocation activities in (a)-(c) sc-SiC and (d)-(f) 12-nm-sized nc-SiC.



Figure 4. Indentation-induced amorphization in (a) and (b) sc-SiC, and (c) and (d) 4-nm-sized nc-SiC.

The indentation-induced amorphization processes in sc-SiC and 4-nm-sized nc-SiC are shown in Figure 4. Different from the case of sc-SiC, the preferential amorphization is observed at the GBs of nanograins in nc-SiC. In Figures 4 (c) and (d), five different grains beneath the surface of the nc-SiC are labeled with the numbers of #1 through #5. After indentation, it is seen that the amorphization process proceeds from the GBs to the interior of the grains. Consequently, the nanograins become smaller (grains #2-4) with the loading of the indenter until they are fully amorphized (grain #1). The behavior is attributed to the lower threshold energies for atomic displacements at GBs.

#### References

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4. HIGH HEAT FLUX MATERIALS AND COMPONENT TESTING **4.1 FABRICATION OF ULTRASONIC WELDED FUNCTIONALLY GRADED TUNGSTEN-STEEL LAMINATE**—L. M. Garrison, G. Hollyer, W. Zhong, (Oak Ridge National Laboratory), M. Norfolk, J. Wenning (Fabrisonic LLC.)

# OBJECTIVE

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

#### SUMMARY

Tungsten foils were ultrasonically bonded to C1020 steel. Nanoindentation studies were done on a direct tungsten-steel bond (trial 34) and a tungsten-steel bond with an Al1100 interlayer (trial 28). No brittle intermetallic layer was found, and a moderate hardness increase near the interface was observed.

# PROGRESS AND STATUS

A feasibility study for ultrasonic welding tungsten to steel was completed with Fabrisonic LLC. The 34 trials varied the parameters of foil thickness, interlayer material, welding force, vibration amplitude, and other welding parameters. Promising results were obtained for joining tungsten directly to steel and tungsten to steel with an aluminum interlayer. The best direct tungsten-steel trial (test number 34) and aluminum interlayer trial (test number 28) were selected for nanoindentation.

For the direct tungsten-steel trial, 55 indents were performed. For the trial with an Al interlayer, 65 indents were performed . Indents were spaced 50  $\mu$ m apart within rows and each row was spaced 100  $\mu$ m apart. A berkovich tip was used with a strain rate of 0.05 s<sup>-1</sup>. Nanohardness was calculated using a Poisson's ratio of 0.28 for W, 0.29 for C1020 steel, and 0.33 for Al1100 alloy.

There is a slight increase in hardness in the tungsten and steel layers near the interface as compared to their respective values far from the interface (Figure 1a). Nanoindentation also measured a slight hardness increase in the steel near the bond interface in the W-AI-steel sample (Figure 1b). In trial 28, significant visible cracking in the tungsten foil may have decreased the measured surface hardness in that region. Hardness indents that lie on the interface of the W and Al1100 have values between that of the W and Al1100, indicating the interaction volume of the indents on the border had contribution from both materials. The Al1100 layer is too thin to truly distinguish the hardness at its interface versus the bulk value. Previous EDS analysis on these samples showed no intermetallic phase was formed at the interfaces. Work hardening and a decrease in grain size may explain this hardness increase near the interfaces. The SEM imagery showed a decrease in grain size near the interface in steel. The mechanical motion of the ultrasonic bonding appears to have work hardened the tungsten and steel near the interfaces.



**Figure 1.** Nanoindentation patterns and surface hardness. (a) Trial 34-direct tungsten to steel baseplate, and (b) Trial 28-tungsten, aluminum interlayer, and steel baseplate.

**4.2 INVESTIGATION OF TUNGSTEN FOILS FOR USE IN COMPOSITES**—L. M. Garrison, C. Wade (Oak Ridge National Laboratory)

#### OBJECTIVE

The objective of this project is to investigate the properties of tungsten foils use in tungsten-based composites for plasma facing components in fusion reactors.

#### SUMMARY

Both tensile and shear punch tests were previously performed on tungsten foils fabricated by ESPI metals in three different thicknesses:  $25 \ \mu$ m,  $100 \ \mu$ m and  $250 \ \mu$ m. Additional shear punch tests were performed on 100  $\mu$ m foils fabricated by PLANSEE. The raw data previously reported was more fully analyzed and tabulated to show the trends of the foil mechanical properties.

#### PROGRESS AND STATUS

#### <u>Tensile</u>

Tensile tests were performed previously, and the raw data presented in the Fusion Materials Semiannual January-June 2015 report. Here a fuller analysis was done on the data to remove the error from the machine compliance. Two tests were done at each condition, with one representative curve from each condition shown in the Figure 1. Full details of the yield stress (YS), ultimate tensile strength (UTS), uniform elongation (UE) and total elongation (TE) of all tests done are reported in the Table 1.

In order to perform tensile tests on the tungsten foils, custom grips were designed and fabricated. Typical SSJ-2 style samples rely on pressure exerted on the shoulder in order to hold the sample in place. However, because the foils are so flexible, they can deform and slip out of the grips. In order to accommodate the minimal thickness of the foils, custom grips were developed that provide pressure to the tabs instead of to the shoulders. Initial tests confirmed that the specialized grips were successful in holding the samples in place.

The three ESPI foils,  $25 \ \mu$ m,  $100 \ \mu$ m and  $250 \ \mu$ m thick, were tensile tested. The tensile samples were cut in three different directions: parallel, perpendicular, and 45 degrees to the rolling direction. The results for the 25 \ \mum m foil may not be representative due to multiple fractures created on several of the samples. As seen in Table 1, several of the 25 \ \mum m foil trials were brittle. However, some clear patterns were still observed. The parallel samples consistently had the greatest UTS. Other patterns detected were that the perpendicular samples had the least ductility and though the 45-degree samples showed some ductility, they had lower UTS than either the parallel or perpendicular samples.



**Figure 1.** Retained plastic deformation for tungsten foils cut parallel, perpendicular and 45 degrees to rolling direction.

**Table 1.** Full details of tensile tests. Yield strength (YS), ultimate tensile strength (UTS), uniformelongation (UE), and total elongation (TE) reported. For brittle samples, the fracture stress is reported in<br/>the UTS column.

Orientation	Sample ID	YS (MPa)	UTS (MPa)	UE (%)	TE (%)					
25 µm W foil	25 µm W foil									
parallel	W01a-1	1640	1656	0.25	0.41					
parallel	W01a-2	Brittle	1553	0.08	0.11					
perpendicular	W01b-1	Brittle	1406	0.06	0.06					
perpendicular	W01b-2	Brittle	1704	0.06	0.07					
perpendicular	W01b-3	Brittle	930	0.04	0.06					
45 degrees	W01c-1	Brittle	704	0.05	0.07					
45 degrees	W01c-2	1504	1633	1.11	1.32					
100 µm W foil										
parallel	W04a-1	2180	2216	0.85	1.50					
parallel	W04a-2	2139	2215	0.88	1.00					
perpendicular	W04b-1	Brittle	1460	0.1	0.28					
perpendicular	W04b-2	2134	2143	0.23	0.23					
45 degrees	W04c-1	1734	1781	0.89	4.25					
45 degrees	W04c-2	1759	1840	1.07	3.83					
250 µm W foil										
parallel	W10a-1	1987	2016	0.52	0.59					
parallel	W10a-2	1879	1948	0.63	0.73					
perpendicular	W10b-1	1806	1856	1.35	3.58					
perpendicular	W10b-2	1814	1884	0.99	4.36					
45 degrees	W10c-1	1650	1699	0.87	4.02					
45 degrees	W10c-2	1605	1630	0.69	1.31					

# Shear Punch

Shear punch tests were analyzed here to compare shear strength and elongation of different thickness foils. Foils fabricated by ESPI metals and PLANSEE were considered. There were 10 trials of the ESPI

metals at each thickness--25  $\mu$ m, 100  $\mu$ m and 250  $\mu$ m, and three trials for the 100  $\mu$ m PLANSEE foil. From the shear punch tests, shear yield strength (SYS), ultimate shear strength (USS), uniform normalized displacement (UND), and total normalized displacement (TND) were measured.

The foil results were compared by thickness. It was found that there was an increase in both USS and SYS from the thinner foils to the thicker foils (Figure 2). The 100  $\mu$ m foil had higher TND and UND than either the 25  $\mu$ m or 250  $\mu$ m foils, which were brittle and had very low elongation (Figure 3).

The 100  $\mu$ m ESPI foil was then compared to a similar sized foil from PLANSEE. The ESPI foil had a higher USS and SYS than the PLANSEE foil. However, the PLANSEE foil had a slightly higher TND and UND.



**Figure 2.** Shear yield strength and ultimate shear strengths were measured for the four different foils and are plotted versus the foil thicknesses. Line segments were used to connect the average values within the ESPI data set.



**Figure 3.** Shear yield strength and ultimate shear strengths were measured for the four different foils and are plotted versus the foil thicknesses. Line segments were used to connect the average values within the ESPI data set

**4.3 FABRICATION OF FUNCTIONALLY GRADED TUNGSTEN STEEL LAMINATE-ROLL BONDED**—L. M. Garrison, S. K. Wonner (Oak Ridge National Laboratory)

# OBJECTIVE

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

#### SUMMARY

As outlined in previous updates, four tungsten steel laminate composites have been fabricated through the extent of this project. The composites had two different fabrication conditions and four different foil stacking patterns. Although macroscopically the composites were fabricated with either an 80% or 20% reduction in thickness, the deformation of each foil in the composite was not the same. Comparisons of these composites is underway, with focus on comparing the composites' cross sections, and their ultimate tensile strengths (UTS) as they relate to the percentage of tungsten present in the composite. The general trend observed from the tensile tests is that the UTS of the composites increase with the percentage of tungsten, but never reaches the UTS of the individual tungsten foils. In addition to the percentage of tungsten, the UTS depends on the shape of the tungsten foils after processing. The composite with segmented tungsten foils had a lower UTS than would have been predicted only based on the percentage of tungsten.

#### PROGRESS AND STATUS

Four tungsten-steel laminate composites were fabricated, and their details are listed in Table 1. This information includes the specific foil thicknesses, the number of foils, the processing parameters, and different tests conducted for each composite. In all cases, the foils were stacked in an alternating tungsten-steel pattern, and with a consistent orientation of rolling direction so that all foils align. Composite 1 is further separated into three sections; this is because the composition was graded from primarily steel to primarily tungsten by using three separate stacking and foil thickness sections. Composite 1 was produced via a combination of hot pressing and rolling at 1000°C and underwent an 80% reduction in height; Composites 2-4 were made by hot pressing at 1000°C and had a 20% height reduction.

		Foil Thickness (µm)		Number of Foils		
Composite		Tungsten	Steel	Tungsten	Steel	<b>Processing Conditions</b>
	Section 1	250	76	10	10	Hot Pressing /Rolling
1	Section 2	100	100	10	10	at 1000°C
	Section 3	25	250	10	10	80% height reduction
:	2	25	250	10	10	Hot Pressed at 1000°C
3		25	100	38	37	20% height reduction
	4	100	100	40	39	

**Table 1**. Information regarding the four tungsten steel laminate composites investigated, which includes:

 foil thicknesses, number of foils used, and processing conditions

After processing, a section of each composite was observed with scanning electron microscopy (SEM). Composite 1 sections 1-3 are shown in Figure 1A, with section 1 located on the right, section 2 in the middle, and section 3 on the left. Some cracking was observed in section 1 of the composite, within the 250

µm tungsten foil. Section 2 showed no signs of delamination, cracking, or segmentation. In section 3, segmentation of the 25 µm tungsten foils was observed. The 80% reduction appears to have been more than the strain limit of the thinnest tungsten foil, so it was separated into segments during the processing. Overall, a large takeaway for composite 1 is that the foils were deformed drastically, such that the layers form a wave-like interface. This is most noticeable in section 2. Although macroscopically the entire composite was subjected to 80% thickness reduction, the deformation in each foil was not uniform, leading to some specific sections in each layer to be thicker than others.

Figure 1B shows a cross section of composite 2. This composite was processed with only 20% reduction, but its stacking sequence is analogous to section 3 of composite 1, as they both share the 25  $\mu$ m tungsten and 250  $\mu$ m steel foil configuration. The tungsten foils in composite 2 did not undergo the same segmentation exhibited by the foils in composite 1. Here, the tungsten foil remains connected. There is also no cracking or delamination observed in this cross section.

Composite 3 is shown in Figure 1C, and composite 4 is shown in Figure 1D. In both, no segmentation, cracking, or delamination was observed in the samples cut from the bulk composite material. Furthermore, the layers do not exhibit as much varied deformation, and do not share the wavelike layers as seen in composite 1. This can certainly be attributed to the decrease in reduction percentage that these generations of composites underwent; as opposed to 80%, composites 2-4 underwent 20%.



**Figure 1**. SEM Micrographs of (A) Composite 1, (B) Composite 2, (C) Composite 3, and (D) Composite 4 polished cross sections. In all the images the W layers appear brighter and the steel layers appear darker. Note that (A) is at a different magnification than the others.

		Before Processing		After Processing					
		Foil Thickness (µm)		Range of Foil Thickness (μm)		Average Foil Thickness (μm)		Foil Percent Reduction	
Com	posite	Tungsten	Tungsten Steel Tungsten		Steel	Tungsten	Steel	Tungsten	Steel
	Section 1	250	76	129 - 188	44 - 59	168	50	33%	34%
1	Section 2	100	100	44 - 73	23 - 59	57	48	43%	52%
	Section 3	25	250	8 - 18	29 - 69	13	42	48%	83%
	2	25	250	16 - 21	182 - 201	18	194	28%	22%
	<b>3</b> 25 100		100	17 - 22	71 - 81	19	76	24%	24%
	4	100	100	90 - 94	87 - 89	92	88	8%	12%

Table 2	Composite's	foil thick	naccae he	fore and	after d	leformation	via	nrocessing	×
I able 2.	Composite a		1103303 00	fille and	aneru	leionnation	via	hincessing	J

The observed reductions in foil thickness after processing for each composite is compiled in Table 2. As expected, composite 1 underwent much more deformation compared to the other composites; This is fitting since during processing, composite 1 underwent a processing reduction of 80%, and the other composites were reduced 20% of the original height. The general trend is that the steel foil deformed more than the tungsten foil during processing. Comparing section 3 of composite 1 and composite 2, which share the same foil configurations, composite 1 deformed the most. The tungsten foils in section 3 deformed from 25  $\mu$ m to an average of 13  $\mu$ m, which is a 48% reduction, whereas the tungsten in composite 2 exhibited a 28% reduction, deforming from 25  $\mu$ m to 18  $\mu$ m. The steel foil in section 3 composite 1 deformed from 250  $\mu$ m to an average of 42  $\mu$ m in thickness, which is an 83% reduction. In contrast, the steel foil in composite 2 underwent a 22% reduction, deforming to 194  $\mu$ m. Similarly, section 2 of composite 1 and composite 4 can be compared. The tungsten in section 2 exhibited a 43% reduction in thickness, starting at 100  $\mu$ m and deforming to 57  $\mu$ m, whereas composite 4 tungsten foil deformed to 92  $\mu$ m with an 8% reduction. The steel foils are also drastically different in the different composites, with the foil reducing 52% from 100  $\mu$ m to 48  $\mu$ m in composite 1 and undergoing a 12% reduction to 88  $\mu$ m in composite 4.



**Figure 2**. Ultimate tensile strength versus percentage of tungsten. Tungsten foils are shown as diamond markers, and the steel foils are shown in square markers.

Tensile tests were conducted on composites 1, 2, and 4; The uniaxial stress in these tests was applied parallel to the rolling direction of the foils in the composites. The samples' geometry was of the SSJ2 type and so they were 0.5 mm thick. Because of the varying foil thicknesses across the composites, each tensile bar had a different amount of tungsten and steel layers across the tensile sample. Therefore, every sample had a different percentage of tungsten and steel. Fractography was utilized to count the number of constituent layers in each tensile sample. This information, along with the average foil thicknesses shown in Table 2, was utilized to calculate each tensile sample's percentage of tungsten and compare it accordingly with its reported UTS.

The relationship between the percentage of tungsten in each composite tensile sample and its recorded UTS is shown in Figure 2. Also plotted are the UTS of each individual tungsten and steel foil. except for the 76 µm steel, which were tensile tested themselves in addition to the composite tests. In all cases, the composite's UTS was lower than that of the tungsten foils. The composites also exhibited higher UTS values compared to the steel foils: However, this trend did not align with the composite 1 section 3 data points, which lie on the 20-25% tungsten range and have UTS values lower than the steel foils. This could potentially be explained by the segmentation of the tungsten foil, which was observed after processing. The tungsten foils splitting apart and ceasing to be continuous could contribute to a lower UTS. Comparing this section to composite 2, which had the same foil constituents but only underwent a 20% reduction during processing, can further illuminate this. Composite 2's tungsten foil did not undergo segmentation and exhibited similar UTS as the other tungsten composites. Further, the segmentation of section 3 also means that the value for percentage of tungsten is likely overestimated and should be lower. This accounts for why composite 2 displays a much lower tungsten percentage. Composite 4, which had the same constituents as composite 1 section 2 but had a different processing reduction percentage, is shown to have very similar tungsten percentages and UTS values as its counterpart; showing that perhaps the processing reduction does not have as big an impact on the UTS of the composite, as long as segmentation of the foils does not occur.

**4.4 TENSILE TESTING OF STEEL AND TUNGSTEN FIBERS FOR APPLICATIONS IN COMPOSITE MATERIALS**—L. M. Garrison, J.R. Echols, M. Gussev (Oak Ridge National Laboratory)

# OBJECTIVE

The goal of this project is to develop a technique for the tensile testing of steel and tungsten fibers to determine their mechanical properties for use in fiber composites.

#### SUMMARY

A method for tensile testing steel and tungsten fibers was developed in order to understand the properties of fiber composite materials for use in fusion reactors. A new fixture was designed for tensile testing fibers. Tungsten fibers were irradiated as part of the PHENIX collaboration RB\*19J capsule. Initial tests on the irradiated tungsten fibers have been completed, and the fibers retain some ductility at room temperature after irradiation. This is in contrast to single and polycrystalline tungsten materials that are brittle at room temperature before and after irradiation.

#### PROGRESS AND STATUS

#### Introduction

Tungsten fiber composites are being examined as a possible way to improve the toughness of bulk tungsten materials. The fibers are able to dissipate the crack energy in the composites, could increase their ductility, and lower their effective brittle to ductile transition temperature. In order to understand the mechanical properties of the tungsten fiber composites, it is important to understand the properties of the fibers that will be used to fabricate them. To accomplish this, a method for tensile testing of steel and tungsten fibers has been developed. This involved developing a new fiber testing fixture and procedure. Unirradiated steel and tungsten fibers were previously tested. Now select irradiated fibers have also been tensile tested.

#### <u>Results</u>

Three types of tungsten foils were neutron irradiated in the PHENIX RB\*19J experiment (Table 1). Types 1 and 2 have potassium doping but were straightened by different means, while Type 3 was unalloyed tungsten. In order to neutron irradiate the fibers, they were loaded into small graphite tubes (Figure 1).

Table 1. Details of three types of tungsten fibers that were neutron irradiated and tensile tested

	Туре 1	Туре 2	Туре 3
Composition	W with 60 ppm K	W with 60 ppm K	W
Straightening method	straightened by plastic deformation (1%) at room temperature	straightened by producer at high temperature	straightened by plastic deformation (1%) at room temperature
Length	40 mm	38.5 mm	37 mm
Diameter	150 µm	150 µm	150 µm



Graphite tube

**Figure 1.** Three types of tungsten fibers were loaded in small graphite tubes for neutron irradiation. (a) fibers partway inserted in the tube, (b) close view of the fibers partially inserted in the tube, (c) side view. After these images, the fibers were pushed fully into the small tubes and the end cap placed on the graphite tube.

To tensile test the fibers, a mounting procedure and special fixture were developed. Figure 2a shows a fiber inside the paper frame, clamped into the tensile fixture after the fiber has broken in a successful tensile test. To track the fiber deformation, they were painted with white and black speckle pattern (Figure 2b) and tracked in a camera using digital image correlation (DIC).



**Figure 2**. (a) Close up view of a fiber after a successful tensile test. Epoxy fixes the fiber ends inside the paper frame, and the paper plus epoxy ensure that the metal clamp of the fixture does not have any direct contact with the delicate fibers. (b) image in the camera of the speckle paint pattern on the fiber surface.

The unirradiated tungsten fibers show increased strength and ductility as compared to single crystal and standard polycrystalline tungsten at room temperature (Figure 3). The Type 2 fiber, which was heat treated, has a lower ultimate tensile strength (UTS) and longer total elongation (TE) than either of the other two fibers. The difference in mechanical properties is echoed in the cross-section microstructure of the unirradiated fibers (Figure 4). Fibers were mounted vertically in epoxy and polished to reveal the cross-section grains. Both the Type 1 with K and the Type 3 without K have similar small, sharp grains that have a crisscross or interlocking tangled pattern with each other. In contrast, the Type 2 fiber which was heat treated to straighten it has much more equiaxed grains. This shows that the microstructure and mechanical properties of the tungsten fibers are sensitive to temperature, even when K is included to try to slow or prevent grain growth.



**Figure 3**. Room temperature tensile tests of the unirradiated tungsten fibers, compared with single crystal tungsten and powder metallurgy produced polycrystalline tungsten in SSJ2 geometry.



Figure 4. Polished cross-sections of the unirradiated fibers.

After neutron irradiation to ~0.2 dpa at 500°C, the Type 3 fiber had a similar UTS and slightly less TE than before irradiation (Figure 5). In the unirradiated state, the Type 1 and Type 3 fibers had very similar fracture surfaces where each small grain has pulled to a knife edge failure (Figure 6). After the ~0.2 dpa at 500°C irradiation, the fracture surface (Figure 7) is also very similar to the before irradiation fracture surface. After further neutron irradiation to ~0.7 dpa at 800°C, the UTS is slightly lower and the TE is more significantly lower, but it is not a fully brittle fracture. The change in the tensile curve is matched by a strong change in the fracture surface. The highest dose Type 3 fiber has a cleavage type fracture surface with the initiation point on the right side and the failure striations radiating out from that point (Figure 8).



Figure 5. Type 3, unalloyed W, tensile curves at room temperature before and after neutron irradiation.



Figure 6. Unirradiated Type 1 W with 60 ppm K fracture surface after room temperature tensile test.



Figure 7. Type 3 W, irradiated to ~0.2 dpa at 500°C, fracture surface after room temperature tensile test.



Figure 8. Type 3 W, irradiated to ~0.7 dpa at 800°C, fracture surface after room temperature tensile test.

**4.5 INVESTIGATION OF DUCTILE PHASE TOUGHENING BEHAVIOR IN TUNGSTEN HEAVY ALLOYS**—James V. Haag IV, Mitsu Murayama (Virginia Tech), Matthew Olszta, Danny Edwards, Jing Wang, Wahyu Setyawan (Pacific Northwest National Laboratory)

#### OBJECTIVE

This study aims to elucidate the nature of complex boundary structures in bi-phase tungsten heavy alloys (WHAs). It is hypothesized that the ductile phase toughening behavior exhibited by these alloys is a result of these unique microstructures. To build upon prior mechanical and microstructural analyses of these materials, this study focuses on ductile phase grain boundaries, and the brittle to ductile phase interface boundary structure in both an as-received and thermomechanical processed WHA. Both samples exhibit remarkable mechanical adherence between brittle tungsten and ductile Ni-Fe-W, which is likely due to the combined effects of crystallographic orientation, nickel's affinity for tungsten boundaries, and the presence of proposed diffusion gradients at the bi-phase interface. Precise micro- and nano- scale characterization techniques will be used to gauge the effectiveness of ductile phase toughening in WHA systems, and the results gained from this study will be invaluable for the modelling of multi-phase strengthening mechanisms in multiphase systems.

#### SUMMARY

Specimens of an unrolled and hot-rolled 90W - 7Ni - 3Fe wt.% WHA were prepared for mechanical testing and electron backscatter diffraction (EBSD) analysis by electrical discharge machining (EDM) followed by grinding and polishing down to a mirror surface. Specimens from the hot-rolled sample were cut in three orientations relative to the rolling direction for multidirectional analysis due to the high degree of anisotropy induced from rolling. Both samples were then analyzed through a combination of EBSD, in- and ex-situ mechanical testing, and transmission electron microscopy (TEM). Efforts have also been made towards the improvement of TEM sample quality through the application and optimization of flash electropolishing TEM foils. The data provided gives a more comprehensive view of WHA grain structure from sample and crystallographic frames of reference, which can be used to generate a more robust description of WHA samples and their behavior.

#### PROGRESS AND STATUS

#### Introduction

Tungsten heavy alloys have been the subject of recent research for potential candidacy in nuclear fusion reactors [1-6]. Their unique combination of high stiffness and thermal stability from tungsten coupled with the deformability of a Ni-Fe-W ductile phase makes them an attractive choice for the extreme environmental conditions of a fusion reactor interior. In an effort to optimize the mechanical properties of WHAs for plasma facing material components (PFMCs), researchers have varied the brittle to ductile phase ratio [4] and experimented with thermomechanical processing [1-3], to tailor the microstructure to exhibit a preferred response to external stimuli. The work presented here deviates from the systematic optimization of WHA microstructures, and instead focuses on the expression of ductile phase toughening in two proposed systems; the first of which is a liquid phase sintered structure, consisting of semispherical tungsten domains suspended in a continuous ductile phase matrix, and the second being the same specimen composition, but hot rolled to resemble a brick and mortar structure. Of particular interest is the accommodation of deformation in these alloys, as the expression of ductile phase toughening behavior is expected to vary between the unrolled and rolled samples.

#### Experimental

In order to characterize the differences in expression of ductile phase toughening behavior in the asreceived and thermomechanical treated samples, it is imperative to maintain a multidirectional and multiscale microstructural view of these materials. To build upon prior 3D reconstruction and mechanical testing, a mechanical analysis of the as-received and three different orientations of the rolled sample has been conducted in triplicate to observe any measurable differences in mechanical behavior after specimen hot-rolling. Micro tensile specimens were fabricated and polished to final gauge dimensions of approximately 5.0×1.1×0.1 mm for in- and ex-situ uniaxial tension testing. Ex-situ mechanical tests yielded similar mechanical properties between the as-received and rolled samples, but in-situ mechanical testing revealed a drastic change in how each respective material deforms until failure. The as-received sample appears to uniformly elongate leading to eventual critical crack propagation through brittle and ductile phase alike, while the hot-rolled sample builds a high density of microcracks at W-W boundaries that eventually link through discontinuous ductile phase ligaments, causing failure. Further TEM in-situ mechanical tests are in process to provide a nanoscale view of this deformation behavior.



**Figure 1.** (a) EBSD micrograph of ductile phase in unrolled sample, (b) EBSD micrograph of ductile phase in hot-rolled sample of 87% thickness reduction.

In addition to added repeatability in mechanical behavior analysis, more recent efforts have been made towards the incorporation of a crystallographic understanding into the description of the WHA samples. The introduction of a diffraction-based approach to these samples allows for further deconvolution of the physics governing WHA behavior through coupling phase differentiation with crystallographic orientation. Texturing analysis, as well as analysis of grain and phase boundary character have been added through EBSD and TEM diffraction. These techniques have revealed that the as-received sample possesses an extremely coarse ductile phase grain structure with seemingly no preferred orientation relationship (OR) between the body centered cubic (BCC) W spheres and the face centered cubic (FCC) Ni-Fe-W matrix. The as-received sample possesses no strong evidence of texturing in either phase, despite the severe thickness reduction via directional processing. There remains no evidence of a preferred OR in the asreceived sample either. The most notable change resulting from the rolling is the refinement of the ductile phase grain structure. Figure 1 compares the ductile phase grains before and after hot rolling. Ductile phase grain size is drastically reduced, as is that of the matrix continuity. More in-depth analysis of the ductile phase grain boundary character, shown in Figure 2, reveals a high density of  $\Sigma$ 3 or twin type boundaries. In the image shown, approximately 87% of the ductile phase grain boundaries are some form of coincidence site lattice (CSL) boundary, and 82% are twin boundaries. This high density of twin boundaries is theorized to be an important factor for the exemplary ductility exhibited by the rolled sample.



**Figure 2.** (a) EBSD micrograph of ductile phase in rolled sample with twin boundaries highlighted in red, (b) plot of CSL boundaries between ductile phase grains in (a).

One potential confounding factor in the interfacial analysis of WHAs is a high degree of curvature present at brittle to ductile phase interfaces. Figure 3 illustrates the difficulties of this characterization, showing a conventional FIB lift out from a bulk sample, and the geometrical tilting necessary to align a particular boundary of interest to the edge-on condition. It can be observed that the contoured nature of the phase boundary leads to difficulty in the characterization of the true nature of the boundary. While this effect has not been confirmed to be present across the specimens tested, it is nonetheless a potential dissenting claim to the proposed diffusion gradient present at the boundary. Assuming a 100-nm thick TEM foil taken at the interface between a 30-µm diameter tungsten sphere and the ductile phase, there is a potential curvature effect ranging between 0.3 and 25 nm. For comparative purposes, the diffusion boundary noted across TEM analysis of multiple samples is on the order of 5-10 nm in width. This boundary curvature could mimic the behavior noted through energy dispersive x-ray spectroscopy and diffraction mapping datasets, showing a gradual transition from the brittle W phase to the ductile phase, even when the boundary appears parallel to the electron beam.



**Figure 3.** Schematic of potential boundary curvature effect in TEM. (a) top down view of FIB lift out region in an unrolled sample, (b) thickness view of lift out with highlighted boundary of interest for analysis, (c) boundary tilted to assumed on-edge condition with respect to incident TEM electron beam, (d) apparent boundary present due to high degree of curvature in W domains.

A study is currently in progress to improve upon prior flash electropolishing trials for surface damage elimination in TEM foils produced via focused ion beam (FIB) preparation. The difficulty of electrochemically thinning multiphase materials is well-known due to the varying electrochemical potentials between different species. Yet it remains imperative that a solution to this issue is found prior to beginning analysis of irradiated WHA specimens, as any remaining defects from FIB preparation may mimic or obscure results on the defect structures resulting from specimen irradiation. As such, the prior setup based on advancements made in [7-8] has been adjusted to 5ms long 15V pulses in a 1% perchloric in methanol solution. A trial run of this process can be seen in Figure 4 on a dimple ground and ion milled sample of the rolled WHA (a). Optical micrographs of the sample surface can be observed at seguential polishing steps 1 - 4 (b - e respectively). TEM observations of these samples would be conducted near the edge of the specimen foil, where it is at its thinnest; this region has been marked with a white arrow in (a). The first polishing step (b) was conducted at 20V for 5ms and lead to pitting of the specimen. The voltage was subsequently stepped down to 15V for 5ms in subsequent polishing steps (c, d, and e respectively) leading to a much-improved surface finish. While both materials are being removed in this process, there is an apparent preferential removal of ductile phase. It has therefore been proposed to implement a dual-step flash electropolishing trial using two electrolyte solutions. The first solution remaining 1% perchloric in methanol, and the second a dilute NaOH solution designed to be more aggressive in the removal of the W phase over the ductile phase. The goal of this trial will be to ensure tunable electrochemical thinning of the samples to produce damage free specimens exhibiting a uniform thickness between the separate phases.



**Figure 4.** Flash electropolishing of TEM foil prepared by dimple grinding and ion milling. (a) sample before any electropolishing, (b) 20V pulse for 5ms pitting noted so voltage stepped down, (c) 15V pulse for 5ms, (d) 15V pulse for 5ms, (e) 15V pulse for 5ms. Preferential sample removal noted in later polishing steps, surface finish notably improved.

# ACKNOWLEDGEMENTS

This research was supported by the Office of Fusion Energy Sciences, U.S. Department of Energy (DOE) under Contract DE-AC05-76RLO 1830. Part of this work was performed at VT and supported by PNNL through Subcontract 510702. The authors would also like to extend thanks to Alan Schemer-Kohrn for his assistance in flash electropolishing and electron microscopy characterization.

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**4.6 SELF-ION AND He ION IRRADIATION OF DUCTILE-PHASE TOUGHENED TUNGSTEN COMPOSITES**—Weilin Jiang, Wahyu Setyawan, Karen Kruska, Libor Kovarik, Dalong Zhang (Pacific Northwest National Laboratory)

# OBJECTIVE

The aim of this experimental work is to study the response of ductile-phase toughened tungsten (DPT W) composites in fusion environments emulated by ion irradiation at elevated temperatures. Specifically, we will focus on the study of (1) Helium (He) bubble distributions in W and NiFeW phases and along the interphase boundaries, (2) relative He retention in W and NiFeW, (3) possible Ni precipitation in W, (4) dislocation loops and cavities in NiFeW and along the interphase boundaries without involving He, and (5) impact of the pre-existing defects on He cavity density and size.

#### SUMMARY

A hot-rolled DPT W (1) composite (90W-7Ni-3Fe) was irradiated with 4 MeV He<sup>2+</sup> ions to 7.8×10<sup>17</sup> He<sup>2+</sup>/cm<sup>2</sup> at 973 K. The material was determined to contain 88 wt.% W and 12 wt.% NiFeW. The NiFeW phase consists of 54.68 at.% Ni, 22.57 at.% Fe and 22.75 at.% W. While a microscopy study is being performed for DPT W (1), a DPT W (2) sample from the same batch has been sequentially irradiated with self-ions (Ni<sup>+</sup>) and He<sup>+</sup> ions to emulate the material response in a fusion power plant for 5 years. The irradiation was performed with 1.2 MeV Ni<sup>+</sup> ions to 2.15×10<sup>15</sup> Ni<sup>+</sup>/cm<sup>2</sup> at 973 K, followed by 90 keV He<sup>+</sup> ions to 6.5×10<sup>15</sup> He<sup>+</sup>/cm<sup>2</sup> at 973 K. SRIM13 simulations suggest that the He concentration peak (depth: 295 nm) is overlapped spatially with the Ni damage peak (depth: 296 nm) in the NiFeW alloy under the irradiation conditions. This condition allows for a study of He atom interaction with irradiation defects in NiFeW. A TEM study of the He bubbles and Ni precipitates in the irradiated DPT W (2) has been initiated.

#### PROGRESS AND STATUS

#### Introduction

**Table 1.** Displacement damage dose and helium gas production in pure W, Ni, and Fe under neutron spectrum in the first wall (FW) of a 1-GW DEMO fusion power plant for 5 years [1.04×10<sup>15</sup> (n/cm<sup>2</sup>)/s]. The composition-averaged helium production in the NiFeW ductile phase of the DPT W (2) (90W-7Ni-3Fe) is also given.

Composition	Percentage (wt.%)	Percentage (at.%)	Dose (dpa)	Helium (appm)
W			27.4 [3,5]	33.6 [3]
Ni				2,442 [4]
Fe			89.6 [3,5]	1,090 [3]
Ni in NiFeW	54.68	63.83		
Fe in NiFeW	22.57	27.69		
W in NiFeW	22.75	8.48		
Average in NiFeW				1,863

In our previous report [1], we presented the characterization results of a hot-rolled high-density DPT W (1) (90W-7Ni-3Fe) composite [2], including the composition of 88 wt.% W and 12 wt.% NiFeW that consists of 54.68 at.% Ni, 22.57 at.% Fe and 22.75 at.% W, the microstructure of W grains in a NiFeW matrix, and the size and orientation distributions of the dual phases. A portion of the DPT W (1) sample was irradiated with a defocused 4 MeV He<sup>2+</sup> beam to 7.8×10<sup>17</sup> He<sup>2+</sup>/nm<sup>2</sup> at 973 K over an area of 3 mm × 3 mm. While a microscopy study is being performed for the sample and some preliminary data will be presented in this report, we have also been emulating irradiation effects in a DPT W (2) composite. Based on the model calculations of elemental transmutation and gas production, Gilbert et al. [3] have predicted the He production in the first wall of a future fusion power plant at a total neutron flux of  $1.04 \times 10^{15}$  (n/cm<sup>2</sup>)/s. Table 1 gives the He concentrations in appm in pure W and Fe over the 5 years in the fusion power plant. Calculations [3] show that He concentration is 1,090 appm produced from Fe and 33.6 appm from W. He production from Ni is at 2,442 appm, which is estimated based on the cross sections of Ni (99.9 mb) and Fe (44.6 mb) reactions with 14 MeV neutrons [4]. Thus, the total He concentration in NiFeW is 1,863 appm or ~0.19 at.%. Also included in Table 1 are the estimated doses in displacements per atom (dpa) for W and Fe based on the data reported in [5] with a proper adjustment in the neutron flux [3]. The results are 27.4 and 89.6 dpa for W and Fe as the first-wall materials, respectively, for 5-year irradiation in the fusion power plant.

#### **SRIM Simulation**

In order to better emulate irradiation effects in NiFeW by  $E_0=14$  MeV neutrons from  ${}^{3}H({}^{2}H,n){}^{4}He$  reaction using ion irradiation, both self-ion and He ion irradiations need to be taken into account. The factor of the maximum primary knock-on atom (PKA) energy  $[E_{max}(PKA)/E_0]$  for the energetic neutrons, Fe, Ni and W



**Figure 1.** Depth profiles of doses and atomic percentages from SRIM13 simulations for (a) 1.2 MeV Ni<sup>+</sup> irradiation W to 2.15×10<sup>16</sup> Ni<sup>+</sup>/cm<sup>2</sup>, (b) 90 keV He<sup>+</sup> irradiation W to 6.5×10<sup>15</sup> He<sup>+</sup>/cm<sup>2</sup>, (c) 1.2 MeV Ni<sup>+</sup> irradiation NiFeW to 2.15×10<sup>16</sup> Ni<sup>+</sup>/cm<sup>2</sup>, and (d) 90 keV He<sup>+</sup> irradiation NiFeW to 6.5×10<sup>15</sup> He<sup>+</sup>/cm<sup>2</sup>.

lon	Material	Damage Peak Depth (nm)	Peak Dose (dpa)	Ni or He Peak Depth (nm)	Ni or He Peak Concentration (at.%)
1.2 MeV Ni <sup>+</sup> 2.15×10 <sup>16</sup> Ni <sup>+</sup> /cm <sup>2</sup>	W	168	27	294	0.98
90 keV He <sup>+</sup> 6.5×10 <sup>15</sup> He <sup>+</sup> /cm <sup>2</sup>	W	160	0.074	215	0.48
1.2 MeV Ni <sup>+</sup> 2.15×10 <sup>16</sup> Ni <sup>+</sup> /cm <sup>2</sup>	NiFeW	296	31	416	0.76
90 keV He⁺ 6.5×10 <sup>15</sup> He⁺/cm²	NiFeW	250	0.17	295	0.39

**Table 2.** SRIM13 simulation results for sequential irradiation with Ni<sup>+</sup> and He<sup>+</sup> ions in DPT W (2)

ions collided with W is 0.0215, 0.716, 0.735 and 1, respectively. Obviously, the factors for Fe and Ni ions are closer to the factor for neutrons than W ions. Thus, the lighter ions are a better choice for self-ion irradiation in terms of better emulation of damage cascades. Because the PKA energy factors for Fe and Ni ions are comparable in value and Ni is the dominant element in the NiFeW phase, Ni ions are selected as self-ions for irradiation to emulate high-energy neutron irradiation of NiFeW. In addition, because He atoms would typically migrate in NiFeW phase with irradiation damage, sequential irradiation is designed with first Ni<sup>+</sup> and then He<sup>+</sup> ions with the He profile spatially overlapped with the Ni damage peak.

In order to estimate dose rates and He atomic distributions in W and NiFeW phases, quick Kinchin-Pease (K-P) SRIM13 (Stopping and Range of Ions in Matter, version 2013 [6]) simulations were carried out for 1.2 MeV Ni ions and 90 keV He ions in W and NiFeW, where the threshold displacement energies of  $E_d(W)=90$  eV and  $E_d(Ni)=E_d(Fe)=40$  eV were adopted [7]. The lattice binding energy was set to 0 eV [8]. The theoretical density is 19.25 g/cm<sup>3</sup> or  $6.3 \times 10^{22}$  at./cm<sup>3</sup> for body-centered cubic W and 9.50 g/cm<sup>3</sup> or  $8.3 \times 10^{22}$  at./cm<sup>3</sup> for face-centered cubic NiFeW. The simulation results for  $2.15 \times 10^{16}$  Ni<sup>+</sup>/cm<sup>2</sup> and  $6.5 \times 10^{15}$  He<sup>+</sup>/cm<sup>2</sup> in W and NiFeW are shown in Fig. 1 and summarized in Table 2. For Ni<sup>+</sup> ion irradiation in W, the peak dose is 27 dpa at 168 nm, corresponding to the dose in W for 5-year irradiation in a future fusion power plant; in NiFeW, the peak dose is 31 dpa at 296 nm. For He<sup>+</sup> ion irradiation in NiFeW, the maximum He concentration is 0.39 at.% at 295 nm. The He peak is well aligned with the Ni damage peak, as desired. The He concentration (0.39 at.%) is doubled on purpose compared to that produced in NiFeW (0.19 at.%) during neutron irradiation because a significant amount (assumed to be ~50%) of the implanted He atoms is expected to be released during He<sup>+</sup> ion irradiation at 973 K.

# Sequential Ion Irradiation

A high-density DPT W composite with a nominal composition of 90W-7Ni-3Fe was produced at Pacific Northwest National Laboratory (PNNL) with powders obtained from Mi-Tech [9,10]. The material was rolled at high temperatures (to 87% thickness reduction), cut into small samples, and polished on one side at PNNL. Figure 2(a) shows a schematic diagram for the sequence of ion irradiation at 973 K. A resistance heater was located behind the copper plate on which the sample was mounted. The temperature was monitored using a thermocouple on the copper plate. An area of 4 mm × 7 mm was irradiated with 1.2 MeV Ni<sup>+</sup> ions to 2.15×10<sup>16</sup> Ni<sup>+</sup>/cm<sup>2</sup>. Subsequently, an area of 4 mm × 8 mm was irradiated with 90 keV He<sup>+</sup> ions to  $6.5 \times 10^{15}$  He<sup>+</sup>/cm<sup>2</sup>. There was an overlapping area of 4 mm  $\times$  4 mm, as shown in Figure 2(a), thus creating He⁺ 3 reaions of irradiation with Ni<sup>+</sup> ions only, Ni⁺ and ions and He⁺


**Figure 2.** (a) Sequential irradiation of DPT W (2) with Ni<sup>+</sup> and He<sup>+</sup> ions at 973 K to create three different irradiation regions with an unirradiated region, and (b) picture of the irradiated sample.

ions only. There was also an unirradiated area of 4 mm  $\times$  2 mm. The irradiations were performed with a rastering system to achieve a uniform irradiation over the intended areas. The average flux was  $4.0 \times 10^{12}$  (N<sup>i+</sup>/cm<sup>2</sup>)/s and  $3.6 \times 10^{12}$  (He<sup>2+</sup>/cm<sup>2</sup>)/s. Figure 2(b) shows the irradiated sample with line markers to identify the four different regions.

# **Preliminary Results**

As described in our previous report [1], a portion of a DPT W (1) composite was irradiated with a defocused 4 MeV He<sup>2+</sup> beam to  $7.8 \times 10^{17}$  He<sup>2+</sup>/nm<sup>2</sup> at 973 K over an area of 3 mm × 3 mm, as shown in Figure 3(a). Focused ion beam (FIB) technique was used to slice a lamella in the indicated area on the irradiated DPT W (1). Figure 3(b) shows the microstructure of the composite with a distinct contrast for W (gray) and NiFeW (dark) phases. A region largely within a W grain was selected for the FIB operation. The lamella was rotated by 90° with the original sample surface welded to the grid, as shown in Figure 3(c). It was thinned and polished to electron transparency using FIB, as shown in Figure 4(a). There are two holes formed as indicated by red arrows. The sample was examined using a Cs-aberration corrected JEOL ARM 200cF Scanning Transmission Electron Microscope (STEM) at PNNL. Figure 4(b) shows a higher resolution of a thin area near a hole, where lattice strain contrast is observed. In an even higher-resolution image shown in Figure 4(c), it is apparent that the area has a high density of dislocations and



**Figure 3.** (a) DPT W (1) sample irradiated with 4 MeV He<sup>2+</sup> ions to  $7.8 \times 10^{17}$  He<sup>2+</sup>/cm<sup>2</sup> at 973 K, (b) microstructure of the irradiated DPT W (1) composite with the FIB lift-out region indicated, and (c) a FIB lift-out lamella from the region. Gray: W, dark: NiFeW



**Figure 4.** (a) Low-resolution STEM image of DPT W (1) irradiated with 4 MeV He<sup>2+</sup> ions to  $7.8 \times 10^{17}$  He<sup>2+</sup>/cm<sup>2</sup> at 973 K, (b) higher-resolution image in a thin region, (c) a high density of defects from FIB process, and (d) depth profiles of dose and atomic percentage from SRIM13 simulation.

dislocation loops from Ga<sup>+</sup> ion irradiation during the FIB process. The significant lattice distortion makes it difficult to observe any dynamical extinction effects in the diffraction disks (data not shown) from the convergent-beam electron diffraction (CBED) for foil thickness determination.

Quick Kinchin-Pease SRIM simulations [6] suggest that the maximum He concentration is 24.6 at.% He at the depth of 6.24 µm, as shown in Figure 4(d). It should be noted that the actual He percentage in the profile could be lower due to likely He outward diffusion and release during irradiation at 973 K. The damage peak located at 6.16 µm [Figure 4(d)] could serve as effective trapping sites for migrating He atoms during irradiation. STEM-EELS (Electron Energy Loss Spectroscopy) analysis of He retention has been performed across the framed region [Figure 4(a)], where the foil thickness is relatively uniform. A series of measurements were made at depths from 5.7 to 8.2 µm. The STEM-EELS data are currently being analyzed. The foil thickness t will be estimated [11] by the STEM-EELS analysis based on the ratio of total number of electrons in the spectrum It over the number of electrons having lost no energy (area of zeroloss peak) I<sub>0</sub>: t/ $\lambda$ =In(I<sub>t</sub>/I<sub>0</sub>),  $\lambda \propto Z^{-0.28}$ , where  $\lambda$  is the characteristic mean free path for inelastic scattering and Z is the effective atomic number. He K edge core-loss line is located at 21.218 eV, which overlaps with the broad plasma peak at ~25 eV. Similar to what has been reported [13], two spectra from the He-rich and He-free regions will be compared. The difference between these thickness-normalized spectra will yield the He core-loss peak. The amount of He atoms N can be determined by [12]: N=I<sub>He</sub>/(I<sub>0</sub>σd), where I<sub>He</sub> is the area of the He peak,  $\sigma$  is the He cross section and d is the He bubble diameter. The relative He retention is proportional to I<sub>He</sub>.

A lamella from the NiFeW phase region will also be prepared for a similar STEM-EELS analysis. The relative He retentions in W and NiFeW at the proper depths for the same He concentration from SRIM13 simulations will be compared to the prediction from a density-functional theory (DFT) calculation. For 1 at.% He in W and NiFeW, for example, the corresponding depths are 5.4 and 6.7  $\mu$ m, respectively. STEM studies of He bubble distributions in W and NiFeW and along the interphase boundaries as well as possible atomic intermixing at the W and NiFeW boundaries will also be investigated.

# Ongoing Efforts

FIB sample preparation and TEM study of DPT W (2) in the Ni<sup>+</sup> and He<sup>+</sup> ion irradiated region have been initiated for the He bubble distributions in NiFeW and W and along the interphase boundaries as well as possible Ni precipitates in W. According to SRIM13 simulations [Figure 1], Ni concentration peak in W is located at the depth of ~300 nm from the surface, while He concentration peaks in W and NiFeW are located at ~200 and ~300 nm, respectively. While the high-fluence DPT W (1)  $(7.8 \times 10^{17} \text{ He}^{2+}/\text{nm}^2)$  is expected to exhibit He bubbles around the He concentration peak [14], the bubbles in the low fluence DPT W (2)

(6.5×10<sup>15</sup> He<sup>+</sup>/cm<sup>2</sup>) could be too small to be visible considering the low fluences applied in this study. The plan is first to work on the Ni<sup>+</sup> and He<sup>+</sup> irradiated region to find out if there are visible He bubbles in W and NiFeW phases and along its interphase boundaries using under- and over-focus TEM. The observed bubble size under the defocused conditions will be corrected to obtain the actual size [15]. At the same time, we will also look for Ni precipitates in W using STEM-EDS (Energy Dispersive X-ray Spectroscopy). Further investigations will also include the Ni<sup>+</sup> irradiated only, He<sup>+</sup> irradiated only and unirradiated regions to study (1) He bubble distributions in W and NiFeW phases and along the interphase boundaries, (2) relative He retention in W and NiFeW, (3) possible Ni precipitation in W, (4) dislocation loops and cavities in NiFeW and along the interphase boundaries without involving He, and (5) impact of pre-existing defects on He cavity density and size. For studies (4) and (5), flash electrochemical polishing (FEP) will be applied to remove the foil surface layer of the Ga<sup>+</sup> ion damage due to FIB process.

#### Acknowledgements

This research was supported by the Office of Fusion Energy Sciences, U.S. Department of Energy and performed at PNNL under Contract DE-AC05-76RL01830. We are grateful to Charles Henager at PNNL for providing the DPT W samples and to Xuemei Wang, Tianyao Wang and Zhihan Hu at Texas A&M University (TAMU) for performing the ion irradiation for this study.

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**4.7 TENSILE TESTING AND MICROSTRUCTURAL CHARACTERIZATION OF DUCTILE PHASE TOUGHENED W-NiFe ALLOYS**—Jing Wang, David Collins, Nicole R. Overman, Wahyu Setyawan (Pacific Northwest National Laboratory)

# OBJECTIVE

The objective of the project is to understand the deformation behavior of ductile phase toughened tungsten heavy alloys, such as W-NiFe, for applications in fusion reactor divertor and plasma-facing-components.

# SUMMARY

This report summarizes the progress in investigating microstructure-mechanical property correlation in ductile phase toughened (DPT) W-NiFe alloys at PNNL. In order to reduce challenges in integration with finite element (FE) model development and validation, the project determined to focus on tensile tests for providing mechanical data. Miniature tensile specimens were fabricated from the bulk specimens via electrical discharge machining (EDM), and they were tested at room temperature under three different strain rates. Preliminary microstructural characterization on the samples were performed using scanning electron microscope (SEM) and electron back-scattering diffraction (EBSD). The W/NiFe interfaces in as-received and hot-rolled 90W-NiFe specimens were investigated using atom probe tomography (APT) via site-specific specimen fabrication with focused ion beam (FIB). Preliminary tensile results and strain-stress curves are also presented and discussed.

# PROGRESS AND STATUS

#### Introduction

Ductile phase toughening (DPT) is a fracture toughness improvement concept being used to develop tungsten-based composites for fusion reactor divertor and plasma facing materials. Tungsten is a promising candidate material for fusion reactor component applications due to its excellent high temperature strength, low sputtering rate, and high melting temperature [1, 2]. However, the potential application of tungsten as structural material is limited due to its low ductility, which could further degrade after irradiation [3]. Introducing a ductile phase for developing W composite could serve as an alternative route to overcome its limitations.

Previously, W-Cu composite materials have been investigated, and it is found that the ductile phase could form a bridge near the crack tip to enhance fracture toughness of the W-Cu composites [4, 5]. A finite element model was developed for understanding toughening mechanism (Dynamic Bridging Model) and for predicting load-displacement curves and crack propagation patterns (Finite Element Continuum Model) [6, 7]. Although W-Cu composite is a good starting model system for exploration, it is not suitable for fusion reactor environment due to low melting point of the ductile phase Cu. An alternative system of W-Ni-Fe composite was proposed and studied.

90W-NiFe as-received samples, in which W powders were embedded in a Ni-Fe matrix, were hot rolled at PNNL to 62%, 74% and 87% thickness reduction to resemble a lamellar structure. In FY19 and FY20, efforts to collect experimental data to understand the effects of hot rolling and deformation behavior of DPT W-NiFe alloys are continued. This report summarizes the progress on mechanical testing and microstructural characterization of the as-received 90W, 95W and 97W, and hot rolled 90W to 87% thickness reduction. The specimen matrix in this report is listed in Table 1.

Specimen ID	Details		
90W-0R	90 wt% W, as received, powder purchased from		
	MiTech, sintered at PNNL		
90W-87R	90 wt% W, hot rolled to 87% thickness reduction		
95W-0R	95 wt% W, as received, MiTech		
97W-0R	97 wt% W, as received, MiTech		

#### **Table 1.** Specimen matrix in this report

#### **Experimental Procedure**

#### Microstructural Characterization

The SEM and EBSD on as-received samples were carried out using a JEOL 7600 field emission SEM at PNNL. Samples for characterization were polished to a 0.05 µm colloidal silica finish. A low-angle backscatter electron (BSE) detector was utilized to examine the general microstructure at various locations. The EBSD was performed using the Oxford Symmetry detector to acquire W grain size distributions and orientations. The results were processed and analyzed using the AZtec software package from the Oxford Instruments.

Atom probe tomography was conducted in a CAMECA Local Electrode Atom Probe (LEAP) 4000X HR at the Environmental Molecular Science and Laboratory at PNNL. The APT specimens were prepared following the standard lift-out procedure. To obtain site-specific specimens, a wedge of ~30 um was extracted near W/Ni boundary. For each material, around five APT specimens have been prepared. The acquisition condition was set to a detection rate of 0.3% (0.003 detected ion/pulse), a laser ( $\lambda$ =335 nm) energy of 60 pJ, and a laser pulse rate of 100 kHz. The specimen was maintained at a temperature of 40 K during operation. The obtained data were reconstructed using the Integrated Visualization and Analysis Software (IVAS) version 3.8.

#### Mechanical Testing

The mechanical properties were characterized using tensile testing as opposed to 3- or 4- point bend testing as the former is considerably simpler and therefore more favorable for model development. Current tests are focused on acquiring strain-stress curves on un-notched tensile specimens, while notched tensile sample testing will be performed in the future to characterize fracture toughness properties. Miniature tensile specimens were fabricated via EDM from the as-received bulk materials into the geometry shown in Figure 1, while Figure 2 features CAD renderings of the fixturing used to test the specimens. This tensile grip geometry aims to improve compatibility with the associated optical extensometer to track the gauge length of the tensile specimen during testing so accurate strain measurements may be obtained. For this set of tests, the samples were shoulder-loaded instead of pin-loaded to avoid tear-out at the pin hole as well as warping of the pins. The samples were tested at room temperature using an Instron 5582 servomechanical test frame equipped with an Epsilon ONE optical extensometer.

In order to create a more accurate and comprehensive model, it is necessary to test these materials under a wide range of deformation rates. For this study, the effects of testing at three different displacement rates (0.1, 1, and 10 micron/s crosshead speed) were explored, and the corresponding strain rates are listed in the results section. The slowest rate was chosen because on a per second basis it is approximately twice the displacement resolution of the test frame (~0.06 microns), which would mitigate the "stair step" pattern that is often seen in servo-mechanical test frames at extremely low displacement rates. The fastest speed was set to two orders of magnitude higher in order to produce significantly contrasting data. To perform the tests, the samples were first preloaded up to 20N, then loaded at the prescribed displacement rate until failure. The resulting data was then smoothed, reduced to approximately 100 points, and plotted.



Figure 1. Drawings of the miniature tensile sample geometry.



**Figure 2.** Drawings of the tensile fixturing. This fixturing features an "open face" design, where fixturing material normally in the vicinity of the specimen is removed to improve compatibility with optical extensometers.

#### June 30, 2020

# **Preliminary Results**

#### **Microstructure**

The general microstructure of W-NiFe alloy samples are shown in Figure 3. The microstructure resembles two typical phases in this set of materials: a NiFe phase, which serves as the ductile matrix; and a W phase, which provides strength and high temperature mechanical performance. In as-received 90W (a), 95W (c) and 97W (d), we can clearly see the W particle size changes as a function of composition. At the same time, area coverage of NiFe phase decreases noticeably. Figure 3 b) shows the surface perpendicular to transverse direction and parallel to rolling direction. It shows that along the rolling direction, the W phase deforms significantly into a plate-like structure. The ductile phase in the rolled specimen seems less continuous, although further quantitative analysis is needed.



**Figure 3.** BSE images of a) 90W-0R; b) 90W-87R; c) 95W-0R; d) 97W-0R. Note that b) was taken on the surface perpendicular to transverse direction. The rolling direction is horizontal (left to right).

Figure 4 shows inverse pole figure (IPF) maps along in-plane (X and Y), and out-of-plane (Z) directions from EBSD analysis of the W-NiFe alloy specimens. The W particles are primarily single crystals in asreceived 90W, 95W, and 97W alloys and does not show any significant preferential orientation relationships in EBSD map. Slight grain rotations, colored as different orientations in IPF maps, are visible within some W particles, e.g. in upper right W-particle for 95W-0R. Most of such minor grain rotations have a disorientation below 5°, and all of them are below 10°. Local variations in texture in these specimens are probably polishing artifact resulting in not perfectly flat W surfaces. The IPF maps also show that in these W-NiFe alloys, the NiFe phase has the same orientation across a large region (hundreds of micrometers), while occasionally smaller regions of NiFe with different orientations from nearby NiFe phase can be found. It is difficult to say that whether NiFe phases with same orientations are from one large grain or they happen to have the same orientations look discontinuous and a 3D EBSD mapping will be necessary to determine the nature of these regions. The texture is much richer in the hot-rolled 90W-87R-RD. It is difficult to obtain any apparent intuition from the IPFs maps directly, but isolating NiFe and W phases reveals that a large quantity of NiFe grains of several micrometers in size compose the majority of matrix.



**Figure 4.** EBSD Inverse Pole Figure (IPF) maps showing grain orientation in plane (X, Y) and the out-ofplane (Z) direction. The scale of the figures is labeled in c).

Figure 5 shows the inverse pole figures for NiFe phase and W phase in each specimen, corresponding to Figure 4. First of all, for NiFe phase in 90W-0R, 95W-0R and 97W-0R, the IPFs show that their orientations are highly concentrated among a few crystallographic directions. This is consistent with the observation of only a few orientations in the IPF maps for NiFe phase shows, while each orientation consists of many discontinuous regions. For the hot-rolled 90W-87R-RD, the grain orientation distribution is less concentrated than as-received materials. Among them, a higher proportion of grain exhibited {101} type texture along Y direction (in-plane). This EBSD result shows that the W-phase particles distribute mostly

randomly in the NiFe matrix without any preferential orientation in as-received materials. Although regions of higher relative density in 90W-0R, 95W-0R, and 97W-0R exist, the actual density differences among different orientations are much smaller. The color scale falsefully exemplify the differences. However, the color scale cannot be easily adjusted in current analysis software. In hot-rolled 90W-87R-RD, a slight preference over {001} type texture along Y has been observed for W phase.



**Figure 5.** Inverse pole figure sets for NiFe phase and W phase in 90W-0R, 90W-87R-RD, 95W-0R, and 97W-0R specimens. The color corresponds to the relative density of detected orientations with respect to the multiples of uniform distribution, which describes whether there are preferential orientations. Due to the limitations of the analysis software we cannot set a same color scale across specimens.

The phase maps and grain boundary maps are shown in Figure 6. The NiFe matrix looks discontinuous in all phases maps and it looks like the higher the W composition, the more isolated each NiFe phase. Between as-received 90W-0R and hot-rolled 90W-87R-RD, it seems hot-rolling father break down the NiFe phase to more smaller regions. The NiFe phase area coverages can be obtained from phase maps. An estimation from the analysis software is 16.5% in 90W-0R, 10.9% in 90W-87R-RD, 5.8% in 95W-0R, and

4.6% in 97W-0R. It is expected that in as-received W-NiFe alloys, area fraction of ductile NiFe phase decreases with increasing W composition. However, the decrease of ductile phase in hot-rolled W-NiFe does not seem intuitive. Assuming a conservation of materials, this implies that either the NiFe area coverage increases on the surface perpendicular to the normal direction, a portion of NiFe phase is embedded into W phase during the hot rolling, or some NiFe phase regions are simply too small to be imaged. Further examinations, likely of ND surface in rolled materials, will be needed to better understand the microstructure changes.

Figure 6 b),df), f), h) shows W-W grain boundary characteristics. Most grain boundaries have a >10° disorientation in all samples, while only a small fraction of low-angle grain boundaries with disorientation from 5-10° is detected. Corresponding grain boundary disorientation angle distributions are presented in Figure 7. In NiFe phase in 90W-0R and 95W-0R specimens, nearly 30% of the grain boundary misorientations are around 60°. While in the 90W-87R-RD specimen, approximately 70% NiFe boundaries have a disorientation angle around 60°. Grain boundary disorientations among W-phases are mostly random in as-received materials. an in hot-rolled materials, two preferential disorientation angles, around 30° and around 60° have been observed.



**Figure 6.** Phase maps (red: NiFe; blue:W), and grain boundaries (red > 5°, black > 10) for W-NiFe alloys.



**Figure 7.** Grain boundary misorientation angles distribution for NiFe and W phases. Note that the analysis software normalized the distribution, rather than showing counts of grain boundaries. The distribution is much noisier in 97W-0R, probably due to fewer grain boundaries in NiFe phase.

Figure 8 shows the estimated grain size distributions for both NiFe phase and W phase. Because the majority of W particles are single crystals, the grain size distribution is roughly equivalent to the particle size. It is clear that the W phase size increases as composition goes from 90W to 97W, which confirms the qualitative observation in the BSE images. Despite containing only 2wt% less W, 95W exhibits a more refined particle size than 97W. At the same time, NiFe phase size slightly decreases as W composition increases from 90 to 97. However, we need to emphasize that the grain sizes for NiFe phase is estimated based on the 2D EBSD phase maps only. There is a chance that these discontinuous NiFe regions with same orientations are actually part of a huge NiFe grain formed during liquid phase sintering. In that case, the grain size distribution must be measured manually instead of using current software generated ones, since the software only treats all discontinuous NiFe regions as individual grains on 2D images. In hotrolled specimen, 90W-87R-RD, the size of NiFe phase is noticeably reduced to a few micrometers, compared to >10 um in as-received materials.



**Figure 8.** Grain size distribution as estimated using EBSD for NiFe phase and W phase. Note the grain sizes for NiFe phase in 90W-0R, 95W-0R, and 97W-0R are measurements on isolated discontinuous NiFe regions showing in the EBSD phase map. Since discontinuous NiFe regions with same orientations may actually be part of a huge NiFe grain formed during liquid-phase sintering, the measurements could be inappropriate in describing the true grain size of NiFe phase.

Chemical compositions near the W/NiFe interface in 90W-0R and 90W-87R-RD are shown in Figure 9. In both cases, the major alloying elements, W, Ni, and Fe, all exhibit sharp profiles with a transition region of width about 2-5 nm. It can be seen W is able to dissolve in NiFe phase to a small percentage (mean=6.8 at%), while Ni and Fe are almost non-soluble in W phase. An extremely minor enrichment of O has been observed in the as-received 90W-0R but it disappears in hot-rolled 90W-87R-RD. Other minor elements segregated near W/NiFe interphase boundaries are H and Si. However, we need to caution that a





**Figure 9.** APT measured composition across W/NiFe interfaces in as-received 90W-0R and hot-rolled 90W-87R-RD samples.

#### Tensile Testing

Tensile testing of all specimens was carried out at room temperature at crosshead displacement speeds of 0.1, 1, and 10 microns per second, as listed in Table 2. The standard procedure calls for three specimens to be tested at each displacement rate. However, due to the limited number of specimens available, only two tensile specimens were tested for the hot-rolled materials, while more than three were tested for some 10 micron/s tests of the as-received materials due to large variations in the failure strain. The orientation of the tensile specimens for the hot-rolled 90W-87R is shown in Figure 8. Due to flexure of the specimens and settling of the contact points in the elastic region, the measured strain rates in the elastic region were inconsistent and, in some cases, negative even though the samples were strictly in tension. Once plasticity had initiated, the strain-time curve became reliably linear, so for all practical purposes the strain rate of this region can be assumed to be the strain rate through the entirety of the test. In general, the 0.1, 1, and 10 micron/s displacement rates correspond to plastic regime strain rates of 0.0016, 0.016, and 0.16 %/s, respectively. A more detailed relationship for each test is presented in the tables following the strain-stress curves.

Specimene	Tensile	Fensile Number of tested specimens		
Specimens	Direction	@0.1 µm/s	@1 µm/s	@10 µm/s
90W-0R	N/A	3	3	6
90W-87R-RD	RD	2	2	2
90W-87R-ND	ND	2	2	2
95W-0R	N/A	3	3	3
97W-0R	N/A	3	3	3

Tahlo	2	Tonsilo	testing	matrix
rable	۷.	rensile	lesting	maunx



Figure 10. Orientation of the tensile sample relative to the rolling direction (RD) of the W-NiFe alloy samples.

A summary of yield strength, ultimate tensile strength, and ultimate elongation is presented in 11. In general, the measured yield strength and ultimate tensile strength increases as test speed increases from 0.1 um/s to 10 um/s for all materials. The ultimate elongation for the as-received 90W-0R material is ~20% at all test speeds; of all the materials tested this one shows the best ductility. The ultimate elongations of the hot-rolled 90W-87R-RD and 90W-87R-ND are on the order of 10%; the as-received 95W-0R shows similar ductility. However, the ultimate elongations are not conclusively different among the three displacement rates for the rolled materials and 95W-0R; for the rolled materials this could be attributed to the limited number of test specimens available. By comparison, the 97W-0R shows very poor ductility, with a maximum measured failure strain of less than 3%. Note that the 97W-0R ultimate elongation is much lower than advertised by the vendor (12% elongation of the 95W and 10% for the 97W in the technical documents on their website) [10].



**Figure 11.** Summary of a) yield strength, b) ultimate tensile strength, and c) ultimate elongation for asreceived 90W-NiFe, hot rolled 90W-NiFe (RD: rolling direction, and ND: normal direction), as-received 95W-NiFe, and as-received 97W-NiFe, at three displacement rates. When a load is applied to a cracked material, it may either store that energy through elastic deformation or it may dissipate that energy through either plastic deformation or crack propagation. For strain rate-sensitive ductile materials such as the NiFe matrix, it is common for sustained elastic energy to be dissipated as plastic deformation through minor viscoelastic effects, leading to work hardening of the matrix. Normally the ductility of materials is better when tested at lower strain rates, due to more time allowed for plastic deformation. However, it has been reported in some materials systems that higher strain rate could lead to better ductility. For example, you et al. have reported a nano twined Cu was significantly reduced tensile ductility at low strain rate due to microstructure evolution during deformation and grain boundary restrictions [11]. Further analysis and experiments on the hot-rolled materials will be needed to understand the increased elongation at higher strain rates, and although statistical error cannot be ruled out, more mechanical testing on these materials will help to confirm or reject current observations. Individual strain-stress curves and strain rate summaries for each test are appended for future reference.





Table 3.	Corresponding plastic region strain rates for 90W-0R specimer	s tested	at three	displacem	nent
	speeds				

Crosshead Displacement Speed	Plastic Region Strain Rate		
(µm/s)	(%/s)		
0.1	0.00167±0.00005		
1.0	0.01653±0.00012		
10	0.16467±0.00505		



Figure 13. Strain-stress curves for 90W-87R-ND tensile testing at three displacement speeds.

Table 4. Corresponding plastic region strain rates for 90W-87R-ND specimens tested at three
displacement speeds

Crosshead Displacement Speed	Plastic Region Strain Rate
(µm/s)	(%/s)
0.1	0.00162±0.00004
1.0	0.01615±0.00007
10	0.16650±0.00071





Figure 14. Stress-strain curves for 90W-87R-RD tested at three displacement speeds.

**Table 5.** Corresponding plastic region strain rates for 90W-87R-RD specimens tested at three displacement speeds

Crosshead Displacement Speed (µm/s)	Plastic Region Strain Rate (%/s)
0.1	0.00170±0.00001
1.0	0.01690±0.00014
10	0.17750±0.00354





Figure 15. Stress-strain curves for 95W-0R tested at three displacement speeds.

Table 6. Corresponding plastic region strain rate	s for 95W-0R0	) specimens	tested at	three	displacen	nent
:	speeds					

Plastic Region Strain Rate
(%/s)
0.00156±0.00004
0.01630±0.00010
0.16700±0.00173







Figure 16. Stress-strain curves for 97W-0R tested at three displacement speeds.

**Table 7.** Corresponding plastic region strain rates for 97W specimens tested at three displacement speeds

Crosshead Displacement Speed	Plastic Region Strain Rate
(µm/s)	(%/s)
0.1	0.00162±0.00003
1.0	0.01640±0.00085
10	0.16533±0.00493

#### FUTURE WORK

Due to the COVID-19 crisis from March until the present, there are some delays in the current work progress, mainly in the experimental work and consequent modeling. The primary areas of delay are:

- Characterizing the fracture surfaces of tested specimens at all conditions.
- Converting the obtained microstructure data to finite element meshes for model development.

The future work at PNNL includes testing and characterizing (before and after failure) the following DPT materials to provide data for model development and validation.

- Exploring the effects of matrix composition on mechanical properties.
- Exploring the high-temperature properties and service limits of these materials.
- Characterizing and testing ion-beam irradiated composites to study the effects of He, H, and atomic displacement damage.

#### ACKNOWLEDGEMENTS

This research was supported by Office of Fusion Energy Sciences, U.S. Department of Energy (DOE) under Contract DE-AC05-76RL01830.

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[11] Z. You and L. Lu, Effect of Strain Rate on Tensile Ductility and Fracture Behavior of Bulk Nanotwinned Copper, Advanced Engineering Materials, 2015, 17, 1754-1759 **4.8 ELECTRICAL CONDUCTIVITY EVALUATION OF NEUTRON IRRADIATED TUNGSTEN MATERIALS FROM THE PHENIX CAMPAIGN**\_J. R. Echols, L. M. Garrison (Oak Ridge National Laboratory)

# OBJECTIVE

The goal of the PHENIX collaboration is to expand the database on neutron irradiation effects in tungsten materials. This task evaluates the effects of irradiation at elevated temperature on electrical resistivity.

# SUMMARY

Electrical resistivity measurements conducted on single and polycrystalline tungsten samples exposed to neutron radiation between 0.2 and 0.7 dpa show increased resistivity, but do not show clear trends on the basis of dpa alone. Polycrystalline samples with elongated grains exhibit measurable changes in resistivity depending on sample orientation and this effect is exaggerated following irradiation – showing that grain boundaries play a role in changes to resistivity upon irradiation.

# PROGRESS AND STATUS

The goal of the US-Japan collaboration, PHENIX, is to investigate tungsten and tungsten-based materials responses to neutron irradiation for use in future fusion reactors. Over 1500 single crystal, polycrystalline, and W-Re alloy samples were exposed to neutron radiation in the RB\*19J irradiation capsule in the High Flux Isotope Reactor (HFIR) to doses of ~0.2-0.7 dpa. The nominal irradiation temperatures were 430-670, 740-960, and 880-1080°C and a gadolinium shield was included in the capsule to reduce the thermal neutron flux, and therefore the rate of W to Re,Os transmutations, to more fusion relevant values.

Tungsten's high thermal conductivity is critical for its use in future fusion reactors and is one of the reasons tungsten is the leading candidate material for high heat flux regions of reactors. Neutron irradiation in a reactor environment, however, degrades the thermal conductivity of tungsten. In order to separate the phonon, electron, and transmutant element contributions to tungsten thermal conductivity, electrical conductivity measurements need to be taken and compared against thermal conductivity measurements.

For the purposes of this report, electrical resistivity (the inverse of conductivity) is given. Measuring resistivity is done by applying a current to a sample of material and determining voltage changes across a known geometry. Ideal resistivity ( $\rho$ ) is defined as the resistance (R) of a uniform specimen multiplied by the cross-sectional area (A) and divided by the length (I) of the specimen, shown in **Equation 1**.

# Equation 1. $\rho = R \frac{A}{l}$

The geometry, radioactivity levels, and HFIR capsule geometry severely limit the size of the samples which can be used. Therefore, to measure the electrical conductivity of the irradiated samples, a miniature electrical resistivity fixtures was designed and constructed for 3 mm diameter discs, which is shown in Figure 1. The measurement system utilizes a Keithley Model 182 Sensitive Digital Voltmeter to measure the voltage drop across the inner two leads. A Model 237 High Voltage Source Measure Unit provides the current source. Resistivity testing was performed at room temperature, between 20°C and 24°C. Resistivity values were then normalized to 20°C for comparison. General test procedures for electrical resistivity testing on metals are given in ASTM B 193-87, Standard Test Method for Resistivity of Electrical Conductor Materials.

Sample surfaces from the 880-1080°C irradiation zone was found to be discolored by an opaque film of presumed impurities following irradiation. An SEM cross-section of sample which fractured during testing, BT07, is shown in Figure 2, and shows this film to be approximately 20-30 microns thick for this sample.



**Figure 1**. Electrical resistivity testing device. a) Disassembled 3 mm disk holder with the apparatus on the left and an example 3 mm disk with the plug on right. b) Assembled 3 mm disk fixture with the disc inserted and the plug clamped to the apparatus to ensure proper contact with the pins. c) Simplified schematic for the apparatus. Circuit schematic specifies length (I), width (w), and thicknesses (t) used in resistivity calculation. Major gridlines in a) and b) are 1 cm apart.



**Figure 2**. SEM micrographs of fractured sample (BT07) highlighting the contamination layer present on the surface. (Left) A cross-section highlighting the change in fractured morphology from the bulk (left side of the image) to the surface (right side of the image), indicating an approximately 20-micron thick contamination layer at the surface. (Right) An angled view, showing the surface of the contamination layer in the foreground, the fractured contamination layer, and the fractured tungsten.

The EDS scans performed on this surface layer are not yet definitive but indicate that the contaminations may be carbides and/or oxides of tungsten. This film was removed on one side for all resistivity evaluated samples from this temperature zone by a series of ~10-micron thick polishes, until the film was no longer present. The polished sample side was placed "down" in the fixture to contact the electrical resistivity probes, and the unpolished side touched the nonconductive plug that fixes the sample in place. Verification steps were taken to assure that resistivity values obtained are consistent regardless of sample thickness.

Electrical resistivity was measured for thick plate ALMT produced polycrystalline tungsten with elongated grains (material codes AT and BT) and single-crystal tungsten (material code UE). For the polycrystalline samples, samples were cut in different orientations with respect to the elongated grains. AT series samples

**BT** Series – No Irradiation

are cut at 90 degrees relative to BT series samples. Examples of the microstructure when viewing the sample face are given in Figure 3. Grain size calculations taken on these images utilizing the linear intercept method indicate an average grain length of 2.1 microns for the AT series, and 1.4 microns / 2.3 microns for the BT series in the horizontal and vertical directions, respectively.

AT Series – No Irradiation



Figure 3. Unirradiated grain structure for AT (isotropic grains) and BT (elongated grains) series materials.

Electrical resistivity measurements for measured samples are shown in Figure 4. Unirradiated tungsten exhibits resistivity around 0.55 n $\Omega$ m. All polycrystalline samples exhibit resistivity in excess of 0.63 n $\Omega$ m following irradiation. There does not appear to be a simple relationship between resistivity and either temperature or dose – with sample irradiated to higher doses and temperatures (e.g. AT04 & BT05) exhibiting lower resistivity than samples at lower doses and temperatures (e.g. AT02 & BT02). This effect is likely a result of higher temperatures enabling better healing of radiation-induced damages that inhibit electron transfer.

A single sample of single crystal tungsten, UE02, exhibits low resistivity, around 0.57 n $\Omega$ m, following irradiation. UE06, however, which was irradiated at higher temperature and approximately double the dose, has resistivity more similar to the polycrystalline samples. Further testing of single crystalline samples is expected to elucidate this data.



**Figure 4**. Electrical resistivity of unirradiated, AT, BT, and UE series materials as a function of dpa. Approximate irradiation temperature for each sample is given in the legend. Measurements were taken between 20°C and 24°C and normalized for 20°C



**Figure 5**. Electrical resistivity as a function of sample rotational orientation relative to the probes for selected polycrystalline samples. Sine waves fit to the BT series samples are shown in yellow. The 0-degree angle is arbitrary for individual samples because the grains are too small to see with the eye when inserting samples in the fixture.

BT series polycrystalline samples, when rotated 45 degrees in the resistivity fixture between measurements, exhibit a periodicity in resistivity. Figure 5 shows the angular/resistivity relationship for these samples, along with a comparison for the equiaxed AT series samples. The equiaxed AT series sample does not show any apparent periodicity. For the irradiated BT specimen, there is an approximately 5% change in resistivity depending on the sample orientation. There is also an apparent difference in amplitude in the BT series samples. The unirradiated amplitude is  $\sim 10^9$  while the irradiated sample BT02 is approximately double that. It is likely that either radiation defect and/or transmutant element segregation to the grain boundaries is responsible for this amplitude increase.

# FUTURE PLANS

Testing will continue for single crystal specimens and for W-Re alloys. Comparisons to irradiation temperature, transmutation, microstructure, and thermal conductivity will be made in to clarify their relationship to irradiation changes in electrical resistivity.

**4.9 MODEL GUIDED DESIGN AND SYNTHESIS OF SOLUTE-STABILIZED TERNARY NANOSTRUCTURED TUNGSTEN ALLOYS**—N. Olynik, W. Wang, J.R. Trelewicz (Stony Brook University), C.M. Parish (Oak Ridge National Laboratory)

# OBJECTIVE

Although tungsten has emerged as a promising candidate for plasma-facing components, there are several outstanding issues yet to be resolved including high temperature stability limited by recrystallization, mechanical performance, and long-term radiation tolerance. The overarching technical aim of this research is to address these limitations in tandem by precisely tailoring the volume fraction, chemistry, and structural state of grain boundaries in nanostructured tungsten alloys. We focus specifically on the W-Ti-Cr ternary system where Ti is introduced to stabilize the nanocrystalline grain boundary network while Cr is added to reduce the required sintering temperatures while simultaneously enhancing the alloy's oxidation resistance.

# SUMMARY

The lattice Monte Carlo (LMC) modelling technique was implemented to identify ternary compositions in the W-Ti-Cr system that simultaneously produce Ti segregation at grain boundaries for alloy stabilization and the formation of Cr-rich nanograins to enhance sinterability at temperatures below the recrystallization temperature of commercially-pure tungsten. Guided by these LMC simulation results, mechanical alloying and grain refinement during high-energy ball milling was studied in the ternary W-Ti-Cr system. Microstructure and phase evolution were mapped as a function of the milling parameters to downselect a processing condition for achieving a nanostructured W alloy containing Ti and Cr in solid solution with a small volume fraction of retained BCC Cr.

# **PROGRESS AND STATUS**

Stable nanocrystalline states in ternary W-Ti-Cr alloys were explored as a function of alloy composition using a LMC formalism that probes a configurational space incorporating chemical mixing collectively with grain boundaries<sup>1</sup>. The relative content of both solute additions (Ti and Cr) was systematically varied from 2 to 20 at. % to produce 16 unique compositions as summarized in Figure 1a; each simulation was constructed to contain 400 x 400 x 6 sites on a BCC lattice. Simulations were initialized with random site assignment of chemical identity and grain allegiance with alloy configurations evolved using the Metropolis method<sup>2</sup> at a series of temperatures from 25-1400 °C. Energy parameterization used distinct interactions for lattice and grain boundary sites using enthalpies of mixing and grain boundary segregation for the binary W-Ti, W-Cr, and Ti-Cr systems. Representative snapshots of energy minimized grain structures at 400 °C are shown in Figure 1b for the constant Cr, varying Ti series and Figure 1c for the constant Ti, varying Cr series with Ti lattice sites colored red and Cr yellow. Ti was observed to grain boundary segregate at concentrations  $\leq$  10 at. %, which transitioned to phase separation as the concentration was increased to 20 at %. At low concentrations, Cr exhibited a combination of segregation and solute rich clustering, and the formation of these nanoclusters dominated at higher Cr contents.



**Figure 1.** (a) W-Ti-Cr ternary phase space summarizing compositions investigated using LMC models to identify thermodynamically preferred states in this alloy system. Energy-minimized nanostructures for (b) varying Ti and (c) varying Cr concentrations at 400 °C. Grain boundary segregation and nanoscale phase separation are evident in both series where the nature of the nanostructure depends on both the Ti and Cr concentration.

While grain boundary segregation stabilizes the nanocrystalline state as illustrated by retention of the nanostructure in Figure 7 up to 1400 °C, the formation of Cr rich nanoclusters has been shown to enable accelerated solid-state phase sintering<sup>3</sup>. Thus, a combination of these two features are desirable from an alloy design perspective and from Figure 2, W-5Ti-(5-10)Cr appears to offer a combination of stability up to 1400 °C and the formation of solute rich nanoclusters. While this behaviour fails to capture the kinetics of solute redistribution at various temperatures, it provides a convenience approach for down-selecting alloy compositions for experimental study.



**Figure 2.** Representative LMC phase diagram for tungsten containing 5 at. % Ti and varying Cr concentrations. While the nanostructure evolves both with Cr content and temperature, it is predictively stable up to 1400 °C albeit accompanied by changes in the grain boundary segregation and phase separation state.

Guided by the LMC simulations, mechanical alloying and grain refinement during high-energy ball milling was studied in the ternary W-Ti-Cr system. The initial composition for optimization of the milling parameters was W-10Ti-20Cr, which represents the maximum alloying content of interest in the LMC results; future studies will consider systematic variations in Ti and Cr of 5, 10, 15, and 20 at.%. From Figure 3, the powder size distributions generally shifted to finer sizes after 4 hours of milling but evolved to a bimodal distribution after 12 hours likely due to agglomeration of ultra-fine particles. Morphologies also evolved as the particle size refined and involved a transient state with platelets morphologies prior to the formation of spherical geometries.



**Figure 3.** (a) Particle size distributions as a function of milling time. Scanning electron micrographs for (b) the initial tungsten powder, and after milling for (c) 4 hours and (d) 12 hours. Note the change in powder morphology from platelets to spheres.

X-ray diffraction (XRD) spectra are shown in Figure 4a as a function of milling time. The minor HCP Ti peaks from the mixed powders disappear after milling for 6 hours, indicating that Ti completely dissolved in the BCC W lattice. Conversely, the BCC Cr peaks remained throughout milling, though their intensity decreased with milling time also denoting dissolution of Cr. The evolution of HCP Ti and BCC Cr, determined through Rietveld refinements, is shown in Figure 4b and captures retention of a small volume fraction of BCC Cr phase while HCP Ti is confirmed to completely dissolve into the solid solution. Refinement of the grain structure accompanied the mixing process due to the high deformation energy imparted through the ball milling process. In order to accurately fit the various spectra, two grain size populations denoted W1 and W2 in Figure 4c were employed in the Rietveld refinements. The convolution of these two populations produced the average grain size trend, which demonstrates that a significant reduction in grain size occurred after 6 hours to produce a nanocrystalline structure with 10-20 nm grain sizes.



**Figure 4.** (a) XRD spectra for the milled W-10Ti-20Cr alloy (at. %) relative to the initial blended powders. Evolution of the (b) BCC Cr and HCP Ti phases and (c) grain size as a function of milling time. A best fit was obtained in the Rieveld analysis using two grain size populations, which are ploted relative to the average grain size.

The transmission electron micrographs in Figure 5 were acquired on regions from two different powder particles from the powder sample used in the above XRD measurements. One powder particle exhibited the fine equiaxed nanocrystalline grain structure shown in Figure 5a with grain sizes of 10-20 nm. An adjacent particle located on the same TEM grid instead exhibited a highly deformed microstructure containing larger elongated nanocrystalline grains as shown in Figure 5b. We refer to this region as a transitional microstructure, which is attributed to non-uniform deformation of the powder particles during high-energy ball milling.



**Figure 5.** Dark-field TEM micrographs highlighting (a) the equiaxed grain structure with a grain size of 10-20 nm and (b) the deformed transitional microstructure containing elongated grains and a generally larger grain size relative to the equiaxed region.

To confirm the origin of the transitional microstructure and its relation to the powder morphologies in Figure 3, we compacted powders into the XRD sample holders such that the flat surfaces of the platelets after 6 hours of milling were parallel to the surface of the holder. The XRD results of from this oriented packing configuration relative to a randomly packed powder sample are shown in Figure 6. As compared with the randomly packed powder sample, (200) and (211) peaks are accentuated in the oriented powder in Figure 6a. The intensity of the (200) peak relative to the (110) peak is plotted as a function of milling time in Figure 6b, where it can be seen to maximized at a milling time of 6 hours. These preferred orientations are attributed to a {110} texture orthogonal to the direction the coarse-grained powders were crushed during early stages of milling process. As grain size was refined, the preferred BCC slip system for coarse-grained tungsten was eliminated, and the cold welding/fracture process evolved to produce the spherical particles shown in Figure 1d. We note that microstructural heterogeneities remain even after 12 hours of milling from the TEM analysis, though the grains in these transitional regions are also nanocrystalline.



**Figure 6.** XRD spectra for the W-10Ti-20Cr powders milled for 6 hours loaded into the sample holder in two different confiruations. The "oriented packing" configuration aligned the platelet with a preferred (200) orentation emerging, which corresponds to a favorable BCC slip system and consistent with the deformed transitional microstructure.

# **FUTURE WORK**

Systematic experiments are underway to correlate structural features at the nanoscale with alloy chemistries and aging conditions. By selecting ternary configurations containing Ti at grain boundaries and a distributed Cr-rich nanophase, bulk nanostructured samples will be produced and characterized via synchrotron x-ray analysis and correlative electron microscopy experiments.

#### ACKNOWLEDGEMENTS

This work was supported by the Department of Energy through Grant DE-SC0017899.

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**4.10 TAILORING MICROSTRUCTURE IN SINTERED Cu-Cr-Nb-Zr ALLOYS FOR FUSION COMPONENTS**—B. Cheng, D. J. Sprouster, L. Snead, J. R. Trelewicz (Stony Brook University), L. Wang, W. Zhong, Y. Yang (Oak Ridge National Laboratory), S. J Zinkle (University of Tennessee)

# OBJECTIVE

The development of next generation fusion energy systems will require high-strength, high-thermal conductivity, and irradiation-tolerant materials for plasma facing components [1]. Unfortunately, commercially available copper alloys have primarily been designed for low-temperature applications and suffer from pronounced creep at temperatures above 300-400°C. Moreover, little effort has been placed on fabrication of irradiation-stable copper alloys. One suggested metallurgical approach to realize superior alloys involves the introduction of a high density of planar interfaces or distributed secondary phases to impede creep, promote radiation-induced defect recombination while retaining high strength. It is in this light that multiple grain/twin boundaries, precipitates, dispersions strengthened Cu alloys have been proposed via different processing methods. The aim of this task is to produce and characterize the microstructure of novel Cu-Cr-Nb-Zr (CCNZ) alloys with tailored precipitate distributions for enhanced stability and creep resistance [1].

# SUMMARY

We have developed a powder metallurgy processing route, incorporating a combination of gas atomization for alloying, and consolidation via direct current sintering (DCS). Synchrotron-based X-ray diffraction (XRD) and small angle X-ray scattering (SAXS) have been leveraged to characterize the crystallographic phases, crystallite sizes, and size distribution of coarse Cr precipitates, Cr<sub>2</sub>Nb precipitates and Cr nanoprecipitates. Conventional TEM has also been employed to directly reveal microstructure of consolidated compacts.

# **PROGRESS AND STATUS**

From our fabrication process, fully dense CCNZ alloys with microstructures representative of cast CCNZ were achieved through direct current sintering (DCS) at 970°C under 50MPa pressure for 10min. Heat treatment of the as-sintered alloy was performed following the procedure outlined by Yang, et al [2]. XRD and SAXS patterns for the as sintered and heat-treated sample is shown in Figure 1. As seen, FCC Cu, BCC Cr and FCC Cr<sub>2</sub>Nb phases are identified in as-fabricated and following heat treatment. Figure 2(a) shows the TEM results for the heat-treated sample. Multiple microstructural characteristics are observable: i) a fine average Cu matrix grain size (~6µm), ii) large Cr2Nb precipitates located at GBs, and iii) Cr nanoprecipitates dispersed in the Cu matrix. Statistical results in Figure 2 (b) indicate that the average size and number density of Cr<sub>2</sub>Nb precipitates are 80.39 ± 14.49nm and 1.46x10<sup>20</sup>/m<sup>3</sup>, respectively. The Cr<sub>2</sub>Nb and Cr particles are consistent with the XRD results. The high-resolution TEM micrograph together with the selected area diffraction pattern for a Cr<sub>2</sub>Nb precipitate in Figure 2(c) shows that it is single crystal with internal stacking faults. In Figure 2 (d), the dark field image of Figure 2(a) is shown with corresponding elemental maps for Cu, Cr, Nb and Zr in Figure 2(e). It is clear that all the precipitates highlighted in Figure 2(d) coincide with the Cr and Nb-rich regions. Figure 2 (f) shows the overlay of the Cr and Nb EDS signals with the dark field TEM micrograph highlighting the Cr<sub>2</sub>Nb. The Zr atoms are evenly distributed throughout the Cu matrix. Figure 2(g) shows a high-magnification TEM micrograph of a region marked (red square) in Figure 2(a), to highlight the Cr<sub>2</sub>Nb precipitates are surrounded by Cr nanoprecipitates. The corresponding Cr and Nb EDS maps are shown in Figure 2 (h) and (i), respectively. The EDS results show that the nanoprecipitates are indeed Cr-rich. A high-density of Cr nanoprecipitates in the Cu matrix are observed from the TEM images shown in Figure 2(g-i). The size distribution and number density are 8.10 ± 1.45 nm and 3.1x10<sup>22</sup>/m<sup>3</sup> respectively. The size, and size distribution for the small Cr nanoprecipitates from SAXS

and TEM are consistent. A summary of the microstructures of the as fabricated and sintered CCNZ alloys from the synchrotron and TEM characterization are given in Table 1.



**Figure 1.** XRD patterns (a) for as sintered (b) heat treated CCNZ specimens. (c) SAXS intensities for as sintered, heat treated, and heat treated - as sintered (to isolate the small Cr nanoprecipitates). (d) SAXS fitting results are shown in panel (d).

A summary of the physical properties for CCNZ and CCZ alloys are presented in Table 2 [3-4]. The multiple precipitates and fine Cu grain size of our DCS CCNZ alloys result in a relatively high hardness for this material (133.2 HV). Moreover, this high hardness was achieved without compromising the electrical (thus thermal) conductivities. The sintered CCNZ achieved an electrical conductivity of 74.6% of the international annealed copper standard value, and a high-thermal conductivity of 298.4 W/m<sup>-</sup>K, which is in the vicinity of the proposed target (>300 W/m<sup>-</sup>K).



**Figure 2.** a) TEM micrograph and (b) the size distribution of  $Cr_2Nb$  precipitates for the heat-treated sample. (c) high-magnification TEM micrograph of a  $Cr_2Nb$  precipitate with selected area electron diffraction pattern inset. (d) dark field TEM micrograph of the same region in (a). (e) EDS maps of Cu, Cr, Nb, and Zr element corresponding to the dark field TEM micrograph. (f) overlay of dark field TEM, Cr and Nb EDS maps. (g) high-magnification TEM micrograph (highlighted by a red dashed square in (a)) and corresponding (h) Cr and (i) Nb EDS maps.

In summary, multiple precipitate populations with different size and number density are achieved in the aged CCNZ alloys with coarse-Cr and Cr<sub>2</sub>Nb precipitates located at GBs, and Cr nanoprecipitates dispersed throughout the Cu matrix. Quantitative size and particle distributions generated from XRD, SAXS, and TEM agree. We have prepared an article discussing and comparing the microstructural properties and performance of our CCNZ to other CCNZ processing routes and propose a precipitation process via our powder metallurgy approach [5]. A high-level result of this work suggests that the CCNZ alloys can be

achieved through DCS and therefore are a candidate for further study as a creep resistant copper alloy to be used in graded HHF structures. Current and planned work include investigating the effects of irradiation and base mechanical properties including mechanical creep.

Microstructure	As-sintered	Heat-treated
Cu Grain size (µm)	8.27 ± 2.73	6.75 ± 2.38
Cu Crystallite size (nm)	507.4 ± 18.8	346.7 ± 11.7
Cu Lattice Parameter (Å)	3.6194 ± 1.6E-5	3.6178 ± 2.2E-5
Cr <sub>2</sub> Nb Precipitate size (nm)		80.39 ± 19.49/
Cr <sub>2</sub> Nb Precipitate number density (m <sup>-3</sup> )		1.46 × 10 <sup>20</sup>
coarse-Cr Precipitate size (nm)		483.07 ± 95.65/
coarse-Cr Precipitate number density (m <sup>-3</sup> )		2.92 × 10 <sup>17</sup>
nanoprecipitate Ćr (TEM) (nm)	-	8.09 ± 1.45
nanoprecipitate Cr (SAXS) (nm)	-	7.16 ± 1.26
Number density (m <sup>-3</sup> )	-	3.11 × 10 <sup>22</sup>

Table 1. Microstructure of Sintered CCNZ alloys

Table 2. Comparison of microstructures and properties at room temperature for CCNZ and CCZ alloys

Microstructure/Property	DCS CCNZ (Sintered and Aged)	Ingot-Casted CCNZ [4]	Ingot-Casted CCNZ (High- purity) [3]	Aged CCZ [3]
Cu Grain Size (µm)	5.7 ± 2.6	~20	40 ± 9	39 ± 5
Cr <sub>2</sub> Nb Precipitate Size (nm)	80.39 ± 19.49	300~500	2000-11000	-
Hardness (Vickers)	133.2 ± 2.8	126.2 ± 2.8	137.9 ± 7.0	135.8 ± 6.2
Electrical Conductivity (%IACS)	74.6 ± 1.3	56.7 ± 0.5	72.1	83.4
Thermal Conductivity (W/m·K)	298.4 ± 1.2	-	-	

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#### 5. MAGNETIC AND DIAGNOSTIC SYSTEM MATERIALS

No contributions this reporting period.
6. FUSION CORROSION AND COMPATIBILITY SCIENCE **6.1 LIQUID METAL COMPATIBILITY IN FLOWING SYSTEMS**—B. A. Pint, J. Jun (Oak Ridge National Laboratory)

## OBJECTIVE

The first goal of this research was to investigate the maximum Pb-Li temperature achievable in the dual coolant lead-lithium (DCLL) blanket concept for the overall system efficiency. FeCrAl alloys are potential candidates and a series of monometallic thermal convection loops (TCL) fabricated from a commercial FeCrAl alloy have been operated to assess the maximum use temperature where FeCrAl is compatible with flowing Pb-Li. New experiments are now focused on examining more fusion-relevant materials such as SiC and ODS FeCrAl in flowing Pb-Li with a peak temperature of 700°C.

## SUMMARY

The fourth and fifth TCL experiments have completed 1000-h exposures with a peak temperature of 700°C and ~80°C temperature gradient. Specimen characterization is in progress from both experiments. The fourth TCL was a monometallic experiment with Kanthal alloy APMT (Fe-21Cr-5Al-3Mo) tubing and specimens. Post exposure tensile properties were more degraded than in prior experiments at lower temperatures. The fifth TCL contained CVD SiC and ODS Fe-10Cr-6Al specimens in a TCL also fabricated from APMT. The mass changes were much larger with mass gains for most SiC specimens and moderate to large mass losses for ODS FeCrAl specimens, 5-100X higher than the previous loop. Initial characterization indicated that the ODS FeCrAl specimens did not form LiAlO<sub>2</sub> in all cases and X-ray diffraction identified numerous Fe-Si, Fe-Cr-C and Li-Al-Si compounds on the SiC specimens.

#### PROGRESS AND STATUS

#### Introduction

To inhibit the direct contact between liquid Pb-17at.%Li and ferritic steels, one strategy is to form a stable, adherent surface oxide such as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> on FeCrAl alloys or Al-rich coatings [1-4]. This strategy has the potential to raise the maximum operating temperature of the DCLL blanket concept for a demonstration reactor. The goal of this ongoing project has been to assess the maximum temperature where an Al-containing alloy could maintain good compatibility with flowing Pb-Li in a temperature gradient using TCLs. A series of monometallic TCL experiments has been conducted using commercially available tubing material Kanthal alloy APMT (Advanced Power Metallurgy Tube) with each TCL having an increased maximum temperature [3,4]. The fourth TCL experiment with a peak temperature of 700°C showed significant mass loss of APMT specimens at the highest temperature, suggesting that 700°C is the highest temperature where this strategy is operable.

The fifth TCL experiment was completed in April 2000 with nominally the same conditions as the 4<sup>th</sup> experiment but including more fusion relevant materials: chemical vapor diffusion (CVD) deposited high purity SiC and low-Cr ODS FeCrAI [5,6] to avoid issues with  $\alpha'$  embrittlement. The characterization is still in progress but the specimen mass changes were significantly higher than in the previous monometallic TCL experiment and it appears clear that having multiple materials resulted in dissimilar materials interactions.

# **Experimental Procedure**

The fourth and fifth TCL experiments followed similar procedures as detailed previously [3,4]. Chains of 20 specimens were exposed in the hot and cold legs of the TCL for 1000 h with a peak temperature of 700°C in the hot leg. Coupon specimens were 15 x 25 x 2 mm and the tensile specimens were 25 mm long SS-3 type. Chemical compositions of the specimens and APMT tubing are given in Table 1. Many of the APMT and ODS Fe-10Cr-6Al specimens were pre-oxidized for 2 h at 1000°C in laboratory air [4]. The APMT loop was pre-oxidized for 8 h at 1050°C as part of the post-weld heat treatment procedure [3]. After the exposure, the PbLi was dumped into a stainless steel tank and the TCL was cleaned using the standard solution of acetic acid, ethanol and hydrogen peroxide [3,4]. Specimens were weighed before and after exposure using a Mettler Toledo X205 balance with an accuracy of  $\pm 0.04$  mg. The coupons were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). Post-exposure room temperature tensile testing was conducted with a ~10<sup>-3</sup> s<sup>-1</sup> strain rate.

# Results

The characterization of the specimens from the 4<sup>th</sup> monometallic APMT loop with a peak temperature of 700°C is nearly complete. Figure 1 shows the post-exposure room temperature tensile properties compared to those in the previous TCL experiment where the peak temperature was only 650°C (open symbols) [4]. In the previous TCL, only minor changes in tensile properties were noted after exposure compared to the as-received APMT tensile properties shown as shaded areas in Figure 1. With a higher peak temperature, there was more variability in the post-exposure results and, in particular, a larger drop in ductility for some specimens, Figure 1b. Previously [7], it was reported that the hot leg chain broke and three specimens were missing and one broken below the first specimen in the chain, thus no information is available from those specimens that may have been significantly attacked (or the APMT wire holding the specimens together) under these conditions.

Figures 2 and 3 show light microscopy of polished cross-sections of APMT specimens from the 4<sup>th</sup> TCL experiment. For the coupon specimens in Figure 2, the surface layers were identified by XRD as either  $\alpha$ - or  $\gamma$ -LiAlO<sub>2</sub> [7], similar to observations from the 3<sup>rd</sup> TCL experiment [4]. Prior work showed that  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> transforms to  $\alpha$ -LiAlO<sub>2</sub> during exposure to Pb-Li [4,8]. For the APMT tensile specimens in Figure 3, flat regions on pre-oxidized specimens suggest little metal loss occurred in these locations. However, in other locations the wavy or pitted interface suggests that some dissolution occurred before a protective Al-rich oxide could form, especially for the bare specimens where the mass change was typically higher [7].

For the 5<sup>th</sup> TCL experiment, all of the operating parameters were repeated including a new APMT TCL. Six coupon specimens of CVD SiC were added to each chain along with ODS FeCrAl coupons and tensile specimens. Four SS3 APMT specimens were included for comparison to the 4<sup>th</sup> experiment. The temperatures measured during the experiment are shown in Figure 4. In the first 200 h of operation, there was a furnace failure and a building power outage that interrupted operation. The experiment was extended ~30 h to account for these events so that there was ~1000 h of hot time with the peak temperature of ~700°C. Figure 5 shows where four "hot-spot" tests [3] were conducted to measure the Pb-Li velocity in the TCL. All of the values were statistically similar between 0.90-0.97 cm/s. Opportunities to check the velocity earlier in the experiment were interrupted by the COVID-19 response.



**Table 1.** Alloy compositions measured using inductively coupled plasma and combustion analyses

**Figure 1**. Post-exposure room-temperature tensile properties of APMT specimens as a function of estimated exposure temperature (a) yield and ultimate tensile strength and (b) total elongation. The open symbols are from the 3<sup>rd</sup> TCL and the closed symbols from the 4<sup>th</sup> TCL. The baseline properties are shown as a shaded band in each case.

After disassembling, it was discovered that the second and fourth specimens in the hot leg had broken due to massive mass loss and the third specimen was missing, similar to the 4<sup>th</sup> TCL, and suggesting that attack was very severe at this location. The chain break disrupted the location of the SiC specimens, which were hung using APMT wire, Figure 6b, so that the SiC specimens were not damaged during loading, unloading or exposure. The location of the six SiC specimens from the hot leg were inferred based on their recovery location. The specimen mass change for all of the TCL experiments is shown in Figure 6a and compared to the mass change from the previous experiment. Many of the mass changes were much higher mass gains (e.g., SiC in cold leg) or larger mass losses (e.g., bare ODS FeCrAl in the hot and cold legs) than the previous experiment. As mentioned previously, massive metal loss (>80% of starting mass) was observed for the 2<sup>nd</sup> and 4<sup>th</sup> specimens in the hot leg chain, both bare ODS FeCrAl specimens. On the cold leg, the ~6 FeCrAl specimens that were pre-oxidized all showed relatively small mass changes but the others were all larger than had been observed in prior experiments. To provide a more direct comparison between the two TCL experiments, four APMT specimens were exposed in the latter experiment with the CVD SiC and ODS FeCrAl specimens. Figure 7 compares the mass change of APMT specimens in the same location in each TCL. Because the temperature distribution was slightly different (based on the temperatures in Figure 4), the estimated temperatures are shown for each specimen. Half of the specimens were bare and the others were pre-oxidized for 2 h at 1000°C. As shown in Figure 7, pre-oxidation reduced the mass losses in the monometallic (4th) TCL and also was beneficial in the 5th TCL but all of the mass losses were significantly higher in the multi-material (5<sup>th</sup>) TCL.



**Figure 2**. Light microscopy of the APMT coupon specimens from the 4<sup>th</sup> TCL experiment showing the oxide layer formed in each case with and without pre-oxidation for 2 h at 1000°C. A protective Cu layer was deposited before mounting.



**Figure 3**. Light microscopy of representative APMT tensile specimens from the 4<sup>th</sup> TCL experiment hot leg (HL) and cold leg (CL). A protective Cu layer was deposited before mounting.



Figure 4. Measured temperatures from the six TCL thermowells during the 5<sup>th</sup> TCL experiment.



**Figure 5**. Measure velocities from hot spot tests performed at four different times during operation of the 5<sup>th</sup> TCL experiment.



**Figure 6**. (a) specimen mass change of TCL specimens as a function of estimated temperature in the hot leg (HL) and cold leg (CL) of the 4<sup>th</sup> (APMT only) and 5<sup>th</sup> (multi-material) TCL experiments (b) all coupons were hung using APMT wire.



**Figure 7**. Specimen mass loss of APMT TCL specimens at similar locations and temperatures in the 4<sup>th</sup> (APMT monometallic) and 5<sup>th</sup> (multi-material) TCL experiments.

Six CVD SiC and all four ODS FeCrAl coupon specimens were selected for XRD analysis. The CVD SiC specimens formed a variety of Fe-Si, (Cr,Fe)C<sub>x</sub> and Li-Al-Si phases. Among the four ODS FeCrAl coupons, only on the bare (not pre-oxidized) hot leg coupon (-44 mg/cm<sup>2</sup>) was an Al-rich oxide detected,  $\alpha$ -LiAlO<sub>2</sub>. For APMT, bare specimens in the 3<sup>rd</sup> and 4<sup>th</sup> TCL formed  $\gamma$ -LiAlO<sub>2</sub> and  $\alpha$ -LiAlO<sub>2</sub> was observed on the pre-oxidized specimen [4,7]. On the pre-oxidized ODS FeCrAl specimens from the hot leg (-52 mg/cm<sup>2</sup>) and cold leg (-16 mg/cm<sup>2</sup>), no oxide phases could be identified. On both bare specimens (-17 mg/cm<sup>2</sup> on cold leg), Pb-rich oxide phases were identified, e.g. Pb(Cr<sub>2</sub>O<sub>7</sub>). All of these results suggest that the ODS FeCrAl specimens with 10%Cr were not able to form a protective Al-rich oxide, compared to the 21%Cr in APMT. The presence of CVD SiC in the TCL may have made forming a protective oxide more difficult as indicated by the higher mass losses for APMT in Figure 7. Particularly at these lower temperatures, the Cr may be critical in assisting alumina (or LiAlO<sub>2</sub>) formation, via the synergistic "third element" effect [9]. Prior work on model FeCrAlY alloys had indicated that Fe-10Cr-5Al had a low mass

loss in a PbLi capsule at 700°C [10]. The ODS FeCrAl contained 6%Al to further improve its oxidation resistance for this and other applications [5,6].

Figures 8-10 show some top-down, plan-view SEM images and associated EDS maps of specimens from the cold leg. In Figure 8, the CVD SiC speicmen from the top of the cold leg (+26 mg/cm<sup>2</sup>) shows a correlation between the Fe and Si maps consistent with an Fe-Si reaction product as identified by XRD (e.g. FeSi, Fe<sub>3</sub>Si, Fe<sub>5</sub>Si<sub>3</sub>, etc.). The Cr map suggests carbide formation but additional characterization is needed to quantify these observations, particularly using cross-sections, which are in progress. Figure 9 shows the CVD SiC specimen from the bottom of the cold leg (+61 mg/cm<sup>2</sup>). In this case, Al-rich precipitates were detected which did not appear to be O-enriched but could be a Li-Al or Li-Al-Si compounds, as identified by XRD.



**Figure 8**. (a) SEM secondary electron image of CVD SiC exposed at 647°C (+26 mg/cm<sup>2</sup>) and associated EDS maps of the same region are shown in (b) Fe, (c) Si and (d) Cr.



**Figure 9**. (a) SEM secondary electron image of CVD SiC exposed at 619°C (+61 mg/cm<sup>2</sup>) and associated EDS maps of the same region are shown in (b) Fe, (c) Al and (d) Cr.



**Figure 10.** SEM secondary electron image of ODS FeCrAl specimens (a) bare specimen exposed at 642°C (-55 mg/cm<sup>2</sup>) and (e) pre-oxidized specimen exposed at 638°C (-3 mg/cm<sup>2</sup>) with associated EDS maps of the same regions (b,f) Fe, (c,g) Al and (d,h) Cr.

Figure 10 shows two different ODS FeCrAl tensile specimens without (-55 mg/cm<sup>2</sup>) and with (-3 mg/cm<sup>2</sup>) pre-oxidation, Figures 10a-d and 10e-h respectively. Obviously in this location, pre-oxidation was very effective in reducing mass loss. In one area, Al-rich oxide was present on the surface of the pre-oxidized specimen in Figure 10g. It is possible that the surface oxide was damaged by handling or cleaning after exposure. For the bare specimen, there was no Al-enrichment detected and significant metal loss occurred.

The characterization work is continuing, especially for the specimens from the 5<sup>th</sup> TCL experiment with polished cross-sections being prepared and specimens sent for tensile testing. In addition, thermodynamic modeling will be conducted to determine what phases are expected to be stable under these conditions. The initial hypothesis is that as the FeCrAl specimens (and possibly the APMT tubing) dissolved, Fe and Cr in the liquid reacted with the SiC as both Fe and Cr are more stable carbides than SiC [11]. The thermodynamic calculations will help determine favorable reactions as Cr carbides and Fe-Si intermetallic phases appear to be the favored reaction products. As Fe and Cr are removed from the liquid, that may accelerate dissolution of the metallic components rather than the liquid saturating.

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#### 7. ADVANCED MANUFACTURING

7.1 ADDITIVE MANUFACTURING: ELECTRON BEAM MELTING OF TUNGSTEN DIVERTOR COMPONENTS—Betsy Ellis, John Echols, Christopher Ledford, Michael Sprayberry, Lauren Garrison, Michael Kirka, Yutai Kato, Ryan Dehoff (Oak Ridge National Laboratory), Sullivan Figurskey, Timothy Horn, Chris D. Rock (North Carolina State University)

#### OBJECTIVE

The objective of this project is to evaluate the electron beam additive manufacturing technique for manufacturing tungsten divertor components. This report will cover the tensile testing of material made previously, as well as efforts to further refine processing parameters for reduced porosity and cracking.

#### Tensile Testing

Two builds (20190613/Sample 3, 20190606/Sample T3) were selected to measure tensile properties. Build properties for both prints are shown in Table 1.

Start temperature (°C)	1350
Speed (mm/s)	70
Current (mA)	4530
Hatch (mm)	0.0325
Power analyze (°C)	1500
Focus offset (mA)	40
Speed function	5

Table 1. Build properties for tensile tested material

Figure 1 shows the layout of samples machined, machining geometries, and an example SS-J3 sample.



**Figure 1.** (Left) Layout of the three tensile testing geometries and relationship to build direction. (Right top) Engineering drawing for the SS-J3 geometry and (right bottom) an example tensile sample, highlighting the level of porosity remaining in the samples.

To determine the effects of build direction on tensile properties, three machining geometries were selected:

- X Side face with tension perpendicular to build direction
- Y Side face with tension parallel to build direction
- Z Top face with tension perpendicular to build direction

Tensile bars in the SS-J3 geometry were machined via wire electrical discharge machining and polished to remove process contamination. Samples were tensile tested on an Instron 1125 with a [???] MPa load cell at an extension rate of 0.2mm/min. All tensile tests were performed at room temperature and pressure and crosshead motion was recorded to estimate strain on the samples. Following failure, fracture surface analysis was performed with a Scanning Electron Microscope (SEM).



Figure 2. EBSD maps and relationship to build direction from the "Sample 3" block.

Porosity in the build volume lead to significant material losses during machining and the resulting samples were extremely fragile. Therefore, only limited tensile data was obtainable. Notably, all samples but one from the "T3" block were lost in machining or handling. The "3" block exhibited better handling durability, but significant porosity was still notable in the individual samples. Example stress-strain curves are given for the 5 tested geometries in Figure 3. Notably, samples from build 3 machined in the 'Y' direction, where tension is parallel to the build direction, exhibited much higher stresses for comparable strains to all other samples and failed at the highest stresses and strains.



Figure 3. Stress-strain curves for example tensile bars from builds 3 and T3.

The relative orientation of the build direction to the tension direction also shows stark contrast in the fractographs, which are shown for build 3 in the X and Y orientation in Figure 4. Transgranular cleavage dominates for samples where tension is parallel to the build direction, whereas intergranular fracture dominates for samples where tension is perpendicular to the build direction (both the X and Z orientations). A more detailed fractograph of a sample loaded in parallel to the build direction is shown in Figure 5. Here, it is clear how the fracture initiation site for these samples is unfused material (circled) and that failure propagates outward from this site.



**Figure 4.** Fractographs and representative EBSD maps for samples from build 3 with tension parallel (3Y03, left) and perpendicular (3X01, right) to the build direction.



**Figure 5.** Fractograph of a sample from build 3 (3Y03) where tension was in the build direction. The circled area highlights the fracture initiation site and arrows show the direction of the propagation of failure.

#### Parameter Development

Previous work on additive manufacturing of tungsten produced dense and crack-free material, but some more recent builds have been of lower quality. Process parameters were refined based on analysis of log files as well as image processing of in-situ near-infrared layer images.

The Arcam EBM system uses a near-IR camera to take an image of each layer of a build, and defects such as cracks or unmelted material may sometimes be identified from these images. Machine learning algorithms may then be used to predict defects in the finished part from these layer images and create a 3-

D reconstruction of the final part. This in-situ defect detection process has been validated for Ti6Al4V and various Ni-base superalloys but has not yet been used for tungsten.



**Figure 6.** Raw in-situ near-IR images (top) and processed images indicating location of pores (bottom) for two tungsten builds.

Figure 6 shows raw near-IR layer images as well as the results of image processing to identify areas of porosity. The following four step image processing flow was used to automate to the detection of anomalies:

1. Image correction and NIR image mapping of the 2D space of the post-melt and post-rake to ensure pixel resolution consistency and accurate localization of anomalies;

2. Correction of temporally dependent emissivity to account for spatially asynchronous thermal decays;

3. Detection of anomalies using spatial statistical analytics; and

4. Measurement of morphological properties of anomalies such as center of mass, volume, orientation, or eccentricity to determine the likelihood of anomaly classification.

Using only those anomalies classified as porosity, an area and volumetric density were calculated. The relative volumetric density of the parts in build 6, shown in Figure 6, is between 99±2 and 100±2%. Further validation of these values is ongoing, as this is the first attempt to use this method for tungsten and the machine learning algorithm requires training on tungsten data for accuracy. In particular, tungsten presents a challenge for this technique because the emissivity's of solid tungsten and tungsten powder are relatively similar, meaning that contrast between melted and unmelted material is not as sharp as in some of the other materials for which this technique has been successfully demonstrated. However, defect detection via in-situ NIR measurements is a very promising technique in that it offers the potential for rapid, non-destructive evaluation of as-built parts and the application of this technique to tungsten deserves further work.

Comparison of two builds with identical melt parameters but different preheat parameters reveals the importance of ambient temperature on cracking in additively manufactured tungsten. Figure 7 shows vertical (XZ) and build-plane (XY) sections of two builds, where the build on the left is uncracked and the build on the right is not. The build on the left (a and c) uses a longer ang higher-current preheat cycle than the build on the right (b and d), with a net preheat of 735 J/mm2 for the build on the left and 395 J/mm<sup>2</sup> for the build on the right. The higher preheat cycle can suppress cracking in the build on the left and will be used for future builds.



**Figure 7.** Influence of preheat on cracking. The part preheated at 735 J/mm<sup>2</sup> (a and c) is not cracked, while the part preheated at 395 J/mm<sup>2</sup> (b and d) is cracked. All parts have a porous support structure beneath the dense region of interest.

Cracking in additively manufactured tungsten is a persistent problem in literature, due to the inherently brittle nature of tungsten. However, Figure 7 shows that crack-free tungsten can be produced via careful tuning of process parameters. As the ambient temperature for both builds in Figure 7 was above 1000°C, merely building above the ductile-brittle transition temperature cannot explain the crack suppression in the 735 J/mm<sup>2</sup> part. The relatively broad beam used in these builds may play a role, as a broad beam will produce a gradual preheat, multiple re-melt cycles, and a gradual tapering re-heat as the beam approaches and then moves away from an individual area. This thermal history is associated with lower-amplitude thermal gyrations, lower thermal gradients, and lower cooling rates, all of which are associated with lower stresses and thus a lower propensity toward cracking. Furthermore, the oxygen content of EBM builds is likely to be lower than those produced using a laser process, as the electron beam melting process occurs under vacuum and uses comparatively large powder, with a correspondingly smaller surface area for oxygen adsorption. Oxygen is well known to contribute to weakening of grain boundaries and consequently cracking in tungsten, so the reduced oxygen content in these builds may also prove to be a necessary factor in the elimination of cracking in tungsten.

## FUTURE PLANS

The refined build and preheat parameters described above will be used to produce larger samples of dense, crack-free tungsten. In addition, further work will be done to understand the nature of the unusual texture seen in additively manufactured tungsten. As seen in Figure 2, additively manufactured tungsten shows a strong (111)/(100) fiber texture parallel to the build direction. This texture has also been observed in other BCC metals produced via additive manufacturing but has yet to be explained. The typical texture observed in additively manufactured FCC metals is a strong (100) texture, without the (111) component. This is attributed to the fact that the (100) is the fast growth direction for cubic materials, and additive processes typically involve a large thermal gradient parallel to the build direction. That explanation would predict a similar (100) mechanism in BCC metals, so the presence of a (111) component requires an alternate explanation. Further modeling and experiments will be performed to explore this texture.

**7.2 CHEMICAL VAPOR INFILTRATION OF BINDER JETTED TUNGSTEN**J. R. Echols, L. M. Garrison, Y. Katoh (Oak Ridge National Laboratory)

#### OBJECTIVE

The purpose of this project is to demonstrate the densification of tungsten produced through binder jet additive manufacturing with chemical vapor infiltration.

#### SUMMARY

Binder-jetted tungsten preforms were produced and initial chemical vapor infiltration runs were conducted to begin optimizing the deposition rate for densification. High densification has been achieved at a depth of  $\sim$ 100µm into the preforms, however, the closure of the surface currently prevents infiltration into the bulk. Studies to optimize deposition rate as a function of temperature and pressure are ongoing.

#### PROGRESS AND STATUS

Because plasma-facing components of fusion reactors can require complex shapes or be composed of many small parts, possess complex internal channels, and/or dissimilar material joins, they make ideal candidates for additive manufacturing (AM). Tungsten, in particular, is attractive for AM because its high melting point and brittleness at room temperature makes it difficult to fabricate through traditional machining methods.

Conventional binder jetting produces parts by selectively depositing a liquid binding agent to join powder particles. Layers of material are bonded to produce a preform. The binding agent is then baked out at high temperature and the part is either infiltrated with liquid material or subjected to hot isostatic pressing (HIPing) to achieve full density. Neither of these solutions, however, are attractive to produce a full tungsten part. Both melt infiltration (which is also impractical due to the extreme melting point of tungsten) and HIPing would likely generate fully recrystallized microstructures, which are potentially unattractive for fusion application. Instead, chemical vapor infiltration (CVI), where tungsten is grown on the particles from gaseous reactants, is proposed.

A diagram illustrating the proposed CVI process is shown in Figure 1. The process occurs by passing gaseous tungsten hexafluoride and hydrogen over the W preform at temperatures in excess of ~350°C as described in the following reaction:

$$3H_2 + WF_6 \rightarrow W + 6HF$$

Disk samples 1.5 mm thick and 8 mm in diameter were produced on an X1-Lab with solvent binder. Initial prints utilizing molybdenum powder were followed by tungsten prints with Tekna W-25 powder. CVI was performed at both Oak Ridge National Laboratory (initial run only), and Archer Technicoat Limited (ATL) in the UK (following runs).

The initial CVI run, with the Mo sample, was carried out at 625°C, and although it successfully deposited W in the preform, the deposition rate was far too high and the sample surface closed too quickly to allow for meaningful densification. The second run with the W preforms, was performed at 450°C. A comparison of the densification from these two runs is shown in Figure 2. This second run produced high densification up to 70µm into the sample bulk and showed evidence of successful infiltration deep into the sample bulk, where limited, but extant, deposition is seen on tungsten particles. A cross-sectional SEM micrograph of this run is shown in Figure 3. Ultimately, the deposition rate at this temperature was also too high and the surface closed off before significant deposition occurred in the sample bulk.



**Figure 1**. CVI allows gaseous reactants to infiltrate the sample bulk and react, depositing tungsten on the particulate surfaces. High density is achieved by allowing the process to carry out over a long time period.



**Figure 2**. Cross-sectional SEM micrographs comparing CVI runs attempted at 450°C (top) and 625°C (bottom).



**Figure 3**. Composite SEM image of a cross section of a sample where CVI was performed at 450°C. Tungsten particles in the bulk demonstrate extremely limited deposition, while high density is produced to around  $70\mu m$  depth.

# **FUTURE PLANS**

Trials are ongoing with ATL to optimize the deposition rate binder-jetted tungsten. Temperature, pressure, and flowrate will be varied to achieve growth sufficiently slow to produce bulk densification.

#### 8. MECHANISMS AND ANALYSIS

8.1 IN-SITU SPECTROSCOPIC ELLIPSOMETRY MEASUREMENTS OF NIOBIUM OXIDE EROSION DURING HIGH-FLUX PLASMA EXPOSURE—R. D. Kolasinski, C. -S. Wong, J. A. Whaley (Sandia National Laboratories)

# OBJECTIVE

Super-permeable membranes are an intriguing approach for pumping and separation of hydrogen isotopes from plasma exhaust. The basic concept involves using a plasma source to implant low energy hydrogen into a high permeability material (typically a Group V metal or Pd alloy.) A layer of chemisorbed oxygen (or a thin oxide layer) prevents recombination and release of hydrogen from the upstream surface, resulting in nearly 100% permeation. The amount of oxygen present at both surfaces is critical to the membrane performance. The goal of this work is to use in-situ diagnostics to determine the resiliency of these oxides during high-flux particle bombardment.

## SUMMARY

In this study, we consider Nb as a model system for super-permeation and use in-situ spectroscopic ellipsometry as a non-perturbing probe of oxide thickness during exposure to high-flux (up to  $1.5 \times 10^{21}$  m<sup>-2</sup> s<sup>-1</sup>) Ar and D<sub>2</sub><sup>+</sup> plasmas. The initial oxide thickness (approximately 4 nm) was determined by fitting these measurements with a model assuming a uniform Nb<sub>2</sub>O<sub>5</sub> layer on a Nb substrate. The ellipsometer was then mounted to an RF plasma with line-of-sight viewing of the sample, which allowed us to measure the rate of oxide removal in real time. Whereas low energy (75 eV) Ar<sup>+</sup> plasmas completely removed the oxide in < 5 min., much higher incident ion energies (400 eV) were required to achieve the same result with D<sub>2</sub><sup>+</sup> exposure.

## PROGRESS AND STATUS

## Introduction

The present understanding of super-permeation through Group V metals was advanced considerably through a series of previously published studies by Livshits [1,2] and Hatano [3]. In this work, surface cleanliness was found to have a strong influence on the permeation behavior, though these effects could only be inferred from indirect methods. This includes depositing Pd coatings to minimize oxide growth and varying the O concentration within the Nb, assuming the oxide segregates to the surface upon heating. Typically, the surface needed to be prepared by sputtering with 600 eV D before reasonable permeation rates were observed, suggesting that an oxide layer was present on the surface prior to exposure.

The nature of the Nb oxide itself has been explored through x-ray photoelectron spectroscopy (XPS) in prior work by Grunder and Halbritter [4]. XPS spectra showed contributions consistent with NbO and Nb<sub>2</sub>O<sub>5</sub> phases within the oxide layer. They also found Nb surfaces easily chemisorb O, N, F, S, and hydrocarbons at temperatures < 1400 °C in ultra-high vacuum conditions (UHV). Grunder and Halbritter also noted that Nb reacts with air at 25 °C to form oxide, with the growth rate initially following a logarithmic dependence and then eventually stabilizing at a thickness of 5-10 nm during air exposure. Grazing incidence diffuse x-ray scattering by Delheusy and co-workers [5] allowed for direct detection of sub-surface O. In this case, heating up to 145 °C caused O to diffuse from the surface into the first 10 nm of the bulk.

## **Experimental Methods**

To carry out the high-flux exposures described in this work, we relied on an RF-plasma source. The instrument consists of an ultra-high vacuum chamber (base pressure <  $5 \times 10^{-8}$  Torr) with four magnet coils along its length. By applying RF power (250 W, ~400 MHz) to a Lisitano coil [6,7], it is possible to generate Ar<sup>+</sup>, D<sub>2</sub><sup>+</sup>, He<sup>+</sup>, and N<sub>2</sub><sup>+</sup> plasma discharges. The discharge parameters, including the electron density and temperature, plasma potential, and the incident ion flux are measured using a Langmuir single probe. We refer the reader to prior publications for a more detailed discussion of the experimental hardware [8,9].

The Nb specimens used in this study were fabricated from 1 mm thick foil (Goodfellow.) The primary impurities within the material included Ta (500 ppm), Si (100 ppm), and O (100 ppm). The Nb material was cut into 25 mm diameter discs via electrical discharge machining. Each disc was then mechanically polished to a mirror finish and then mounted on a sample holder that allowed for sample heating (up to

1000 °C) while applying a bias voltage. We monitored the sample temperature with a type-C thermocouple.

For ex-situ surface characterization, we used a spectroscopic ellipsometer sensitive to wavelengths spanning UV to near IR (245 nm – 1000 nm). The instrument measures two raw parameters,  $\Psi$  and  $\Delta$ , that are used to determine the polarization state of the reflected light. It is possible to relate these data to more physically meaningful quantities such as the index of refraction *n* and extinction coefficient *k*:

$$\tan(\Psi) e^{i\Delta} = \rho = r_p/r_s$$

Here,  $\rho$  indicates the reflectivities of p-polarized and s-polarized light (denoted as  $r_p$  and  $r_s$ , respectively.) Then, *n* and *k* can be determined as follows:

$$(\langle n \rangle + i \langle k \rangle)^2 = \sin (\phi)^2 \left[ 1 + \tan (\phi)^2 \left( \frac{1-\rho}{1+\rho} \right)^2 \right]$$

In the expression above,  $\phi$  indicates the angle of incidence of the incoming light. Note that both *<n>* and *<k>* appear in brackets to indicate that they are "effective" values that do not account for surface roughness.

For in-situ measurements, the spectrometer was mounted to the RF-plasma source with direct line-ofsight to the sample surface (70° relative to the surface normal.) We used strain-free viewports along the optical path to minimize any effect of birefringence on the ellipsometry measurements. The source and detector for the ellipsometer were mounted on adjustable gimbals to allow for precise alignment.

#### In-situ Ellipsometry Measurements

In our previous work, we used in-situ ellipsometry to study the growth of W nanostructure produced by high-flux He plasma exposure [9]. The corresponding increase in surface roughness (including growth of nanostructure layers exceeding 1  $\mu$ m in thickness) was easily observable in this case. However, the problem of interest for super-permeation involves the removal of a thin (~ 5nm) oxide layer from a Nb surface by plasma bombardment, which is a subtle change by comparison. Whether it would be possible to reliably detect the oxide removal during plasma exposure is an open question.



**Figure 1.** Reference data showing  $\langle n \rangle$  and  $\langle k \rangle$  as a function of wavelength for (a) Nb and (b) Nb<sub>2</sub>O<sub>5</sub>. Panels (c) and (d) include simulations that show the effects of varying oxide thickness on the ellipsometry measurements. For the relatively thin oxide layers considered here, the increased thickness appears to reduce  $\langle n \rangle$  and  $\langle k \rangle$  over the visible and near-IR portions of the spectrum.

To provide more insight into the effects of the oxide on the optical properties of the surface, we performed simulations using published standards, as shown in Figure 1. Here panels (a) and (b) show the variation of <n> and <k> as a function of wavelength for Nb and Nb<sub>2</sub>O<sub>5</sub>. Like many oxides, the Nb<sub>2</sub>O<sub>5</sub> has a high extinction coefficient at UV wavelengths, which quickly decreases to nearly zero through the visible to near-IR range. Figure 1(c) and (d) contain simulations showing how the optical properties of a Nb surface change with varying levels of oxide growth. Growth of a 2.5 nm thick oxide results in a change of in the peak value of <n> of <10% at 600 nm, which is expected to be well within the range that can be detected by our instrumentation.

Figure 2 shows in-situ spectroscopic ellipsometry results during high-flux Ar<sup>+</sup> exposure. In this case, variations in  $\Delta$  and  $\Psi$  are shown as a function of time for three wavelengths (245 nm, 624 nm, and 999 nm.) The instrument is initially allowed to stabilize for 20 min. prior to starting the plasma discharge. We then biased the specimen to -75 V and exposed it to an Ar<sup>+</sup> flux of  $4.0 \times 10^{20}$  m<sup>-2</sup> s<sup>-1</sup>. The duration of the plasma exposure is indicated by the shaded band in Figure 2, during which rapid changes in both ellipsometric parameters are observed. The magnitude of these changes depends on the wavelength of light considered. Using 624 nm as a reference,  $\Delta$  changes by 12° and  $\Psi$  changes by 1°. The differences before and after plasma exposure are easily detected by our instrumentation. Figure 3 illustrates the effects of 400 eV D<sub>2</sub><sup>+</sup> plasma exposure, with spectra taken before and after plasma exposure. The post-test exposure data shows an index of refraction that is consistent with a nearly clean surface, with fitting of the data revealing only a 0.8 nm thick oxide layer remaining on the surface. A much higher flux plasma exposure ( $1.5 \times 10^{21}$  m<sup>-2</sup> s<sup>-1</sup>) was required to observe any removal of the oxide. This resulted in considerable sample heating during the exposure, which can also affect the optical properties of the surface. Analysis of temperature effects is ongoing and will be needed for interpretation of the in-situ data.



**Figure 2.** In-situ ellipsometry measurements showing the variation of  $\Delta$  and  $\Psi$  is a function of time during high-flux Ar exposure. Three wavelengths (245 nm, 624 nm, and 999 nm) are shown. The duration of the plasma exposure is highlighted by the blue band, and a model fit to the data is indicated by the dashed line.



**Figure 3.** Ellipsometry measurements taken prior to and after 400 eV  $D_2^+$  plasma exposure. The higher index of refraction following plasma exposure is consistent with removal of nearly all the oxide layer. Both spectra were acquired at 25 °C.

#### DISCUSSION AND OUTLOOK

The above results illustrate the capability to detect minute changes in the thickness of the oxide layer present on Nb surfaces during plasma exposure. In-situ techniques provide several significant advantages for this type of work. First, transferring the specimens in air to other characterization chambers would result in chemisorption of impurities such as O and C, distorting any information on the state of the oxide. Using in-situ techniques avoids this problem altogether. Also, the ability to probe the removal of the oxide in real-time allows us to observe dynamic effects, which would not be possible with post-mortem analysis alone.

To enable more quantitative analysis of the oxide thickness, several additional factors must be considered. First, the emissivity of the surface changes with temperature. This may require a more systematic study to calibrate out the effects of sample heating during plasma exposure. In addition, accounting for differences resulting from small variations in surface preparation and microstructure between samples may also need to be considered to achieve the best possible accuracy. These are areas are intended to be topics of forthcoming work.

The strong affinity of Nb for O and other impurities has mixed consequences for permeation. On the upstream side, the chemisorbed impurity layer must be resilient against exposure to low-energy plasmas. If the oxide layer is eroded, replenishment may be possible by simply dosing the surface with O. On the other hand, contamination of the downstream surface could limit recombination and release of hydrogen. Periodic sputter cleaning with heavier species such as Ar (as in the present study) may be a reasonable way to avoid this issue.

#### ACKNOWLEDGEMENTS

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

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# **8.2 QUANTITATIVE INVESTIGATION OF SURFACE STRUCTURE AND INTERATOMIC POTENTIAL WITH IMPACT-COLLISION ION SCATTERING SPECTROSCOPY**—C. -S. Wong, R. D. Kolasinski, J. A. Whaley (Sandia National Laboratories)

#### Abstract of a manuscript in Journal of Physics: Condensed Matter.

Helium ion beam interactions with materials have important implications for magnetic confinement fusion, material modification, and helium ion microscopy. These interactions depend on the precise physics of how helium ions channel into the materials, which can vary greatly based on the local crystalline orientation. In this work, we performed a dedicated experiment to investigate helium ion channeling in a well-characterized tungsten single crystal. Time-of-flight (TOF) impact-collision ion scattering spectroscopy (ICISS) was used to obtain multi-angle maps of the backscattering intensity for 3 keV He<sup>+</sup>  $\rightarrow$  W(111). We found that the backscattering intensity profile arising from helium ion channeling could be well described by a shadow cone analysis. This analysis revealed that subsurface W atoms as deep as the ninth monolayer contributed to the backscattering intensity profile. Binary collision approximation simulations were performed with MARLOWE to model the experimental maps with sufficient accuracy to allow for quantitative comparisons using reliability factors. These quantitative comparisons were applied to investigate how the W lattice structure and He-W interatomic potential affect the multi-angle maps.

#### ACKNOWLEDGEMENTS

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

**8.3 HELIUM EFFECTS ON THE SURFACE AND SUBSURFACE EVOLUTIONS IN SINGLE-CRYSTALLINE TUNGSTEN**—Cuncai Fan, Xunxiang Hu, Chad M. Parish, Yutai Katoh (Oak Ridge National Laboratory), Congyi Li (University of Tennessee)

#### OBJECTIVE

The objective of this project is to explore the effects of helium irradiation on the surface and subsurface evolutions in single-crystalline tungsten with different orientations.

#### SUMMARY

Tungsten (W) has been perceived as one of the most promising plasma facing materials (PFMs) for future fusion reactors. In the past decade, its behavior under irradiation and helium (He) plasma interaction has been extensively studied [1]. In this project, we focus on the He ion-beam irradiation damage effects in mirror-polished single-crystalline W samples with three different surface planes of {100}, {110} and {111}. The microstructures of He-irradiated W before and after heat treatment were characterized by scanning and transmission electron microscopy. Subsurface He bubbles were imaged in all irradiated samples, but newly formed <111>-oriented surface grains and surface blisters were only observed in W {100} and {110} starting orientations. These results reveal that the surface/subsurface evolutions of W are strongly dependent on crystallographic orientation.

#### **PROGRESS AND STATUS**

Ultra-high purity (nominal 99.999%) single-crystalline W {100}, {110} and {111} discs, ~1mm thick and ~5 mm in diameter, were purchased from Goodfellow, USA. They were mechanically polished to a mirror-like surface, followed by irradiation of 40 keV He<sup>+</sup> to a fluence of  $1 \times 10^{16}$  cm<sup>-2</sup> at RT, with the incident ion beam perpendicular to sample surface during irradiation. After irradiation, thermal desorption spectroscopy (TDS) treatment was carried out on the irradiated samples, which were heated up to ~1920 K with a constant ramp rate of 0.5 K/s.

Figure 1 compares the EBSD results of He-irradiated W samples. It shows that abundant <111>- oriented surface grains are formed only in the cases of He-irradiated W {100} and {110}, while the He-irradiated W {111} remains its original orientation. The TEM micrograph of He-irradiated W {110} in Figure 2 reveals that the irradiation-induced surface grains are within ion range and have their boundaries located at ~100-150 nm to surface. In addition, according to the pole figures in Figure 3, the formation of these surface grains in both He-irradiated W (100) or (110) can be regarded as the rotation of matrix around its in-plane <110> axis, as schematically illustrated in Figure 3.



Figure 1. EBSD studies of He-irradiated (a1)-(a3) W {100}, (b1)-(b3) W {110}, and (c1)-(c3) W {111}.



Figure 2. Surface grains formed in the (a) He-irradiated W {100} and (b) He-irradiated W {110}.



**Figure 3.** {100} and {110} pole figures and corresponding schematic illustrations of surface grainmatrix orientation relationships for (a) He-irradiated W {100} and (b) He-irradiated W {110}.

After TDS annealing, surface blisters are only formed in the cases of W {100} and W {110}, as shown in Figure 4. However, the subsurface He bubbles are found in all cases (see Figure 5), indicating the important role of surface gains or surface diffusion in the surface modifications of He-irradiated W.







**Figure 5.** Subsurface He bubbles formed in TDS annealed (a1)-(a3) W {100}; (b1)-(b3) W {110}; (c1)-(c3) W {111}. From top to bottom, the same area is shown, imaged in in-focus, under-focus, and overfocus conditions.

We attribute the formation mechanism of surface grains to ion channeling effects. It has been pointed out that channeling can reduce the probabilities of collisions between incident ions and target atoms [2]. The channeling grains are thus less damaged and have lower volume free energies than nonchanneling grains. Consequently, the transition from non-channeling grains to channeling grains would occur under ion bombardment, which is driven by the difference of their free volume energies [3]. Assume an incident ion beam that enters the crystal lattice at a random crystallographic direction < uvw >. The degree and probability of its resulting channeling angle  $\psi_{uvw}^c$  [4-6]. First,  $\chi_{uvw}$  is a related to the sputtering yield. Basically, a larger  $\chi_{uvw}$  corresponds to a higher sputtering yield, and vice versa, because strong channeling results in less energy deposition near the surface, where sputtering occurs. The non-channeled fraction  $\chi_{uvw}$  is expressed as [4,7]:

$$\chi_{uvw} = \pi N t_{uvw}^{3/2} \left[ \frac{\frac{3A^2 Z_1 Z_2 \left(\frac{e^2}{4\pi\varepsilon_0}\right)}{E}}{E} \right]^{1/2}$$
(1)

where N is the atomic density of target material (~ $6.32 \times 10^{22}$  cm<sup>-3</sup> for W),  $t_{uvw}$  is the atomic distance along  $\langle uvw \rangle$  direction,  $Z_1/Z_2$  is the atomic number of incident/target, *e* is the elemental charge (~ $1.6 \times 10^{-19}$  C),  $\varepsilon_0$  is the permittivity constant (~ $8.85 \times 10^{-12}$  C<sup>2</sup>N<sup>-1</sup>m<sup>-2</sup>), *E* is the incident ion energy, and *A*  is the Thomas-Fermi screening length in the form of [4]:

$$A = \frac{(9\pi^2/128)^{1/3}}{(Z_1^{2/3} + Z_2^{2/3})^{1/2}} a_0$$
 (2)

where  $a_0$  refers to the Bohr radius, ~0.053 nm. Substituting  $Z_1$ = 2 (He),  $Z_2$  = 74 (W), and E = 40 keV into Equations (1) and (2) yields  $\chi_{100}$ = 0.065,  $\chi_{110}$ = 0.109, and  $\chi_{111}$ = 0.051. Second,  $\psi_{uvw}^c$  describes the angular width of the channeling directions, a measurement of the probability of channeling effect. For the low-energy irradiation of 40 keV He<sup>+</sup> into W,  $\psi_{uvw}^c$  can be calculated by [4]:

$$\psi_{uvw}^{c} = \left[\frac{_{3A^{2}Z_{1}Z_{2}}\left(\frac{e^{2}}{4\pi\varepsilon_{0}}\right)}{_{Et_{uvw}^{3}}}\right]^{1/4}$$
(3)

where all the parameters are defined the same as those in Equation (1). Equation (3) gives  $\psi_{100}^c = 5.75^\circ$ ,  $\psi_{110}^c = 4.45^\circ$ ,  $\psi_{111}^c = 6.53^\circ$ . The calculating results of  $\chi_{uvw}$  and  $\psi_{uvw}^c$  are summarized in Table 1. After comparing the calculated values, we can conclude that W {111} will suffer the least radiation damage. Therefore, <111> grains are expected to form in W {100} and {110} or other non-<111>- oriented grains, which is in good agreement with our experimental results demonstrated in Figure 1.

< uvw >	Non-channeled fraction, $\chi_{uvw}$	Critical angular width, $\psi_{uvw}^c$ (°)	
<100>	0.065	5.75	
<110>	0.109	4.45	
<111>	0.051	6.53	

Table 1. Calculations of ion channeling effects

#### CONCLUSION

New surface grains were observed in W {100} and {110} after He ion irradiation at RT, but none of them were found in He-irradiated W {111}. These irradiation-induced grains are primarily <111>-oriented with their bottom GBs located within ion range, approximately at a penetration distance ~100-150 nm to surface. Their formation mechanism can be well explained by ion channeling effects. Micrometer-sized blisters were only formed on the surfaces of W {100} and {110} after TDS annealing, indicating the important role of surface diffusion in the surface modifications of W under He irradiation.

#### **FUTURE PLANS**

Our future work will be focused on the effects of He on the surface and subsurface evolutions in polycrystalline W. Preliminary work has shown that the implanted He can highly enhance the thermal stability of surface grains. This could be caused by a high density of He bubbles formed at grain boundaries and grain interiors. More detailed investigations will be conducted using various characterization techniques.

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9. MODELING PROCESSES IN FUSION SYSTEM MATERIALS **9.1 OKMC SIMULATION OF HELIUM IRRADIATION OF TUNGSTEN SURFACE: IMPLEMENTATION OF DEPTH-DEPENDENT DIFFUSION & TRAP MUTATION PROCESSES IN THE NEAR-SURFACE REGION OF TUNGSTEN**—Giridhar Nandipati, Kenneth J. Roche, Richard J. Kurtz, Wahyu Setyawan (Pacific Northwest National Laboratory), Karl Hammond (University of Missouri), Dimitrios Maroudas (University of Massachusetts), Brian D. Wirth (University of Tennessee)

#### OBJECTIVE

The aim is to study evolution of helium (He)-bubble microstructure in a near-surface region of plasmaexposed tungsten using object kinetic Monte Carlo (OKMC) method. KSOME (kinetic simulations of microstructural evolution) [1,2], an OKMC code, is used to evolve the microstructures to experimentally relevant spatial- and time-scales under isothermal and variable-temperature conditions caused by and edge-localized mode in the plasma.

#### SUMMARY

This report documents upgrades made to KSOME to enable simulation of diffusion of point defects and point defect clusters considering their long-range interactions with extended defects, particularly with free surfaces and grain boundaries. Furthermore, calculation of depth-dependent migration barriers for helium clusters to diffuse toward or away from the free surface is also discussed.

#### PROGRESS AND STATUS

#### Introduction

Molecular dynamics studies [4,5,6] show the migration of He clusters and their transition into He bubbles (helium-vacancy complexes) are influenced by their long-range interaction with the free surface. More importantly, the strength of the interaction increases with the size of the clusters or bubbles.[5] Furthermore, in a recent study of near-surface He accumulation using KSOME, it was found that even though the qualitative behavior of He retention as a function of fluence was similar to the result from molecular dynamics simulations [7], KSOME predicted a higher retention. The lower helium retention was attributed to the drift-diffusion of helium clusters toward the surface. The drift-diffusion is due to the elastic interaction between the clusters and the free surface, decreasing the activation energy barrier for helium clusters diffusion towards the surface with decreasing depth. Therefore, KSOME was upgraded to handle point defect cluster diffusion under the influence of long-range interactions with extended defects. In this case with free surfaces.

## **Brief Summary of KSOME Upgrades**

One of the critical upgrades to KSOME was the ability to parse mathematical (or analytical) expressions from a text-file and subsequently the read expressions are used to calculate various defect parameters. The present version of KSOME can parse analytical expressions with basic math operations ( $\times$ ,  $\div$ , +  $x^y$ ,  $\sqrt{}$ , *log* and *trigonometric* functions). This feature is being used to read analytical formula to calculate capture radii of various defect types or sub-defect types (e.g., vacancy loop or void). That is, it is now possible to give different capture radii expressions for multiple combinations of defect parameters. More importantly, it is no longer necessary to hardwire the analytical expressions for capture radii, thus eliminating recompilation of the code as simulation becomes more and more complex and/or when additional defect types are required to simulate a material system.

The ability to parse mathematical expression is also used to calculate distances of a defect from different extended defects on-the-fly. For simplicity, extended defects are considered to have regular geometric shapes. For example, a free surface or grain boundary is considered as a planar object, while a dislocation can be considered as a line object. These geometric objects are described by four-dimensional coordinates. For example, an XY-plane at Z = 100 is represented as (0, 0, 1, -100) and a straight line of equation  $a_xx + a_yy + a_zz = 0$  is represented as  $(a_x, a_y, a_z, 0)$ . Distance of a mobile point defect from an extended defect is used as one of the defect parameters and it is updated every time the defect moves, and appropriate activation energy barriers are selected accordingly. In the present version, activation energy barriers as a function of distance are provided via an input file. In the future, KSOME will be upgraded so that appropriate

analytical expressions required to calculate the modified activation energy barriers of a mobile point defect diffusion in the vicinity of an extended defect.

#### **Calculation of Depth-Dependent Migration Barriers of He Clusters**

Molecular static simulations [5,7] show that elastic interaction energy of a  $He_n$  cluster of size n (*i. e.* consisting of n helium atoms) with a surface scales inversely with the third power of the distance (d) of its center of mass from the surface

$$\Delta E\{n, d, O\} = -\frac{A\{n, O\}}{(d - d_0\{O\})^3}$$
(1)

where,  $A\{n, \mathcal{O}\}$  is the interaction strength of a surface with crystallographic orientation  $\mathcal{O}$  for a helium cluster of size *n*. Distance *d* is between the helium cluster's center of mass and the free surface. The *minus* sign in eq.(1) implies attractive interaction between a helium cluster and the free surface.  $d_0$  corresponds to the characteristic length which is introduced to avoid singularity on the surface as  $d \rightarrow 0$ .  $d_0$  depends only on the crystallographic orientation of the surface and is on the order of inter-planar spacing. Accordingly, in the near-surface region, helium clusters perform drift-diffusion toward the surface and the drift becomes larger with decreasing depth. Furthermore,  $A\{n, \mathcal{O}\}$  increases with increasing helium cluster size [5]. Hence, the drift towards the surface at a given depth increases with helium cluster size. More importantly, trap mutation processes, where a He cluster displaces a lattice atom and transforms into a He bubble, in the near-surface region occur at a much higher rate than in the bulk.[4-6] The calculation of depth-dependent activation energy barriers and prefactors using their occurrence probabilities was described in Ref. [3]



**Figure 1.** a) Illustration of potential energy surface (PES) in bulk (red curve) and near-surface region (black curve);  $\Delta E_A$ ,  $\Delta E_B$  and  $\Delta E_S$  are the energy changes at the minimum energy sites (A & B) and at the saddle point (S), respectively. b) Potential energy surface as seen by a He<sub>2</sub> cluster as it approaches tungsten (100) surface from molecular dynamics simulation, arbitrary  $1/d^3$  curves are drawn to guide eyes and to reveal the inverse-cube depth dependence of minimum energy sites and saddle points.

It can be seen from the figure 1(b), the potential energy surface of a  $He_2$  cluster as it approaches the (100) surface shows that both the energies of local energy minima (red curve) as well as the saddle point energies (blue curve) seem to scale as  $1/d^3$ . Therefore, for a given surface crystallographic orientation and helium cluster size, the value of  $A\{n, O\}$  is taken to be the same both at the energy minima and saddle points. Accordingly, in the near-surface region, the energies of He cluster at *A*, *B* and *S* are given as

$$E_{i}\{n, d, O\} = E_{i}^{bulk}\{n\} + \Delta E_{i}\{n, d, O\}$$
  
=  $E_{i}^{bulk}\{n\} - \frac{A\{n, O\}}{(d_{i} - d_{0}\{O\})^{3}}$   $i = A, B, S$  (2)

where  $d_i$  i = A, B, S are the distances of sites A, B and S from the free surface (see figure.1(a)). Then the activation energy barriers  $(E_m)$  from  $A \rightarrow B$  and  $B \rightarrow A$  in the near-surface region is are given as

$$E_{m}^{i \to j} \{n, d, \mathcal{O}\} = E_{S}\{n, d, \mathcal{O}\} - E_{i}\{n, d, \mathcal{O}\} = (E_{S}^{bulk}\{n\} + \Delta E_{s}\{n, d, \mathcal{O}\}) - (E_{i}^{bulk}\{n\} + \Delta E_{i}\{n, d, \mathcal{O}\}) = E_{S}^{bulk}\{n\} - E_{i}^{bulk}\{n\} + (\Delta E_{S}\{n, d, \mathcal{O}\} - \Delta E_{i}\{n, d, \mathcal{O}\})$$

$$\begin{cases} i, j = A, B \ (i \neq j) \\ (3) = A, B \ (i \neq j) \\ (3) = A, B \ (i \neq j) \\ (3) = A, B \ (i \neq j) \\ (3) = A, B \ (i \neq j) \\ (3) = A, B \ (i \neq j) \\ (3) = A, B \ (i \neq j) \\ (3) = A, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B, B \ (i \neq j) \\ (3) = B,$$

In eq. (3), the term  $E_S^{bulk}\{n\} - E_i^{bulk}\{n\} = E_m^{bulk}\{n\}$  is the activation energy barrier in the bulk (or far away from the surface). The second term is the difference in the change in the energy of the He cluster at *A* and *S* due to the presence of the free surface. Also, this difference is the change in the activation energy barrier for a He cluster to move toward or away from the surface due to the elastic interaction when compared to its value in the bulk. Hence eq. (3) can be rewritten as

$$E_{m}^{i \to j} \{n, d, \mathcal{O}\} = E_{m}^{bulk} \{n\} + (\Delta E_{S}\{n, d, \mathcal{O}\} - \Delta E_{i}\{n, d, \mathcal{O}\}) \\ = E_{m}^{bulk} \{n\} - A\{n, \mathcal{O}\} \left(\frac{1}{(d_{S} - d_{0}\{\mathcal{O}\})^{3}} - \frac{1}{(d_{i} - d_{0}\{\mathcal{O}\})^{3}}\right) \right\}^{i, j} = A, B \ (i \neq j)$$
(4)

Considering the potential energy surface seen by a helium cluster is symmetric around at the mid-point between initial and final states [9], the saddle point in our calculation was always assumed to be at the mid-point.

It can be seen from Table I that the activation energy barrier for a He atom to diffuse toward the surface decreases with decreasing depth and vice versa. Furthermore, it can be seen the barrier for the He atom to diffuse toward the surface from layer 2 to layer 1 (note that layer 0 corresponds to the surface layer) becomes negative. In this case, He atom is assumed to hop from layer 2 to the free surface directly. The same approach is used even for larger He clusters.

**Table 1.** List of activation energy barriers for a He atom to hop toward and away from tungsten (100) surface at various layers (*l*) from the surface. Here, l = 0 corresponds to the surface layer.  $d_s$  and  $d_l$  are the distances of the saddle point and lattice layer from the surface.  $d_0 = 0.8$  Å and  $A\{n, O\} = 2.28 \text{ eV} \cdot$ 

		$d_l - d_0 \qquad d_s$		Away fro	n Surface	Toward	Toward Surface	
l	$d_l$		$d_s - d_0$	Direction	$E_m$ (eV)	Direction	$E_m$ (eV)	
1	1.585	0.785						
			1.5775	$1 \rightarrow 2$	4.28	$2 \rightarrow 1$	- 0.26	
2	3.17	2.37						
			3.1625	$2 \rightarrow 3$	0.25	$3 \rightarrow 2$	0.12	
3	4.755	3.955						
			4.7475	$3 \rightarrow 4$	0.17	$4 \rightarrow 3$	0.14	
4	6.34	5.54						
			6.3325	$4 \rightarrow 5$	0.15	$5 \rightarrow 4$	0.15	
5	7.925	7.125						

Å<sup>3</sup> for the (100) surface and  $E_m^{bulk} = 0.15 \ eV$ .

#### Acknowledgements

The work was performed at the Pacific Northwest National Laboratory, which is operated by Battelle for the United States Department of Energy (US DOE) under contract number DE-AC05-76RL01830. This study has been supported through the SciDAC-4 program on Plasma-Surface Interactions, which is funded by the U.S. Department of Energy, Office of Fusion Energy Sciences (FES) contract number AT1030200-70230 and Office of Advanced Scientific Computing Research (ASCR) contract number KJ0403010-70444. All computations were performed on PNNL's Research Computing Clusters.

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**9.2 DESIGN OF HIERARCHICAL TUNGSTEN-BASED COMPOSITES FOR FUSION ENERGY APPLICATIONS**—Ba Nghiep Nguyen, Charles H. Henager Jr., Jing Wang, Wahyu Setyawan (Pacific Northwest National Laboratory)

This is the Extended Abstract for a recently published paper [1]: B.N. Nguyen, C.H. Henager Jr., J. Wang, W. Setyawan "Tailoring Ductile-Phase Toughened Tungsten Hierarchical Microstructures for Plasma-Facing Materials", Journal of Nuclear Materials, 540 (2020) 152382, doi: 10.1016/j.jnucmat.2020.152382.

Biological materials, such as bones, nacre, etc., have been found to exhibit attractive and unique combinations of stiffness, strength and fracture toughness. Research has been conducted in various engineering areas to mimic the naturally hierarchical microstructures or nanostructures of these materials to produce materials with optimum stiffness, high strength and fracture toughness for their intended structural applications. In the same objective, this work applies our multiscale microstructural approach previously developed [2] to investigate the deformation and fracture behavior of ductile phase toughned tungsten (W) materials such as tungsten-nickel/iron (W-Ni/Fe) composites that possess lamellar-like and hierarchical "brick-and-mortar" (BAM) microstructures. First, the approach is used to simulate tensile loading of W-Ni/Fe specimens cut out from hot-rolled W-Ni/Fe plates which possess lamellar-like microstructures. The finite element (FE) model of the gage section of the specimen consists of a W-Ni/Fe dual-phase microstructural domain in which the constitutive behaviors of W and Ni/Fe phases are described using an elastic-plastic damage model. Predicted material stress-strain response and crack pattern development as a function of loading are then compared to the corresponding experimental data to determine the constitutive model parameters for W and Ni/Fe.

Figure 1 shows a magnified view of a local area inside the microstructural domain to illustrate damage mechanisms and fracture patterns that develop as a function of loading. A failure indicator, defined as the value of damage variable normalized by its value at saturation, is used to detect fracture initiation in the domain. After initiation, crack propagation is modeled by a vanishing element method [3]. At 0.04 applied strain, damage has already initiated in some Ni/Fe elements (Figure 1b) and at 0.085 strain these elements start to fail (failure indicator = 1) and microcracks are formed through linking-up of failed elements; as shown in Figure 1c. Figures 1b and 1c illustrate the ductile-phase toughening (DPT) mechanism associated with damage and failure of the ductile Ni/Fe elements between W elements. At 0.12 strain, the microcracks can also penetrate W elements and cause them to fail. The linking-up of microcracks through both W and Ni/Fe regions forms a visible macrocrack shown in Figure 1d at this loading level. Two important failure mechanisms are illustrated in Figure 1: 1) ductile-phase toughening and 2) fracture of W. Figure 1e shows an SEM of a local crack that propagates through W regions adjacent to Ni/Fe regions and appears similar to the predicted crack paths in Figure 1d.

Subsequently, the model parameters are used to analyze W-Ni/Fe BAM microstructures that have been designed to investigate the effect of microstructural feature and morphology on composite elastic modulus, stress-strain response, damage, and fracture pattern. Figure 2a shows an example of a BAM microstructure consisting of two hierarchical levels. Level 0 corresponds to a single W "brick" with length *L* and height *H* while Level 1 includes a representative W-brick-and-Ni/Fe-"mortar" unit cell that is repeated in both horizontal (x) and vertical (y) direction to build the microstructural domain. A series of BAM microstructures similar to the one shown in Figure 1a with L/H = 5, 10, 20, 30 and 40 are generated for the study. In these microstructures, the thickness *t* of the Ni/Fe mortar (Figure 2a) is adjusted while the W volume fraction is kept at 0.8 in the model domain. In addition, the size of this domain is kept constant and is equal to that of the hot-rolled W-Ni/Fe microstructure from which the damage model parameters are determined. Figure 2b shows the stress-strain curves up to failure of the BAM composites compared to the predicted response of the hot-rolled composite. The results show that increasing the brick aspect ratio L/H from 10 to 40 leads to a significant increase in strength but a reduction in fracture strain. In addition, strength saturation with increasing L/H from L/H = 30 has been found. For small brick aspect ratios such as the case for L/H=5, the model predicts a significant increase in strength combined with an important increase in fracture strain.







(e)

Figure 1. (a) A magnified view of a local area inside the microstructural domain (yellow arrow indicating a preexisting weak path favoring crack propagation), (b) predicted local damage distribution at 0.04 strain, (c) predicted local damage distribution and crack propagation at 0.085 strain, (d) predicted cracks formed by the linking-up of failed Ni-Fe and W elements at 0.12 strain, and (e) SEM image of cracks near the fracture path in the tensile sample strained to failure [1].



**Figure 2.** (a) An example of BAM microstructure for W/Ni-Fe showing two hierarchical levels: Level 0 corresponds to a single W "brick" with length *L* and height *H*; Level 1 includes the representative W-brick-and-Ni/Fe-"mortar" unit cell - (b) predicted tensile stress-strain responses for the BAM W-Ni/Fe composites compared to the predicted response of the hot-rolled W-Ni/Fe material [1].

The modeling shows that regular BAM microstructures that experience bridging mechanism combined with crack penetration across W-phase regions exhibit significantly higher strengths than the rather random lamellar-like microstructures obtained from hot rolling. More significantly, by adjusting the brick's length-to-height ratio, the BAM microstructure can be designed to allow a more distributed damage zone which leads to increased strength, ductility, and fracture energy. The microstructure study reveals several toughening mechanisms that control the composite material mechanical properties. In addition to ductile-phase toughening mechanism, crack penetration through W phases combined with crack distribution and interaction over the domain can significantly contribute to the increased fracture energy, thus increased strength and fracture strain. Future work will explore high-temperature mechanical behavior and irradiation effect. The developed capability may be useful for finding an optimum BAM composite architecture that can be fabricated via additive manufacturing.

# ACKNOWLEDGEMENTS

This research has been supported by U.S. Department of Energy (DOE), Office of Science, Office of Fusion Energy Sciences under Contract DE-AC05-76RL01830. PNNL is a multi-program national laboratory operated by Battelle Memorial Institute for the US DOE under DE-AC05-76RL01830.

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# **9.3 AB INITIO STUDY OF He SEGREGATION AND DECOHESION EFFECT IN W110/Ni111 INTERPHASE BOUNDARY**—W. Setyawan (Pacific Northwest National Laboratory)

#### This is an Extended Abstract of a paper "Density Functional Theory Calculation of Helium Segregation and Decohesion Effect in W110/Ni111 Interphase Boundary" that has been submitted to Journal of Applied Physics.

W-NiFe heavy alloys containing > 90 wt.% of W are being explored as a potential crack-arrest layer below a tungsten armor for use in plasma-facing components. The alloys (composites) consist of W particles embedded in a Ni-based NiFeW ductile matrix. W-NiFe composites are significantly tougher than tungsten at room temperature. An important factor in the toughening is the strong cohesion of W/NiFe interphase boundaries. High-temperature mechanical behavior and the effect of neutron irradiation remain to be investigated. Fusion neutrons will cause atomic displacement damage as well as activation of the composite constituents. Nickel exhibits a higher activity than Fe and W which may pose a radiological concern. Activity assessment of the 97wt.% W composite, if used in the first wall of a DEMO reactor, shows the dose rate of the irradiated composite after 1 year (following 5 years of operation) is similar to that of W, and it is less than two times higher than W after 10,000 years. A study on the limit of elements to qualify as a class C waste puts the limit of Ni at about 10 at.%. For comparison, 97W composite contains 2.1 wt.% (or 6.2 at.%) of Ni. The studies suggest that W-NiFe composites containing a small percentage of Ni are acceptable.

If the composite is used as a crack-arrest layer underneath a pure W armor, direct He plasma bombardment may not be a concern, although, depending on the thickness of the armor, He diffusion through the armor, particularly if cracks develop, may remain a concern. Another challenge is He gas production from the transmutation of Ni, Fe, and to a lesser extent W. Helium production from Ni is expected to be several times larger than from Fe. The He gas production could cause significant embrittlement, particularly if He segregates to the W/NiFe interphase boundary whose cohesion is key to the composite excellent toughness. Studies have shown that He promotes decohesion in tungsten grain boundaries; therefore, it is pertinent to study the decohesion effect in the composite.

First-principle density functional theory calculations are performed to study the preferential distribution and decohesion effect of He in a W-NiFe composite model. A slab containing {110}<100>W//{111}<110>Ni interface is used as a surrogate model for the W-NiFe system. Firstly, the fracture energy of the W/Ni interphase boundary (IB) (4.37 J/m<sup>2</sup>) is higher than the cleavage energy of Ni{111} (3.82 J/m<sup>2</sup>) and lower than the cleavage energy of W{110} (6.60 J/m<sup>2</sup>). The comparison reveals that the cohesion of the IB is stronger than the Ni{111} planes that are away from the IB. The strong IB cohesion would allow plastic deformation to occur in the ductile Ni phase before the IB fractures, hence making the W-NiFe composite tough. However, the cohesion between the Ni{111} planes adjacent to the IB is found to be the weakest in this system, with a cleavage energy of 3.11 J/m<sup>2</sup>. Subsequently, formation energy of He is calculated in the Ni slab, W slab, and various interstitial sites in the IB. The calculations show that He is significantly more stable in Ni than in W by about 1.75 eV. Interestingly, He does not prefer to segregate at the IB as compared to bulk Ni. Nevertheless, it prefers to segregate to the region between the Ni{111} planes adjacent to the IB and decreases the cohesion of the already weakest region. Based on an estimated amount of He gas production in five years under first wall neutron irradiation (neutron flux of 1.04x10<sup>15</sup> n/cm<sup>2</sup>/s), He will decrease the cleavage energy of the weakest region by 21.2%, 15.4%, and 12.2% at 800, 1000, and 1200°C, respectively. Future studies are needed to investigate the cohesion trend in other IB systems and the effect of solid solution in the ductile phase.

# ACKNOWLEDGEMENTS

This research has been supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences and performed at the Pacific Northwest National Laboratory under contract number DE-AC05-76RL01830.

**9.4 POTFITML COMPUTER CODE TO IMPROVE INTERATOMIC POTENTIAL FITTING WITH MACHINE LEARNING**—W. Setyawan (Pacific Northwest National Laboratory)

#### OBJECTIVE

The objective of this research is to develop a computational framework to explore the feasibility of using machine learning to improve fitting of interatomic potentials.

#### SUMMARY

A computational framework (*potfitml*) has been developed that uses machine learning (ML) model to capture property-to-parameter relationship of an interatomic potential. The trained model is used to produce a new trial potential by inputting a set of target properties. In this report, *potfitml* was used fit an embeddedatom method (EAM) potential for Re to explore the feasibility of using ML to improve the Re potential previously fitted with a force-matching (FM) method and to reveal any limitation of the EAM parameterization to concurrently reproduce elastic moduli and formation energies of point defects in Re as obtained from first-principles calculations or experiments. To generate the dataset, force-matching fits are performed, resulting in 2153 sets. Five datasets each containing 1000 randomly selected sets from the 2153 sets are used to run five independent *potfitml* runs. A dense neural network with two hidden layers and 32 nodes per layer with sigmoid activation function is used. The average property error in each dataset decrease as iteration progresses, indicating *potfitml* is successfully tested. However, no new best sets are found. Different property weights will be explored in the future before we can infer on the limitation of the EAM parameterization for reproducing all the specified target properties which include defect formation energies and elastic moduli.

### PROGRESS AND STATUS

In this research, we explore the idea of using machine learning (ML) to improve fitting of an interatomic potential. The idea is based on the fact that a large number of fitted trial potentials is typically generated in developing a potential in which the best one is selected. The question is, how can we utilize the dataset of these trial potentials to improve the best set in the dataset? To answer this question, we use the dataset to train a ML model to solve an inverse problem. That is, rather than using ML to describe the typical parameter-to-property relationship, we use it to describe the property-to-parameter relationship, connecting the properties predicted by a potential to the parameters of the potential. Subsequently, a set of target properties is used to evaluate the trained model to produce a set of potential parameters (a new trial). Ideally, the new trial would represent the "target" potential. In practice, this is not the case. Therefore, if the new trial is better than the worst set, it can be used to replace the worst set in the dataset and the process can then be iterated. *potfitml* is a computational framework that is developed in this research to automate the iteration. As a framework, it manages external codes to perform the following jobs, 1) a ML job to train and evaluate the ML model and to produce a trial parameter set, 2) a FORMAT job to format the trial parameter set into a potential file format that can be used directly in molecular dynamics (MD) codes, and 3) an MD job to perform MD simulations to obtain the properties of the trial potential.

In the previous report [1], the development of *potfitml* has been completed where the code can be run interactively or run as a daemon. In this report, *potfitml* is tested to improve the fitting of an embedded-atom method (EAM) potential for Re. The EAM potential is parametrized as follows. The pair potential energy function  $\phi(r)$  is given as

$$\phi(r) = \sum_{i=1}^{N} f_i (r_i - r)^3 \theta(r_i - r)$$
(1)

where  $\theta(r)$  is a Step function, N = 15, and the knot position  $r_i$  is uniformly positioned between 2 and 5.5 Å (inclusive) and fixed. The electron density  $\rho(r)$  due to an atom at a distance r from the atom is taken from

[2] where a consistent set of universal atomic electron density of all elements in the periodic table has been derived. The form of the atomic density is

$$\rho(r) = \rho_e \exp\left(-\beta(r/r_e - 1)\right) \tag{2}$$

where for Re,  $\rho_e = 0.242$  Å<sup>-3</sup>,  $\beta = 5.684$ , and  $r_e = 2.040$  Å. With a cutoff set at  $r_c = 5.5$  Å, the atomic density at each atom position in an equilibrium hcp lattice due to its neighbors is  $\rho_{eq} = 0.39409$  Å<sup>-3</sup>. The embedding energy for inserting an atom in a location with a total electron density of  $\rho$  is

$$F(\rho) = a_1 \sqrt{\rho} + a_2 \rho + a_3 \rho^2 \tag{3}$$

The initial dataset is obtained from the results of force-matching fit performed using the *potfit* code [3]. The IAP parameters to fit are  $f_1$  to  $f_{15}$ ,  $a_1$ ,  $a_2$ , and  $a_3$ . The force-matching method fits the parameters based on energies, forces, and stresses in reference atomistic structures from first-principles quantum mechanical calculations. The list of reference structures and the detail of the first-principles calculations are described in our previous study [4]. The force-matching fit is performed with a ratio of the effective weights of the force component, energy, and the stress component of 1:50:10. To start the force-matching fit, the pair energy is set to zero, the embedding energy parameters are also set to zero except  $a_1 = -0.1$  to give a small negative potential energy. In an equilibrium hcp lattice, the initial parameters correspond to an energy of -0.0628 eV per atom. A fit run consists of a simulated annealing optimization followed by a conjugate gradient minimization. In a simulated annealing optimization, each  $f_1$  to  $f_{15}$  is allowed to change randomly within -50 and 0,  $a_2$  within -50 and 50, and  $a_3$  within 0 and 50. During simulated annealing, which parameter to change is also randomly selected. A different random number of seed is generated for each trial set.

3000 force-matching fits are performed. Each fit produces a trial IAP set. The property of the trial sets is then calculated with MD. The list of the properties is given in Table 1. Trial sets that produce negative elastic constants or defect formation energies are removed. There are 2153 trial sets left which constitute the dataset for testing the *potfitml* code. At the beginning, *potfitml* is run with N\_ITER set to 0 in the input file, which means that *potfitml* is run to execute only initial functions; including detecting and removing redundant sets and calculating the errors of the initial dataset and then it simply exits. Note that it is possible that some of the trial IAP sets have converged to a similar set of IAP parameters during the force-matching fit. A redundant set is a set in which each parameter is within the TOL\_REDUNDANCE of the corresponding parameter in another set. The redundancy check is performed with TOL\_REDUNDANCE = 1e-3. It is found that all the 2153 sets are unique.

Modes to calculate the weighted sum of property error that are currently implemented in *potfitml* are meanabsolute-error (*mae*) and root-mean-squared-error (*rmse*):

$$e_j = (p_j - q_j)/q_j \tag{4}$$

$$mae = \frac{\sum_{j=1}^{L} g_j |e_j|}{\sum_{j=1}^{L} g_j}$$
(5)

$$rmse = \sqrt{\frac{\sum_{j=1}^{L} g_{j} e_{j}^{2}}{\sum_{j=1}^{L} g_{j}}}$$
(6)

Where *L* is the number of properties,  $p_j$  is property-j,  $q_j$  is target property-j,  $e_j$  is relative error of property-j, and  $g_j$  is the effective error weight of property-j calculated:

$$g_j = w_j \text{ if } (p_j * q_j > 0)$$
 (7)

$$g_j = w_j s_j \text{ if } (p_j * q_j < 0) \tag{8}$$

Where  $w_j$  is property-j weight and sj is property-j sign-weight. The property sign-weight is useful to assign additional weight factor for properties with opposite sign from the target values. For this study, the *mae* is used as the error with the property weights and property sign weights given in Table 1. The property of the best initial trial set is also shown in Table 1, labelled as FM.

**Table 1.** List of properties of the Re potential, property weight (*w*), property sign-weight (*s*), target values (Target), and properties of the best initial trial set from the force-matching dataset (FM). Unless specified otherwise, the target values are DFT data from [4]. Defect formation energies (*E<sub>f</sub>*) with the Re potentials are calculated with a 1440-atom hcp cell, while in DFT a 180-atom cell is used. For unstable defects, the final configuration is listed instead of the formation energy. Units are Å, eV, K, and GPa.

Property	Target	W	s	FM set152	Run1 iter1821	Run2 iter890	Run3 iter1552	Run4 iter1103	Run5 iter1796
а	2.761*	1	1000	2.823	2.872	2.875	2.880	2.86	2.87
c/a	1.614*	1	1000	1.585	1.612	1.619	1.619	1.619	1.616
Ecoh [hcp]	8.03*	10	1000	8.05	6.25	5.93	5.86	6.17	5.97
⊿E <sub>coh</sub> [hcp-fcc]	0.06	10	10	0.06	0.003	0.003	0.002	0.002	0.002
⊿E <sub>coh</sub> [hcp-bcc]	0.31	10	10	0.18	0.21	0.24	0.24	0.21	0.23
E <sub>f</sub> [Vac]	3.08	1000	1000	3.43	1.93	1.67	1.65	1.81	1.67
<i>E</i> <sub>f</sub> [C]	6.52	1000	1000	7.42	6.64	6.94	7.12	6.11	6.59
<i>E</i> <sub>f</sub> [O]	8.13	1000	1000	6.87	7.48	7.52	7.74	7.37	7.76
$E_f[S]$	6.53	1000	1000	6.87	6.18	6.30	6.54	6.70	6.44
$E_f[T]$	6.52	1000	1000	6.86	6.65	6.57	6.98	6.86	6.76
E <sub>f</sub> [BO]	7.41	1000	1000	5.88	6.26	6.93	6.89	6.06	6.40
Ef [BS]	8.09	1000	1000	5.92	6.63	7.14	7.11	8.62	6.95
E <sub>f</sub> [BT]	BO	1000	1000	7.50	7.98	7.80	7.52	7.50	7.49
Ef [BC]	BO	1000	1000	5.65	7.93	7.68	7.47	7.93	8.06
C <sub>11</sub>	613*	1	1000	591	441	427	441	429	444
C33	683*	1	1000	715	380	393	394	391	388
C <sub>12</sub>	270*	1	1000	365	270	264	267	270	272
C <sub>13</sub>	206*	1	1000	417	261	260	258	268	268
C44	163*	1	1000	191	71	73	74	73	77
mae				0.179	0.216	0.208	0.206	0.216	0.212

\*experimental data

A subset of the dataset is generated by randomly selecting 1000 sets from the 2153 sets and referred to as dataset1. Firstly, ML models with different activation functions are explored using a dense network with 2 hidden layers and 128 nodes per layer (denoted as 2x128 network). Five-fold cross-validation method is used to study the under/over fitting behavior as a function of number of epochs. The ML model is trained using the Adam optimizer with a learning rate of 0.001 and with a mean absolute error as the loss function. The training is performed with a batch size = 16. Figure 1 shows the mean absolute error of the training set and the validation set as a function of the number of epochs. The number of epochs where the validation error starts to saturate is identified as the optimum value; which is 60 for tanh activation function, 80 for sigmoid, 20 for relu, 100 for softmax, 20 for softplus, and 80 for softsign.



**Figure 1.** mean absolute error of training set and validation set obtained with five-fold cross-validation method as a function of the number of epochs. A dense neural network with 2 hidden layers and 128 nodes per layer is used. Arrows indicate the number of epochs where the validation error starts to saturate.

Subsequently, the six activation functions are used in *potfitml* test runs up to 500 iteration using dataset1. Figure 2 shows the performance of these activation functions with a dense neural network with 2 hidden

layers and 128 nodes per layer (2x128 model). A similar test is performed with (2x32 model) (the result is shown in Figure 3) and with (8x32 model) (the result is shown in Figure 4). Comparing the results, 2x32 model with sigmoid is selected for subsequent *potfitml* runs.



**Figure 2.** Property error of Re EAM potential trial set obtained with *potfitml* at each iteration (blue curve) calculated with Equation 5. The shaded area spans the worst and the best errors in the dataset (dataset1), while the average error is plotted as a black curve. The trial sets are obtained with a dense neural network with 2 hidden layers and 128 nodes per layer.



**Figure 3.** Property error of Re EAM potential trial set obtained with *potfitml* at each iteration (blue curve) calculated with Equation 5. The shaded area spans the worst and the best errors in the dataset (dataset1), while the average error is plotted as a black curve. The trial sets are obtained with a dense neural network with 2 hidden layers and 32 nodes per layer.



**Figure 4.** Property error of Re EAM potential trial set obtained with *potfitml* at each iteration (blue curve) calculated with Equation 5. The shaded area spans the worst and the best errors in the dataset (dataset1), while the average error is plotted as a black curve. The trial sets are obtained with a dense neural network with 8 hidden layers and 32 nodes per layer.

In addition to dataset1, four more datasets are generated, each by selecting 1000 sets randomly from the 2153 sets. Five independent *potfitml* runs are performed; run1 with dataset1, run2 with dataset2, and so on. Figure 5 shows the property error of trial potential at each iteration. In all the runs, the average error over the sets in the dataset decreases with iteration and appears to saturate after 2000 iterations. This indicates that *potfitml* is successfully tested. Nevertheless, no trial sets are found that are more accurate than the already best set in the initial dataset. The predicted properties of the best trial set in each run are summarized in Table 1. Interestingly, the properties of the best trial sets are similar. This could be driven

by the choice of the property weights. Hence, different weights will be explored in the future before we can infer on the limitation of the EAM parameterization to reproduce all the target properties.



**Figure 5.** Property error of Re EAM potential trial set obtained with *potfitml* at each iteration (blue curve) calculated with Equation 5 using a) dataset1, b) dataset2, and c) dataset3. The shaded area spans the worst and the best errors in the dataset, while the average error is plotted as a black curve. The trial sets are obtained with a dense neural network with 2 hidden layers and 32 nodes per layer. The predicted properties of the best trial set in each run are shown in Table 1.



Figure 5. (continued) Panels d) and e) are results obtained with dataset4 and dataset5, respectively.

# ACKKNOWLEDGEMENT

This research has been supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences (DE-AC05-76RL0-1830).

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9.5 ANALYSIS OF DISLOCATION LOOP IMPINGEMENT PROBABILITIES IN IRRADIATED MATERIALS—Peter Doyle, Steven Zinkle (The University of Tennessee)

#### OBJECTIVE

The objective of this work is to quantify the probability of dislocation loop impingement in irradiated materials as a function of loop size and density, and correlate that impingement to observations of loop-to-network dislocation transformation as defect densities increase. Irradiation damage leads to the formation and evolution of dislocation loops and lines. The fractional abundance of lines increases with radiation damage and a critical transition density and size to dislocation lines is hypothesized. The interaction probability depends chiefly on the size and density of the loops.

#### SUMMARY

A Monte Carlo simulation tool has been developed to evaluate the extent of loop impingement (overlap) as a function of dislocation loop size and density. Preliminary simulations have been performed on face-centered cubic (FCC) Cu and body-centered cubic (BCC) Fe systems with loop densities up to  $10^{23}$ /m<sup>3</sup> and average loop radii of 2 to 50 nm. For small loops (<10 nm average radius) interactions were uniformly less than 15 % of total loops and limited to 1-2 interactions per loop. A much larger maximum interaction fraction of 60% and 95% for 25 and 50 nm sizes was observed at the maximum density. Further, low to medium diameter loops were found to predominately interact only one time, while high diameter loops interacted several times/loops with 5+ interactions being the most common at high density.

### PROGRESS AND STATUS

A Monte Carlo algorithm has been designed and written in Fortran and screened for coding errors. Initial data has been gathered for up to a few thousand histories as part of this programming analysis for dislocation loop habit plane conditions ({111} for FCC and both {110} and {100} for BCC crystals) and loop sizes and densities relevant for pure BCC Fe and FCC Cu. Preliminary analysis on these data has been accomplished to quantify the probability of interaction between loops up to densities of 10<sup>23</sup>/m<sup>3</sup>. Correlation of parameters to interaction fractions and comparison to experimental data is reserved for future work where the critical density range will be evaluated.

#### Simulation Algorithm and Input Parameters

The following conditions were assumed in the algorithm generation.

- 1. The transition from dislocation loops to network dislocations will be related to the fraction of defects interacting with each other.
- 2. Interactions can be estimated by creating a static "interaction volume" around each defect. Any two defects with overlapping interaction volumes can be said to have interacted.
- 3. Loops will form randomly on the various crystal planes, depending on the crystal structure. In BCC, loops will form on {110} and {100} planes, while in FCC, loops will inhabit {111} planes.
- 4. Loop motion was not included in the simulation result

Together, the validity of these assumptions can be evaluated by comparison of the model results to experimental findings, which will be the subject of future work. Per these assumptions, a Monte Carlo simulation algorithm was developed using the following inputs, listed in Table 1, maximum loop density  $(\rho_{max})$ , loop average radius (r) and standard deviation, crystal structure, lattice parameter  $(a_0)$ , interaction distance normal to a loop  $(L_{\perp})$ , interaction distance in the direction of the loop plane as measured from the loop center  $(L_{\parallel})$ , number of histories, and size of simulation cell  $(L_{cell})$ . The number of histories was either

10, 10<sup>2</sup>, or 10<sup>3</sup>. Loop size and standard deviation were varied across  $2 \pm 0.4$ ,  $5 \pm 1$ ,  $10 \pm 2$ ,  $15 \pm 3$ ,  $25 \pm 5$ , and  $50 \pm 5$  nm. Standard deviations were determined as 20% of the average loop size.

**Table 1.** Input parameters for the simulations in this work. Number of histories and loop parameters are given in the text.

Parameter	$a_0(nm)$	Crystal	$L_{\perp}$	$L_{\parallel}$	L <sub>cell</sub> (μm)	$ \rho_{max} (m^{-3}) $
Value	0.29, 0.36	FCC, BCC	$2a_0$	$r + 4a_0$	0.8	10 <sup>23</sup>

The simulation algorithm is as follows. Data is read in and cubic cells with length  $L_{cell}$  are constructed and divided into sub-cells for computational efficiency and distinguishing between interior and exterior regions of the cell. In the exterior region of the simulation cell, the number of interactions will be reduced compared to the interior due to a lack of loops outside of the cell to provide additional interactions. Data were thus compiled for each of interior, exterior, and all cells.

For a single history, loops are added until the maximum density is reached. Each loop is added by first choosing a random sub-cell and then a random location within that sub-cell. Random numbers for this assignment were obtained with a uniformly distributed pseudo-random number obtained from the intrinsic Fortran generator. The new loop is also given a plane to reside on, with probability of choosing a plane equally distributed between all {110} and {100} planes (for BCC crystals) or {111} planes (for FCC crystals). Finally, a radius is assigned by the rejection method based on a Gaussian distribution, with a cutoff at 3 standard deviations from the mean.

All loops in the sub-cell the new loop was placed in as well as in adjacent sub-cells are compared to the new loop to determine if there is any overlap in interaction volumes. When overlap is found the number of interactions of both overlapping loops is incremented and counters updated to keep track, of how many loops have 1, 2, 3, 4, or 5+ interactions with other loops. Once all loops have been added, this process is repeated for N histories and the data is cleaned up and output.

#### PRELIMINARY RESULTS

Across the range of histories, 10 to  $10^3$ , no significant difference in mean or error estimates was obtained, indicating a highly reproducible system. The following preliminary results are related to the BCC Fe system simulations with  $10^3$  histories. Figure 1 compares the external cells, internal cells, and full simulation cell calculations of the fraction of loops having any interaction with other loops in the simulation. The figure includes 5, 15, and 50 nm average loop radii. As shown in that figure, there is little difference, and no statistically meaningful difference, in the results except at high loop density (> $10^{22}$  m<sup>3</sup>) and size (50 nm).



**Figure 1.** Comparison of the fraction of loops with any interaction with another loop using data from external cells, internal cells, and all cells. Simulation parameters from 5, 15, and 50 nm average loop size are presented.

The effect of loop size on the loop interaction fraction is presented in Figure 2. Simulations with loops from an average 2 to 50nm radius are presented. At the highest density of  $10^{23}$  m<sup>-3</sup>, interactions were limited to less than 5% of loops for loops with an average radius of 2 and 5nm. Increasing the loops size exponentially increases the interaction fraction to 30 and 60% with 15 and 25nm loops, respectively.





Figure 3 shows the interaction fraction data aggregated over all the interior cells. These data include the fraction of loops that have any interactions (black curve) in addition to the fraction of loops with specifically

1, 2, 3, 4, or 5+ interactions with other loops for three different loop diameters. Figure 3a) shows that >50% of loops have at least one interaction at densities above  $10^{22}$  m<sup>-3</sup>. The interaction fraction drops exponentially with size (20% with 25nm loops and 5% with 15nm loops at  $10^{22}$  m<sup>-3</sup>). Moreover, the size of the loops dramatically influences the number of interactions per loop. Of the 15nm loops which interact, Figure 3c), almost all interact only one time, with double interactions only being relevant at high density. In contrast, 50 nm loops, Figure 3a) significantly interact, but the single interactions only dominate at lower density (< $10^{22}$  m<sup>-3</sup>) with interactions above 5/loop becoming dominant by  $10^{23}$  m<sup>-3</sup> density.



**Figure 3.** Evaluation of the number of interactions per loop as a function of density for a) 50nm, b) 25nm, and c) 15 nm average radius loops ( $\pm$ 20% of the average loop size). Error in the evaluation is given by shading around the line.

# **FUTURE WORK**

Additional simulations are being performed up to 10<sup>6</sup> histories to attempt to minimize error in the simulation at low loop density. Additionally, low density and larger loop size simulations will be performed to bolster understanding of the loop size effects. These data will be evaluated to determine the appropriate correlations between the interaction parameter and the size and density of loops. The resulting correlation will be compared to experimental observations of irradiated materials.

# 10. FUSION SYSTEM DESIGN

No contributions this reporting period.

#### 11. IRRADIATION & TESTING METHODS, EXPERIMENTS AND SCHEDULES

**11.1 NEUTRON FLUENCE MEASUREMENTS AND RADIATION DAMAGE CALCULATIONS FOR THE JP28 AND JP29 EXPERIMENTS IN HFIR**—L. R. Greenwood, B. D. Pierson, M. G. Cantaloub, T. Trang-Le (Pacific Northwest National Laboratory)

# OBJECTIVE

Measure the neutron fluence and energy spectra during irradiations in HFIR and calculate fundamental radiation damage parameters including dpa and gas production.

# SUMMARY

The JP28 and JP29 experiments were irradiated in target positions F3 and C6, respectively, of HFIR. The JP28 was irradiated in cycles 404 starting April 6, 2005 through cycle 448 ending July 13, 2013 for a total exposure of 1050.18 EFPD (effective full power days) at a nominal power level of 85 MW. The JP29 was irradiated in cycles 403 starting January 26, 2005 through cycle 449, ending August 24, 2013 for a total exposure of 1059.26 EFPD at a nominal power of 85 MW. Neutron dosimetry monitors fabricated by PNNL were inserted in the JP28 and JP29 experimental assemblies at various elevations. After the irradiation, the neutron fluence monitors were recovered and sent to PNNL for analysis. The activated monitor wires were analyzed to determine activation rates that were used to adjust the neutron fluence spectrum at each irradiation position. The adjusted neutron fluence spectra were then used to calculate radiation damage parameters.

# PROGRESS AND STATUS

Neutron dosimetry monitors were fabricated by PNNL for insertion in the JP28 and JP29 irradiation assemblies. The vanadium monitors measure 0.050" in diameter by 0.340" long. Each monitor has a 2-digit code stamped on the bottom. The monitors were filled with small wire segments of Fe, Ti, Nb, Cu, and 1% Co-V alloy. Each capsule was electron beam welded to maintain integrity throughout the irradiation. The irradiated monitors were received at PNNL for analysis in June 2016 following irradiation. The monitors from the JP30 and JP31 irradiations were received in the same containers that had the monitors from the JP28 and JP29 experiments which will be reported separately. The monitors were identified, when possible, using the 2-digit ID stamp on the bottom. The monitors were also weighed after irradiation so that the mass values could be compared with the fabrication records in cases where the 2-digit code could not be determined due to damage. Table 1 provides a list of all the monitors that were initially inserted along with the monitors that were recovered and analyzed for this report.

JP28			JP29			
Monitor	Height, cm	Status	Monitor	Height, cm	Status	
К	20.44	Recovered	J8	19.68	Recovered	
Н	16.50	Lost	10	15.71	Recovered	
U8	5.70	Recovered	5U	-3.31	Lost	
18	-8.44	Recovered	EA	-9.11	Recovered	
7J	-24.72	Recovered	8V	-25.04	Recovered	

 Table 1. List of neutron fluence monitors and recovery status

All the monitors were gamma counted as received. The monitors were then opened, and the individual wires were gamma counted separately to avoid any possible interference as well as to detect weaker nuclides that could not be detected in the whole monitor counts due to the <sup>60</sup>Co activity. The nuclear reactions and activation products that were detected are listed in Table 2. The "90% neutron energy range" represents the energy range of the neutrons that produced 90% of the listed reaction; 5% of the activity was produced by neutrons with energies below the lower energy and 5% above the higher energy. The "90% neutron energy ranges" listed in Table 2 represent the maximum spread from all eight dosimetry monitors. The different energy ranges for the four threshold reactions are very useful in defining the neutron spectrum, as discussed later in this report.

Nuclear Reaction	Half-life	90% Neutron Energy Range, MeV
63Cu(n,a)60Co	5.27 a	4.5 to 12.0
54Fe(n,p)54Mn	312 d	2.0 to 7.4
46Ti(n,p)46Sc	83.8 d	3.7 to 10.0
93Nb(n,n')93mNb	16.1 a	0.78 to 5.5
59Co(n,g)60Co	5.27 a	Thermal/Epithermal
93Nb(n,g)94Nb	20,300 a	Thermal/Epithermal

Table 2. Nuclear reactions with half-lives and	l energy sensitivity ranges
------------------------------------------------	-----------------------------

The gamma detectors are calibrated using NIST traceable standards obtained from Eckert and Zeigler. Control counts are performed every day that a detector is used to check the continuing calibration of the energy, efficiency, and resolution. All nuclear data was adopted from the Nudat 2 database at the National Nuclear Data Center at Brookhaven National Laboratory[1]. The weights of the individual wires were measured during fabrication and all results are reported as activity per gram of the elements with natural abundances using the before irradiation masses. The measured activities corrected back to the end of irradiation time are provided in Table 3. The activities were not corrected for nuclear burnup or gamma absorption because these corrections are applied to the reaction rates using the SigPhi calculator from the STAYSL\_PNNL software suite [2].

**Table 3.** Measured activities in Bq/g for the JP28 and JP29 irradiations; uncertainties are ±2%. Resultsare corrected to the end of irradiation times July 13, 2013 (JP28) and August 24, 2013 (JP29) but are notcorrected for decay during irradiation as discussed in the report.

ID	Height,cm	<sup>54</sup> Mn	<sup>93m</sup> Nb	<sup>94</sup> Nb	<sup>60</sup> Co(Co)	<sup>46</sup> Sc	<sup>60</sup> Co(Cu)
JP28		Bq/g	Bq/g	Bq/g	Bq/g	Bq/g	Bq/g
К	20.44	6.56E+09	4.81E+10	4.29E+08	1.83E+11	2.74E+08	2.74E+08
U8	5.7	9.98E+09	6.57E+10	4.34E+08	1.61E+11		6.36E+08
18	-8.44	9.66E+09		3.63E+08	2.42E+11	3.29E+09	
7J	-24.72	4.95E+09	2.77E+10	3.97E+08	2.11E+11	7.24E+08	1.97e+08
JP29							
J8	19.68	6.35E+09	4.87E+10	4.41E+08	1.74E+11	2.08E+09	2.77E+08
10	15.71	7.56E+09		4.00E+08	1.67E+11	2.63E+09	3.26E+08
EA	-9.11	8.87E+09	6.50E+10	4.04E+08	1.59E+11		3.83E+08
8V	-25.02	4.10E+09	3.24E+10	3.87E+08	1.93E+11		4.38E+08

The <sup>93m</sup>Nb activities were determined by x-ray counting of the 16.6 and 18.6 keV x-rays using a low energy photon spectrometer (LEPS) detector. The high purity niobium wires were dissolved in a mixture of nitric and hydrofluoric acid using small Teflon beakers. A small aliquot (about 0.5%) of the solution was accurately weighed and dried on thin filter paper covered by 0.25 mil Mylar for LEPS counting. The very small mass and thin cover nearly eliminated concerns over x-ray absorption, backscatter, and fluorescence as discussed in ASTM practice E1297 [3].

The saturated reaction rates are calculated from the measured activities in Table 3 by applying corrections for decay during irradiation, gamma absorption, and nuclear burnup of the target and product nuclides. These corrections are included with the BCF and SIG-PHI Calculator modules of the STAYSL PNNL computer suite. (2) The irradiation history was provided by ORNL and is described briefly in the Summary section of this report. The BCF program breaks the irradiation up into periods of nearly constant reactor power and calculates the growth and decay of each activation product (see pg. 47 [2]). The resultant correction factor corrects for decay during the irradiation and normalizes to 1050.18 and 1059.26 EFPD at full reactor power using the nominal value of 85 MW for JP-28 and 29 respectively. Gamma absorption in the small wire segments is based on the XCOM database (see Reference [4]) as described Section 7.3 of Reference [2]. Neutron burnup corrections for thermal neutron reactions use an iterative procedure using a ratio of the burnup reaction rates for the target and product nuclides. The uncorrected reaction rate is used to determine a correction and this procedure is iterated until convergence is achieved. The resulting thermal reaction rates are then used as the basis for calculating the burnup corrections for the threshold nuclear reactions using known thermal neutron cross sections and resonance integrals. For complete details regarding the iterative neutron burnup correction see Figure 28 of Reference [2]. Due to the very high burnup of the thermal neutron monitors (up to 99% for Co-59), the constrained, iterative technique did not converge in some cases. It was expected that the reaction rates match those of the JP30 and JP31 experiments. To verify this, we developed a separate minimization scheme to determine the reaction rates for the thermal reactions. Figure 1 is a plot of the specific activity of <sup>60</sup>Co in monitor K over the irradiation period. The standard iterative technique fails in this case since the measured value matches two points on the curve. Figure 2 represents the minimization space as it relates to the thermal and epithermal flux; from this figure the sensitivity to the epithermal flux is limited. The thermal-epithermal flux ratio used in the SigPhi Calculator program was thus set to agree with the calculated neutron spectra used for the JP30/31 experiments. After verifying that the reaction rates for the 59Co(n,g)60Co and 93Nb(n,g)94Nb reactions were comparable to JP30/31, the thermal reaction rates from JP30/31 were plotted together and fit using a common curve. Reaction rates for the two thermal reactions for JP28/29 were estimated using the fitted curves. The calculated saturated reaction rates are listed in Table 4.



Figure 1. The specific activity of <sup>60</sup>Co in monitor K of experiment JP28 over the irradiation period.



**Figure 2.** Minimization space for simultaneously solving for the thermal and epithermal flux using the  ${}^{59}Co(n,g){}^{60}Co$  and  ${}^{93}Nb(n,g){}^{94}Nb$  reactions.

ID	Height,cm	<sup>60</sup> Co (Co)	<sup>60</sup> Co (Cu)	<sup>54</sup> Mn	<sup>94</sup> Nb	<sup>46</sup> Sc	<sup>93m</sup> Nb
JP28							
К	20.44	4.11E-08	2.36E-13	3.33E-11	1.61E-09	4.64E-12	7.92E-11
U8	5.70	5.26E-08	*	5.46E-11	2.17E-09	*	1.12E-10
18	-8.44	4.99E-08	*	5.18E-11	2.07E-09	7.57E-12	*
7J	-24.72	3.00E-08	1.56E-13	2.31E-11	1.17E-09	*	4.39E-11
JP29							
J8	19.68	4.20E-08	2.40E-13	3.23E-11	1.65E-09	4.72E-12	8.02E-11
10	15.71	4.64E-08	2.92E-13	3.96E-11	1.80E-09	6.01E-12	*
EA	-9.11	4.94E-08	3.48E-13	4.72E-11	2.05E-09	*	1.09E-10
8V	-25.04	2.93E-08	*	1.91E-11	1.14E-09	*	5.11E-11

**Table 4.** Saturated reaction rates in product atoms/(target atom – second) for the JP28 and JP29 experiments. Uncertainties are ±2% except for <sup>93m</sup>Nb which are estimated at ±5%.

\*data not usable due to loss of sample or contamination

The saturated reaction rates are equal to the integral of the neutron activation cross section times the timeaveraged neutron flux over all neutron energies. At each irradiation position we thus have at most 6 integral equations that are solved simultaneously using a generalized least-squares procedure in the STAYSL PNNL computer suite. The neutron activation cross sections were adopted from the IRDFF database compiled by the Nuclear Data Section of the International Atomic Energy Agency [5]. The input neutron spectrum was provided by Joel McDuffee at ORNL (see Figure 1, blue) [6]. The input to STAYSL PNNL consisted of the measured saturated reaction rates, the input neutron spectrum, the irradiation length, and the IRDFF neutron activation cross sections including all known uncertainties and covariances. Matrix inversion was then used to determine the adjusted neutron flux spectrum and uncertainties including the complete cross-section covariance matrices and a Gaussian formalism-based flux covariance matrix. The results are presented in Table 5 and a typical neutron spectral adjustment is shown in Figure 3. The neutron fluences are plotted in Figures 4 and 5.

ID	Height,cm	Thermal		Epithermal		> 0.11 MeV		> 1 MeV	
JP28		< 0.5 eV	±%	0.5 eV to 110 keV	±%		±%		±%
К	20.44	1.13E+23	13	7.15E+22	27	6.27E+22	6	3.21E+22	5
U8	5.70	1.49E+23	13	1.21E+23	25	1.04E+23	6	5.17E+22	5
18	-8.44	1.35E+23	13	1.10E+23	25	9.41E+22	7	4.72E+22	6
7J	-24.72	8.28E+22	13	5.20E+22	26	4.15E+22	6	2.04E+22	5
JP29									
J8	19.68	1.17E+23	13	7.24E+22	26	6.33E+22	6	3.25E+22	5
10	15.71	1.28E+23	13	8.40E+22	24	7.28E+22	7	3.66E+22	6
EA	-9.11	1.43E+23	13	1.10E+23	25	9.52E+22	6	4.86E+22	5
8V	-25.04	8.61E+22	13	5.42E+22	26	4.64E+22	6	2.32E+22	5

Table 5. Neutron fluences for the JP28 and JP29 irradiations



**Figure 3.** Neutron spectral adjustment with STAYSL PNNL for the JP18 18 position at -8.4 cm. Flux per lethargy is shown both before and after adjustment. The top curve shows the size of the adjustment using the percent difference scale on the right side.



**Figure 4.** Neutron fluence values are plotted vs. height in the HFIR JP28 experiment. The solid lines are trend lines used as eye guides. The epithermal fluence has a higher uncertainty than the thermal and fast fluences.



**Figure 5.** Neutron fluence values are plotted vs. height in the HFIR JP29 experiment. The solid lines are trend lines. The epithermal fluence has a higher uncertainty than the thermal and fast fluences.

# **Radiation Damage Calculations**

The adjusted neutron spectrum determined at each positon in the irradiation assemblies was used to calculate the dpa and helium production in various elements and alloys using the SPECTER computer code [7] and the damage parameters are listed in Table 6 and plotted in Figures 6 and 7. The radiation damage calcultions do not take into account the significant transmutation that occurs during irradiation. In most cases the transmutation does not significantly change the dpa or helium production but may lead to changes in the alloy composition. The tungsten in the alloy F82H was converted by more than 90% to Re and Os, as discussed in Reference [8].

ID	Height, cm	F82H		Fe		Ni	
JP28		dpa	He,appm	dpa	He,appm	dpa	He,appm
К	20.44	45.01	13.56	45.18	14.21	100.47	28569
U8	5.70	73.81	26.56	74.13	27.86	144.91	36024
18	-8.44	66.96	22.65	67.24	23.75	132.45	33237
7J	-24.72	29.34	9.01	29.46	9.45	70.19	21060
JP29		dpa	He,appm	dpa	He,appm	dpa	He,appm
J8	19.68	45.41	13.83	45.59	14.50	102.52	29423
10	15.71	52.10	17.05	52.32	17.88	114.29	31929
EA	-9.11	68.04	21.16	68.32	22.19	136.66	34957
8V	-25.52	29.56	8.82	29.67	9.24	72.38	22168

Table 6. Radiation damage parameters for the JP28 and JP29 experiments



**Figure 6.** F82H dpa for the JP28 and JP29 experiments. The solid lines are polynomial fits to the data, as described in the text and Table 6.



**Figure 7.** Helium production (appm) in F82H for the JP28 and JP29 experiments. The solid lines are polynomial fits to the data, as described in the text and Table 6.

The neutron fluence and radiation damage parameters can be well described by a polynomial function as shown by the trend lines on the plots. The form of the polynomial is given as equation (1) below where a is the maximum value, and b is the quadratic parameter. The flux, dpa, and helium (appm) values at any location in the assembly can then be determined using the height, z in cm, and the coefficients listed in Table 7. The functions are symmetric about core midplane.

$$F = a (1 + b z^2)$$
 (1)

Table 7. Polynomial coefficients for Equation 1 to calculate neutron fluence and damage parameters

JP28	а	b
Thermal	1.49E+23	-6.791E-04
Epithermal	1.21E+23	-9.514E-04
>0.1 MeV	1.05E+23	-9.810E-04
> 1 MeV	5.23E+22	-9.788E-04
F82H dpa	74.41	-9.792E-04
F82H He,appm	26.05	-1.098E-03
JP29	а	b
Thermal	1.54E+23	-6 780E-04
		0.1002 01
Epithermal	1.13E+23	-8.733E-04
Epithermal >0.1 MeV	1.13E+23 9.86E+22	-8.733E-04 -8.810E-04
Epithermal >0.1 MeV > 1 MeV	1.13E+23 9.86E+22 5.03E+22	-8.733E-04 -8.810E-04 -8.915E-04
Epithermal >0.1 MeV > 1 MeV F82H dpa	1.13E+23 9.86E+22 5.03E+22 71.85	-8.733E-04 -8.810E-04 -8.915E-04 -9.556E-04

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11.2 IAEA SMALL SPECIMEN TEST TECHNIQUE DEVELOPMENT: MASTER CURVE FRACTURE TOUGHNESS ROUND ROBIN TEST PLAN—X. Chen, M. Sokolov (Oak Ridge National Laboratory), R. Hernandez Pascual, M. Serrano (Centre for Energy, Environment and Technology), D. Andres, H. Nolles (UK Atomic Energy Authority)

# OBJECTIVE

This task aims to develop reliable fracture toughness testing and analysis method for small size specimens. Under the framework of the International Atomic Energy Agency (IAEA) Coordinated Research Projects (CRP), the work eventually aims for standardization of fracture toughness test technique for small size specimens.

#### Extended Abstract

Under the auspices of International Atomic Energy Agency (IAEA), a Coordinated Research Project (CRP) entitled "Towards the Standardization of Small Specimen Test Techniques for Fusion Applications" has started since 2017. The overall objective of the project is to provide a set of guidelines for small specimen test techniques (SSTT) based on commonly agreed best practices on main test techniques including tensile, creep, low cycle fatigue, fracture toughness, and fatigue crack growth rate. This will act as the first step of a full standardization of the SSTT. Fusion structural materials, i.e., reduced activation ferritic/martensitic (RAFM) steels, are used for testing. In addition, the project will create a comprehensive mechanical property database of RAFM steels tested by SSTT.

For the fracture toughness task of the CRP, three testing methods including Master Curve, local approach for ductile crack growth and cleavage fracture, and ductile approach at room temperature will be evaluated. This project focuses on the Master Curve method based on the ASTM standard E1921-19b "Standard Test Method for Determination of Reference Temperature, T<sub>0</sub>, for Ferritic Steels in the Transition Range" [1] and commonly agreed best practice from researchers at Oak Ridge National Laboratory (ORNL), Centre for Energy, Environment and Technology (CIEMAT), and UK Atomic Energy Authority (UKAEA).

The materials used in the round-robin testing are Eurofer 97 batch-3 and F82H-BA12. Table 1 summarizes the test matrix adopted in the round-robin testing. The specimen machining plan is highlighted in Figure 1 with individual specimen drawings given in Figures 2-8. Each participating laboratory will perform machining independently. The testing and data recording will strictly follow the testing guidelines and data reporting template in Reference [2]. The testing is expected to commence in September 2020.

Participants	Materials	Specimen configuration	# of specimens	Orientation	Size of raw material*	
	Eurofer97	rofer97 (Fig.2) miniature bend bar 16		ΙT	460mm(L) x 125mm(T) x	
X Chen/M	batch-3	miniCT (Fig.3)	10-12		33mm (S)	
Sokolov		0.5TCT (Fig.4)	8-10			
(ORNL)		miniature bend bar (Fig.2)	16	1.7	100mm(L) x 300mm(T) x	
	F02H-BAIZ	miniCT (Fig.3)	10-12		26mm (S)	
		0.5TCT (Fig.4)	8-10			
		PCCVN (Fig.5)			600mm(L) x	
R. Hernandez Pascual/ M.	Eurofer97 batch-3	0.5TCT (Fig.6)	8-10	LT	125mm(T) x 33mm (S)	
Serrano		PCCVN (Fig.5)	(Fig.5)		200mm(L) x	
(CIEMAT)	F82H-BA12	0.5TCT (Fig.6)	8-10	LT	300mm(T) x 25mm (S)	
		miniCT (Fig. 7)	10-12		50mm(L) x	
	Eurofer97 batch-3	miniCT-DONES (Fig. 8)	10-12 LT		120mm(T) x 33mm (S)	
ΔFΔ)		miniCT (Fig. 7)	10-12		40mm(L) x	
ALA)	F82H-BA12	miniCT-DONES (Fig. 8)	10-12	LT	60mm(T) x 25mm (S) (TBD)	

<b>Table 1.</b> Master Curve round-robin testing matrix	Table 1.	Master	Curve	round-robin	testing	matrix
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\* L: longitudinal, T: transverse, and S: short transverse based on the plate orientation



(a)



(b)



(c)



Eurofer97-3 machining plan (Specimens from left to right: DONES tensile, SSJ3 tensile, mCT-MRF, mCT-DONES, mCT-MRF for FCG) (TBD) (e)



UKAEA F82H-BA12 machining plan (Specimens from left to right: DONES tensile, SSJ3 tensile, mCT-MRF, mCT-DONES.) (TBD)

(f)

Figure 1. Specimen machining plans for ORNL in (a) and (b), CIEMAT in (c) and (d), and UKAEA in (e) and (f).



Figure 2. ORNL miniature bend bar specimen drawing.


Figure 3. ORNL miniCT specimen drawing.



Figure 4. ORNL 0.5TCT specimen drawing.







Figure 6. CIEMAT 0.5TCT specimen drawing.





## NOTES

1. DIMENSIONS IN BRACKETS ARE FOR REFENCE ONLY

2. ALL CUT OR MACHINED SHARP EDGES TO BE DE-BURRED

3. TOLERANCE APPLY +/-0.04

4. 0.12 OR SMALLEST WIRE MAX 0.2



(a)



Figure 7. UKAEA miniCT specimen drawing: (a) general layout, (b) details of the drawing.



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**Figure 8.** UKAEA miniCT-DONES specimen drawing based on the proposed DONES mCT with W=9.2mm: (a) general layout, (b) details of the drawing.

### References

- ASTM E1921-19be1, Standard Test Method for Determination of Reference Temperature, T<sub>0</sub>, for Ferritic Steels in the Transition Range, ASTM International, West Conshohocken, PA, 2019, www.astm.org
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**11.3 MINIATURE MECHANICAL TEST DEVELOPMENT FOR TUNGSTEN-BASED MATERIALS**—L. M. Garrison, N. C. Reid, M. N. Gussev (Oak Ridge National Laboratory)

# OBJECTIVE

The aim of this work is to develop miniature mechanical test methods that can be used to evaluate neutronirradiated tungsten and tungsten composite samples in LAMDA.

### SUMMARY

Three-point bending will be used to observe failure from flexural stresses in tungsten-based samples. Because of its simplicity and economy, it is a fitting test to perform on samples of TEM disc geometry that have been irradiated in HFIR. The test is conventionally performed on beams of rectangular cross sections. This test has been adapted to be performed on disc specimens at the plane of symmetry in the center of the sample. A fixture has been modelled and procured for testing of tungsten materials in LAMDA.

### PROGRESS AND STATUS

A custom three-point bend test fixture was designed for neutron-irradiated disk specimens that are 3 mm in diameter, which is the typical size for transmission electron microscopy (TEM) disks. An initial finite element deformation analysis was performed (Figure 1) to evaluate the mechanical stress field of disk bend specimens; however, a more complete study of the deformation analysis will be completed using ANSYS software.



**Figure 1.** Stress analysis of a simplified model of miniature three-point bend performed on a disk-shaped specimen. (A) Orthographic view, (B) bottom view. For scale, the disc is 3 mm in diameter and 0.25 mm thick.

The experimental setup for this stress analysis was performed using 7 bodies with sliding contacts and no separation. Experimental data from PHENIX unalloyed polycrystalline tungsten was used as inputs. The meshing for this model is coarse, but useful for observing the trends and to minimize computational time. More extensive meshing will be performed in ANSYS for publication quality. The deformation in the direction of load and the maximum tensile stress to the bottom layer of the disk at the center of symmetry agree well with the analytical analysis performed previously. The rods that are in contact with tungsten will be tungsten carbide material to be able to handle large contact pressure with minimal deformation. Based on this model, the tungsten disk will undergo plastic deformation at a mere 15-25 microns of deflection at around 200 N

for a 0.25 mm thick tungsten disk. Due to the squared proportionality between load and thickness, this value is approximately 800 N for a 0.50 mm thick disk specimen.

A bend test fixture has been designed and fabricated to enable testing of these specimens with precisely engineered tolerance and minimal machine compliance (Figure 2-3). The deformation of the tension side of the disk can be measured in-situ through an opening at the bottom of the fixture (Figure 4). Post-mortem examination of the fracture surfaces can additionally be performed. Size and geometry effect will be discussed following preliminary testing through comparison of this test to a conventional three-point bend and uniaxial tensile testing.



**Figure 2.** Exploded view CAD model of a three-point bend fixture assembly for use in LAMDA universal testing frames.

The construction of the fixture was inspired by and reflects that of the shear punch fixture, and so procedures and parts can be adapted and recycled between these two tests. The major changes of the design as compared to the shear punch fixture are a thicker upper half section to support constrained movement of the loading nose, and major changes to the bottom half involving a removable support piece that is tightly fitted and held by a screw from the side. Testing with various centering methods will be performed to find the best method for getting the disk in the exact center of the supports prior to testing.



**Figure 3.** Loading of the sample and nose. The opening is large enough to fit the disk specimen and have a view of it before adding the loading nose. (A) View of the loading nose inside the transparent button guide, (B) top view of the fixture looking down at the sample, which is 3 mm in diameter.

The fixture is self-contained and can be inserted right into the testing frame. Much like the shear punch test, any major movements that may move the inner pieces must be avoided to risk invalidating the test. Centering methods using the clamping mechanism of the upper to lower halves will be considered to keep the disk from moving in place.



**Figure 4.** Opening at the bottom of the fixture allows for a viewpoint of the bottom side of the disk in tension to analyze the stress state during testing and have capability of video of the fracture initiation and propagation.

**11.4 HFIR IRRADIATION EXPERIMENTS**—N. Russell, C. On, J. L. McDuffee, J. W. Geringer (Oak Ridge National Laboratory)

### SUMMARY

Neutron irradiation experiments were performed in support of the research and development of fusion reactor materials using various materials irradiation facilities in the High Flux Isotope Reactor (HFIR).

The HFIR operated for about 3 total cycles between January 1 and June 30, 2020. Cycle 485 was completed on January 19 (2139.36 MWD), Cycle 486 was completed on February 24 (2126.02 MWD), and Cycle 487 on May 23 (2136.99 MWD). Cycle 488 began on June 9 and is expected to complete on July 7.

Thirty-four target zone rabbit capsules remain in the reactor to complete the scheduled irradiations. These capsules are listed in Table 1 along with condensed information on material, specimen type, temperature, fluence, and period of irradiation. Eleven rabbits completed the scheduled irradiation.

Table 1.	The HFIR	fusion	materials	program	n rabbit	capsules	to con	tinue	irradiation	with	reactor	startup
1 4010 11	1110 111 11 (	1001011	materiale	program	Tabbit	oapoaloo	10 0011	unao	maaladon		rouotor	otartap

Experiment Designation	Primary Materials	Specimen Types	Irradiation Temperatur e (°C)	Max Exposure (dpa)	Number of Reactor Cycles	HFIR Cycles Start – End		3
F13B4	FeCrAlY Steel	Tensile	300	50	29	451	-	497
JCR11-03	SiC/SiC	Mini bend bars	950	200	100	487	-	586
JCR11-05	SiC/SiC	Mini bend bars	950	200	115	444	-	568
JCR11-07	SiC/SiC	Mini bend bars	950	100	47	444	-	492
JCR11-08	SiC/SiC	Mini bend bars	950	200	115	444	-	560
JCR11-11	SiC/SiC	Mini bend bars	950	100	55	448	-	524
SCF4	SiC/SiC	Miniature flexure bar	250	100	90	457	-	547
SCF5	SiC/SiC	Miniature flexure bar	250	200	45	457	-	511
SCF8	SiC/SiC	Miniature flexure bar	600	100	45	457	-	502
SCF9	SiC/SiC	Miniature flexure bar	600	200	90	457	-	548
SCF11	SiC/SiC	Miniature flexure bar	950	100	57	458	-	517
ES01	EUROFER 97	Tensile/MPC**	220	20	12	479	-	491
ES02	EUROFER 97	Tensile/MPC**	275	20	12	480	-	492
ES03	EUROFER 97	Tensile/MPC**	275	20	12	479	-	491
ES04	EUROFER 97	Tensile/MPC**	300	20	12	479	-	491
ES05	EUROFER 97	Tensile/MPC**	325	20	12	479	-	491
ES06	EUROFER 97	Tensile/MPC**	350	20	12	479	-	491
ES07	EUROFER 97	Tensile/MPC**	375	20	12	479	-	491

ES11	EUROFER 97	Bend bars	220	20	12	479	-	492
ES12	EUROFER 97 Bend bars		240	20	12	479	-	492
ES13	EUROFER 97	Bend bars	275	20	12	479	-	492
ES14	EUROFER 97 Bend bars		300	20	12	479	-	492
ES15	EUROFER 97	Bend bars	325	20	12	479	-	494
ES16	EUROFER 97	Bend bars	350	20	12	479	-	494
ES17	EUROFER 97	Bend bars	375	20	12	479	-	494
FMP01*	Cu Alloys	Tensile/MPC**	100	5	3	485	-	487
FMP02*	F82H	Tensile	250	5	3	484	-	486
FMP03*	F82H	Tensile	200	5-7	3	484	-	486
FMP04*	F82H	Tensile/MPC**	300	5	3	484	-	486
FMP05*	F82H	Tensile/MPC**	350	5	3	484	-	486
FMP06*	F82H	Tensile/MPC**	300	5-7	3	484	-	486
FMP07	F82H	Tensile	300	20	11	487	-	497
FMP08	F82H	Tensile	300	80	45	487	-	531
FMP09*	F82H	Tensile/MPC**	350	5-7	3	484	-	486
FMP10*	F82H	Tensile/MPC**	385	5-7	3	484	-	486
FMP11	F82H	Tensile	385	20	11	488	-	498
FMP12	F82H	Tensile	385	80	45	488	-	532
FMP13*	F82H	Tensile	450	5-7	3	484	-	486
FMP14	F82H	Tensile	525	20	11	484	-	494
FMP15*	F82H	Tensile/MPC**	650	5-7	3	484	-	486
FMP16	F82H	Tensile/MPC**	650	20	11	484	-	494
FMP17	F82H	Tensile/MPC**	650	80	45	484	-	528
FMP19*	Celia, W	Discs	500	1.6	1	487	-	487
FMP22	F82H	Bend Bars	300	20	11	488	-	498
FMP23	F82H	Bend Bars	300	80	45	488	-	532

\*Completed irradiation this reporting period \*\*MPC= Multi-Purpose Coupon