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Ion-irradiation-induced clustering in W–Re and W–Re–Os alloys: A comparative study using atom probe tomography and nanoindentation measurements

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Abstract—This study examines clustering and hardening in W–2 at.% Re and W–1 at.% Re–1 at.% Os alloys induced by 2 MeV W^+ ion irradiation at 573 and 773 K. Such clusters are known precursors to the formation of embrittling precipitates, a potentially life-limiting phenomenon in the operation of fusion reactor components. Increases in hardness were studied using nanoindentation. The presence of osmium significantly increased post-irradiation hardening. Atom probe tomography analysis revealed clustering in both alloys, with the size and number densities strongly dependent on alloy composition and irradiation temperature. The highest cluster number density was found in the ternary alloy irradiated at 773 K. In the ternary alloy, Os was found to cluster preferentially compared to Re. The implications of this result for the structural integrity of fusion reactor components are discussed.

Keywords: Tungsten rhenium osmium alloys; Nuclear fusion; Atom probe tomography; Ion irradiation; Nanoindentation

1. Introduction

Tungsten is the prime candidate for plasma facing applications in future nuclear fusion reactors, being one of only a handful of materials that are capable of withstanding the harsh operating conditions of up to ~1300 K, power densities of 1–20 MW m^{-2} and irradiation from both 14 MeV neutrons and 2 MeV alpha particles [1,2]. As well as causing large degrees of cascade damage (up to 20 displacements per atom per full-power year) [3], the neutron irradiation will cause pure tungsten to transmute into Re and subsequently Os, yielding potential solute contents as high as 3.8 at.% Re and 1.38 at.% Os after 5 years of reactor operation [4]. Although the equilibrium W–Re–Os phase diagram predicts complete solubility at this composition [5], the mechanical properties of components could be severely degraded due to the formation of irradiation-induced solute-rich clusters as the precursors to sigma and chi precipitates [6,7]. Previous studies of the irradiation responses of these systems are sparse and limited to compositions with more than 3 at.% rhenium and/or osmium present [8–11]. Tanno et al. [8] irradiated W–3Os, W–5Re and W–5Re–3Os in the JOYO Japanese nuclear research reactor. Over a one-year period the alloys were exposed to a neutron dose (>0.1 MeV) of 1.2×10^{26} nm^{-2}, corresponding to 1.54 dpa at ~1032 K, conditions designed to mimic those of the ITER environment [12]. Needle-shaped precipitates were identified by transmission electron microscopy (TEM). Osmium appeared to promote nucleation of precipitates, while Re encouraged their growth [11]. Where Os and Re coexisted in the ternary W–5Re–3Os alloy, Os had a dominant effect, and the precipitation characteristics closely mirrored that of the W–3Os alloy. However, the precipitates were too small to accurately ascertain the compositions and full structures by TEM. Microhardness tests showed increases in hardness in all irradiated samples, with osmium-containing alloys (either binary or ternary) showing a larger increase (up to 8 GPa at 1.54 dpa) than W–Re alloys [11] (up to 5 GPa at 1.54 dpa).

The most detailed chemical characterization of irradiation-induced precipitates in W–Re alloys has been conducted by Herschitz and Seidman [13,14]. Their work used field ion microscopy to image the platelets formed in W–Re alloys post-neutron irradiation. They were able to determine, using 1-D atom probe mass spectrometry, that the precipitates contained either ~50 or ~75 at.% Re. However, the alloys they considered were of much higher

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rhenium content (10 and 25 at.%) than are currently of interest for fusion applications.

Tungsten ion implantation experiments were performed on a commercial W–5 at.% Re alloy by Armstrong et al. [15] from 0.04 to 33 dpa damage levels at 300 °C. Atom probe tomography (APT) showed that a large increase in hardness above the 13 dpa damage level was associated with the formation of rhenium clusters ~3 nm in diameter, though no study of the composition or density of these clusters was performed.

In this study, ion irradiation was used as an analogue for neutron damage in W–Re–Os binary and ternary alloys. APT was used to study clustering and nanoindentation to measure the mechanical properties of the ion-irradiated layer.

2. Experimental methods

Alloys of W–2 at.% Re and W–1 at.% Re–1 at.% Os and were produced using vacuum arc melting of high-purity powders (Sigma Aldrich and AEE), as described in a previous study [16]. Both alloys were found to have large grain sizes (0.5–2 mm measured via optical microscopy) and to be of high purity (>99.99 at.%, with trace impurities of Al, Si and Ca), as measured using APT and electron probe microanalysis. The ingots were cut into 1 mm thick slices, which were ground and polished with SiC paper and diamond paste. A final colloidal silica (40 nm) finish was used to produce a damage-free surface suitable for implantation and subsequent analysis.

Ion irradiation was performed at the National Ion Beam Centre, University of Surrey, UK. Samples were mounted on a stainless steel temperature-controlled stage (held at either 573 or 773 K) under a vacuum pressure $<10^{-6}$ Pa; for full details see Armstrong et al. [16]. These temperatures were chosen to lie on either side of the stage III vacancy recovery temperature for W of 743 K [17]. A tandem accelerator was used to irradiate the samples with 2 MeV W^+ ions to a fluence of 2.64×10^{15} ions cm^{-2} at a flux of 1.96×10^{10} ions cm^{-2} s^{-1}. A SRIM (stopping range of ions in matter) calculation predicts a damage profile extending to 300 nm below the surface, yielding an equivalent peak damage level of 33 dpa (calculated using the full cascade damage model with a binding energy of 68 eV) [15,16,18].

A dual-beam focused ion beam system (Zeiss Nvision) was used to manufacture lift-out samples for APT analysis pre- and post-irradiation, following procedures described elsewhere [19,20]. Materials were analysed using a Cameca LEAP3000X HR (37% total detection efficiency) in laser mode, running at pulse energies of 0.6–0.8 nJ and a sample stage temperature of 50 K. A minimum of three samples were studied for each alloy and each condition, the data from which were reconstructed using Cameca's IVAS (3.6.6) software.

Nanohardness measurements were made using a Nanoindenter XP (MTS, TN, USA) with a Berkovich diamond indenter calibrated against fused silica. The continuous stiffness measurement mode was used, allowing the hardness to be calculated as a function of depth [21]. The indents were made to 1 μm final depth at a target indentation strain rate of 0.05 s^{-1}, significantly deeper than the 300 nm deep damage layer. Grids of 16 indents were made on each of three different grains at room temperature for each sample and condition. There are difficulties with extracting hardness values from such thin irradiated layers where there will be significant penetration of the plastic zone into the unirradiated material. The method described by Armstrong et al. [15] was used to identify the region in which the hardness of the implanted layer dominates over the unimplanted layer, thus reported hardness values are taken at 125 nm indenter penetration.

3. Results and discussion

3.1. APT analyses

In the unirradiated materials, rhenium and osmium atoms are seen to be homogeneously distributed within the tungsten (see Supporting information for atom maps). The measured solute composition is 1.90 at.% Re in the binary alloy and 1.06 at.% Re/1.11 at.% Os in the ternary (wt.% equivalent to two significant figures). Following ion irradiation, solute clustering was observed in both alloys at both irradiation temperatures, and the level of clustering was seen to vary with implantation depth. This is apparent in Fig. 1a, which shows 4 nm thick sections through an atom map of the W–2Re sample following 33 dpa irradiation at 773 K. The outer surface of the alloy is marked by the carbon layer visible on the left-hand side of the map, below which a region of approximately 200 nm has prominent clustering of Re atoms; at greater depths, the structure returns to being a homogeneous solid solution. Fig. 1b shows the calculated average cluster diameter and volume fraction determined within 10 nm thick bins of the dataset (see below for further cluster analysis details). The cluster volume fraction profile strongly correlates with the damage profile from the SRIM calculation for tungsten at 33 dpa.

To compare the effects of different irradiation conditions/alloy compositions on the microstructures, Fig. 2 shows further 4 nm thick slices over the full set of irradiation conditions and samples, confining the analyses to a depth range of 50–200 nm below the implanted surface, where the peak dose would correspond to 33 dpa.

Fig. 2a shows that the irradiation has induced the formation of a high volume fraction of Re-rich clusters in the binary alloy, approximately 5 nm in diameter. Increasing the temperature to 773 K (Fig. 2b) yields a lower number density of clusters but of larger size, up to 15 nm in diameter. However, this is significantly altered when 1 at.% Os is added to the alloy; at 573 K only slight clustering is noticeable in W–1Re–1Os (Fig. 2c), suggesting that Os is suppressing cluster formation. However, following the 773 K irradiation (Fig. 2d), a high number density of very small (<4 nm dia.) precipitates is formed, enriched in both Re and Os.

To quantify the size, chemical composition and density of clusters observed the maximum separation method algorithm [20] was used to identify and separate any clusters present in the 50–200 nm depth range of each dataset. The method classifies two solute atoms as part of the same cluster if the inter-solute distance falls below a user-defined d_{max} value. Clusters containing fewer solute atoms than a user-specified term N_{min} are rejected to eliminate any small random clustering. An optimum d_{max} value was selected for each irradiation condition/alloy combination based on the procedure proposed by Chen et al. [22] and by Williams