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Effect of nano-oxide particle size on radiation resistance of iron–chromium alloys

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ABSTRACT

Radiation resistance of Fe–14Cr alloys under 200 keV He irradiation at 500 °C was systematically investigated with varying sizes of nano oxide Zr, Hf and Cr particles. It is found that these nano oxide particles acted as effective sites for He bubble formation. By statistically analyzing 700–1500 He bubbles at the depth of about 150–700 nm from a series of HRTEM images for each sample, we established the variation of average He bubble size, He bubble density, and swelling percentage along the depth, and found them to be consistent with the He concentration profile calculated from the SIRM program. Oxide particles with sizes less than 3.5–4 nm are found most effective for enhancing radiation resistance in the studied alloy systems.

1. Introduction

One of the key ingredients in engineering irradiation tolerant materials is through the use of nano-size particles (or dispersoids) [1–7]. This has been demonstrated by Y–Ti-enriched nano-oxides, which are found to enhance the irradiation resistance and creep strength of oxide dispersion strengthened (ODS) alloys at elevated temperatures [3,5,8–10]. The nano-oxide particles not only provide large fractions of interfaces for vacancy and self-interstitial recombination, but also serve as preferential trapping sites for helium [11–15]. Helium, as an unavoidable byproduct from neutron-induced (n,α) transmutation reactions in the nuclear reactor environment, is insoluble in ferritic alloys and has the potential to deteriorate materials via void swelling, blistering or embrittlement upon their accumulation [16]. These adverse effects are found to be minimized by the incorporation of nano-oxides in the microstructure to trap helium in fine-scale bubbles [16–21]. Therefore, understanding the effect of nano-oxide particles and their interaction with helium in the irradiation environment becomes a critical factor in designing irradiation resistant materials for nuclear applications.

Current studies of nano-size oxide particles are mostly focused on Y–Ti-enriched oxides in ODS alloys. They are incorporated into the ferritic alloy via mechanical alloying with 0.2–0.3 wt.% Y_2O_3 and ~0.2 wt.% Ti [1,3,5,22–29], and subsequent heating in the temperature range of 1000–1150 °C [3,30]. The addition of Ti particles helps to refine the oxide size down to about 1–15 nm by forming complex non-stoichiometric Y–Ti-enriched oxides. The suppression of nano-oxide particles on swelling and embrittlement is largely attributed to its strong He trapping capability [17,28,31,32]. This scenario is directly supported by transmission electron microscopy (TEM) observations from Refs. [17,31], indicating that small He bubbles are preferentially formed at the metal-oxide interfaces. A recent APT study by Edmondson et al. revealed that the coverage of He atoms on the nano-oxide particle interfaces can be as large as 50% [20]. Such high tendency of He attraction by the oxide interface could be due to the strong interaction between He and vacancy-oxygen at the oxide interface according to the first-principle calculations [33]. Recently, the effectiveness of nano-oxide particles on the promotion of He bubble formation was examined in ODS alloys. The highly dispersed nano-scale oxide particles were found to be an effective nucleation sites for He

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bubbles [20]. Smaller bubble sizes and smaller volume fraction occur in ODS alloys containing nano-oxide particles compared to those without them under He irradiation [8].

Recent studies by our group have revealed high densities of nano particles of ZrO_2 and HfO_2 dispersed in the ferritic matrix [34,35]. These particles are in the size range of 1–10 nm, which is comparable to the nano particles in conventional ODS alloys. It is still not clear how effective these nano-size oxide particles are in enhancing irradiation resistance. Here we report a systematic study on He bubble characteristics in six types of Fe–14Cr alloy samples with different oxide particles subjected to 200 keV He irradiation. This includes Fe–14Cr alloys with Zr/Hf additions as well as Fe–14Cr base alloys. Direct microstructural characterization and statistical analysis are performed to reveal the bubble size, bubble density, and swelling percentage in these alloys. The effectiveness of the size of nano oxide particles in enhancing irradiation resistance is systematically studied.

2. Materials and methods

2.1. Materials synthesis

Fe–14Cr based alloys were synthesized by mechanical alloying using a SPEX 8000M Mixer/Mill. To produce Fe–14Cr–1.5Zr alloys (atom %), powders of Fe, Cr, Zr (from Alfa Aesar, with 99.9%, 99.9%, 99.5% purity, respectively) were mixed, sealed, and mechanically milled for 20 h under purified Ar atmosphere (with less than 1 ppm of oxygen and H_2O). The ball to powder mass ratio was 10:1. The as-milled powders were then annealed in a quartz tube under a Ar–2% H_2 protective atmosphere at 800 °C and 900 °C for 1 h. The starting powder mixture contained excess oxygen according to our previous work [34,35], nanoscale oxide particles will thus be formed. Annealing the powders at different temperatures is expected to produce Fe–14Cr–1.5Zr alloys with very different nano-oxide particle sizes and grain sizes. To prepare the samples for He irradiation, the annealed powders were further cold compressed into discs under 2.5 GPa and mechanically polished with an Allied Mulitprep system. Fe–14Cr–2Hf alloy was synthesized in the same way using 99.6% purity Hf powder from Alfa Aesar, followed by a 700 °C annealing for 1 h. The Fe–14Cr base alloys were also produced for comparison. The as-milled Fe–14Cr powders were subsequently annealed at 900 °C for 1 h, 500 °C for 1 h, and 500 °C for 26 h. This produced the as-annealed Fe–14Cr alloy samples with very different grain sizes.

In this paper, we use the nomenclature of “A_B” to name all six alloy samples. Here, “A” refers to the alloy composition. “B” refers to the annealing temperature and time. Therefore, sample Fe14Cr2Hf_700C1h represents the Fe–14Cr–2Hf alloy annealed at 700 °C for 1 h. Similarly, the Fe–14Cr–1.5Zr alloy annealed at 800 °C for 1 h and 900 °C for 1 h are designated as Fe14Cr1.5Zr_800C1h and Fe14Cr1.5Zr_900C1h, respectively. The Fe–14Cr base alloys annealed at 500 °C for 1 or 26 h and 900 °C for 1 h are designated as Fe14Cr_500C1h, Fe14Cr_500C26h, and Fe14Cr_900C1h thereafter.

2.2. Irradiation conditions

Ion irradiations were performed at the Ion Beam Materials Laboratory at Los Alamos National Laboratory, using a Danfysik High Current Research Ion Implanter operating at 200 kV. Samples were irradiated with 200 keV He ions perpendicular to the sample surface to a fluence of 6.5×10^{20} ions/m^2 and a flux of 2.2×10^{17} ions/m$^2\bullet$s. The temperature of the specimen during irradiation was maintained at 500 °C under pressure of 8×10^{-5} Pa. The estimated damage profile and He ion concentration in the Fe–14Cr alloy were simulated using the SRIM (Stopping and Range of Ions in Matter) program [36]. The simulation was performed using the detailed calculation mode with full damage cascades using a damage displacement threshold energy value of 40 eV for both Fe and Cr. The peak irradiation damage is about 5 dpa at the depth of about 500 nm. The peak He concentration is about 4 at% at a depth of about 550 nm. A slight grain growth was observed in the Fe–14Cr–1.5Zr alloy samples after He ion irradiation at 500 °C for 50 min.

2.3. TEM sample preparation

Scanning/transmission electron microscopy (S/TEM) samples were prepared using the focused ion beam (FIB) ‘lift-out’ technique in an FEI Quanta 3D FEG dual-beam instrument. To protect the specimen top surface from Ga^+ ion sputtering/damage, the specimen was coated with 200 nm Pt using electron beam deposition followed by 3 μm Pt deposited using Ga^+ ion beam. Note that the thick Pt layer is deposited on the top surface of specimen to help prevent the specimen from bending in the final FIB thinning and polishing procedure. The FIB specimen was cut using 30 keV Ga^+ ions, followed by final thinning and polishing at 5 keV and 2 keV.

2.4. TEM/STEM techniques

Conventional and high-resolution TEM images were taken in a JEM-2010F microscope operated at 200 kV. The HRTEM was done in the defocus condition for the values of −512 nm at 80 k× magnification, −256 nm at 200 k× magnification, and −192 nm at 300 k× magnification depending on the field of view and size of He bubbles. The characterization of the He bubble size and distribution is based on a series of HRTEM images acquired located along the irradiated depth. The statistical analysis of void swelling, bubble size and density along the depth from the top surface inward was performed on 750–1500 bubbles using a self-developed program. With the publication of this paper, the code is available upon request.

HAADF-STEM images were taken in an aberration-corrected FEI Titan G2 microscope operated at 200 kV. The probe size, convergence angle and collection inner semi-angle were 0.1 nm, 21 mrad and 77 mrad, respectively. EDS elemental mapping was acquired using the a Titan G2 microscope equipped with four quadrant windowless silicon drift detectors (SDDs) with a total X-ray collection angle of 0.7 sr. The probe current was about 100 pA. The utilization of large-area detectors in the Titan improves the signal/background ratio of EDS mapping and allows the low level solute to be detected. In addition, EELS elemental mapping was acquired using a Gatan Enfinium ER spectrometer equipped Titan microscope. This helps distinguish Cr and O element distribution at nanometer scale. The EELS collection angle is about 39 mrad.

3. Results and discussion

3.1. Nano-oxide particles

He bubbles are observed near nano-sized ZrO_2 particles in the Fe14Cr1.5Zr_900C1 h sample after He irradiation. Fig. 1a shows the HRTEM images with relatively small He bubble concentration and damage concentration at the depth of 350–400 nm below the surface. Nano-size particles with lattice fringes are found in the ferritic matrix, as pointed out by yellow triangles. These nano-sized particles were identified as ZrO_2 in our previous study [34]. Interestingly, He bubbles are formed at the boundaries of these oxide particles, as indicated by the green triangles. The He bubbles are mostly spherical or near-spherical in shape with diameters less