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Helium solubility and bubble formation in a nanostructured ferritic alloy ☆

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ABSTRACT

The response of a nanostructured ferritic alloy to He implantation and post-irradiation annealing (PIA) at 750 °C was characterized by atom probe tomography and transmission electron microscopy. The supersaturated He concentration in the ferrite at a dose of ~2.1 displacements per atom was similar for the as-implanted, 75 ± 7 appm, and a 10 h PIA treatment, 71 ± 7 appm, but decreased to 38 ± 2 appm after a 100 h PIA treatment. Approximately 91–97% of the He bubbles were present as isolated bubbles in the ferrite and ~1–5% on the surface of the nanoclusters in the ferrite. The remainder were associated with the grain boundaries with a small fraction on the surface of Ti(N,C,O) precipitates. Their average size and number density were similar for the as-implanted and 10 h PIA treatment with a small increase in the size and a significant increase in the number density after the 100 h PIA treatment. Swelling in the high dose region increased from ~1% in the as-implanted and 10 h PIA conditions to ~5% after the 100 h PIA treatment but the estimated number of He atoms per unit volume in the He bubbles decreased by an order of magnitude. Number densities increased from $\sim 8 \times 10^{23}$ m^{-3} in the as-implanted to $\sim 15 \times 10^{23}$ m^{-3} in the 10 h PIA condition, with little change (to $\sim 12 \times 10^{23}$ m^{-3}) in the 100 h PIA condition. This trend may indicate nucleation of new bubbles up to 10 h, with growth and possible consumption of the smaller bubbles between 10 and 100 h.

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1. Introduction

The extreme conditions that are likely to be present in future generations of advanced energy systems will place severe demands on the stability of the structural materials. During service, neutron irradiation of ferritic structural materials generates large numbers of displacement cascades and introduces He though a (n,α) transmutation. The resulting He causes swelling and the formation of He bubbles that could lead to helium embrittlement [1–12]. As the migration energy is low, 0.078 eV [9], He migrates rapidly to and becomes trapped at available microstructural defects, such as dislocations, grain boundaries, and the surfaces of precipitates, thereby reducing the highly supersaturated He level in the ferritic matrix. Helium will also be trapped at native vacancies and those introduced during the displacement cascades produced by irradiation. This trapping could produce small He-vacancy clusters in the matrix [13–19]. Therefore, evaluating the response of the microstructures to long-term high-dose neutron irradiation is required for candidate materials for advanced energy systems.

A potential candidate material that has been developed for use in these types of extreme conditions is a nanostructured ferritic alloy (NFA). These NFAs are a specialized subcategory of oxide dispersion strengthened (ODS) steels with truly outstanding properties of high stability to high temperature creep and radiation tolerance [20–37]. However, the microstructures of the NFAs are significantly different from traditional ODS alloys [38–45]. The general microstructure of NFAs after neutron irradiation or He implantation is shown schematically in Fig. 1. The ultrafine grained alloy has a typical grain size of 200–400 nm, and is dominated by the presence of a high number density of 1–2 nm diameter precipitates, which will hereafter be referred to as nanoclusters (NCs) to prevent confusion with the coarser precipitates which are also present. The grain boundaries are decorated with Ti(N,C,O) and $Y_2Ti_2O_7$ precipitates, NCs, and W- and Cr-segregation, which pin the grain boundaries for excellent stability against high temperature creep [24–26]. After neutron irradiation or He implantation, a high number density of He bubbles are found in the high dose regions. Previous research indicated that the helium bubbles are preferentially located on dislocations, grain boundaries, and the surfaces of the precipitates, as well as distributed throughout the

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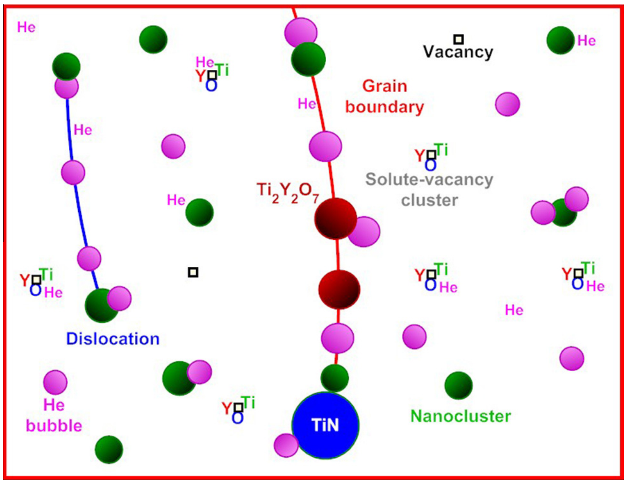

Fig. 1. Schematic diagram of the microstructure of the nanostructured ferritic alloy showing the presence and locations of the microstructural features present (not to scale).

matrix [46–48]. Recently, atom probe tomography (APT) revealed that they are also observed on the surfaces of the NCs [49,50]. It was hypothesized that the trapping of He at the NCs would reduce the amount of free He available to diffuse to and coarsen the He bubbles at the grain boundaries, and hence reduce the susceptibility of the NFA to He embrittlement [49].

Important factors required to understand the stability of these NFAs are the changes in the He concentration in solid solution in the ferrite and in the He bubbles for different conditions and temperatures. The solubility of He in body centered cubic iron is generally assumed to be negligible [9,51] or present at only a few atomic parts per million (appm). Surprisingly, no experimental measurements for iron appear to be cited in the literature. The precise value of He in solid solution in only the ferrite matrix is difficult to experimentally estimate due to the extremely low level present, the complex nature and trapping potential of the microstructural defects, the other microstructural features present, the sensitivity of most experimental techniques to measure this light element, and difficulties in excluding ultrafine He bubbles from the matrix.

Measurement of the helium level within the bubbles, as opposed to the matrix, is established. The helium 1s → 2p electron transition sits at ~21.2 eV [52], which is in the range of energies usually studied by vacuum ultraviolet (VUV) or valence electron energy loss spectroscopy (VEELS) methods [53]. Nuclear magnetic resonance (NMR) methods have also been used for examining helium bubble ensembles [54]. EELS-based methods in the scanning transmission electron microscope (STEM) are particularly attractive because of the high resolution achievable with modern field-emission columns [52,55,56], allowing individual bubbles, instead of ensembles, to be probed. Early work on many aspects of He in metals, particularly methods for measurement, was reviewed by Donnelly [53]. Importantly, equations of state must be invoked to convert atomic density within a bubble to or from pressure, and that a blueshift of the 1s → 2p transition of several eV is expected for increasing pressurization of bubbles. Walsh et al. described a procedure for the use of EELS spectra to measure the helium density via blueshift [56], and this technique has been applied with great success to tritides [52] and a ferritic/martensitic (F/M) steel [55]. The Fe and Fe–Cr alloy bulk plasmon sits at ~22 eV, greatly complicating the extraction of the He signal and blueshift, thus requiring high signal-to-noise ratios for such an experiment. He desorption from bubbles in Si under electron beam interrogation has also been observed [57]. In the matrix outside of the bubbles, however, the use of EELS is probably unrealistic. From the data presented by Frechard et al. [54] a 2-nm-radius bubble might contain ~1500–2000 He atoms, and requires high signal-to-noise and careful data analysis to interrogate, whereas at 1 ppm level in a 50-nm-thick foil of Fe–Cr alloy, an electron-illuminated area ~15 × 15 nm square might be expected to contain only a single He atom, so the EELS He signal will be immeasurable. Therefore, a totally different approach to estimate these parameters has been adopted in this study.

The primary microstructural characterization tool used in this study is APT [59,60] combined with focused-ion beam (FIB) methods for site-specific specimen preparation [60]. One of the major advantages of APT is the ability to simultaneously image both the NCs with iso-concentration surfaces and the He bubbles with iso-density surfaces [49], which enables the number of He bubbles on the surfaces of the NCs and other precipitates, and the grain boundaries, to be visually counted so that an estimate on the effectiveness of the NCs as He trapping sites can be made. Another advantage is that APT permits the He concentration in solid solution in the ferrite matrix to be estimated, as the technique is equally sensitive to all elements. The amount of swelling in the high dose regions due to the extra volume of the helium bubbles can also be estimated.

The time required to achieve high doses with neutrons under normal operating conditions, and the resultant high activity of the specimen, are important experimental factors. Therefore, He implantation followed by thermal annealing is used as a surrogate for neutron irradiations. However, the non-uniform dose and the He concentration profiles typically produced during high dose ion irradiation, results in a non-uniform microstructure that requires specimens to be fabricated at relevant depths beneath the implantation surface corresponding to the high dose regions (see below). The distribution, in terms of dose and resultant He concentration, is also advantageous, as it enables specimens to be obtained at different dose conditions from the same sample.

In this study, the stability of the He bubbles has been investigated by APT after post-irradiation annealing (PIA) at a temperature (750 °C) close to the anticipated service temperature of this material in future advanced energy systems. The level of He remaining in solid solution in the ferritic matrix after high dose He implantation (up to ~2 displacements per atom (dpa) and ~3.8 at.% He) and PIA for 10 and 100 h at 750 °C was estimated from APT data and compared to the as-implanted condition and the equilibrium concentration of He in ferrite. The changes in the size, size distribution, and location of the He bubbles with respect to the various microstructural features, were also determined. A new APT-based method to estimate the amount of swelling in the high dose regions is also introduced.

2. Experimental

The material used in this study was a mechanically alloyed 14YWT NFA. The mechanically alloyed flakes were canned in mild steel, soaked, and extruded into solid form at a temperature of 850 °C. The resulting bar was heat treated for 1 h at 1000 °C. The composition of the alloy was Fe–13.1 wt.% Cr–0.54W–0.19Ti–0.25Y_2O_3.

Coupons were cut from the extruded bar and one surface was mechanically polished to a 0.05 μm finish. The mechanically polished surface was implanted normal to the surface with 335 keV $^4He^+$ ions to a fluence of 6.75 × 10^{20} He m^{-2} at a temperature of 400 °C. Helium ion irradiations have the advantages of attaining high doses in relatively short times, as well as not activating the material and thereby facilitating the experimental procedures.