Helium sequestration at nanoparticle-matrix interfaces in helium + heavy ion irradiated nanostructured ferritic alloys

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Abstract

We irradiated four ferritic alloys with energetic Fe and He ions: one castable nanostructured alloy (CNA) containing Ti-W-Ta-carbides, and three nanostructured ferritic alloys (NFAs). The NFAs were: 9Cr containing Y-Ti-O nanoclusters, and two Fe-12Cr-5Al NFAs containing Y-Zr-O or Y-Hf-O clusters. All four were subjected to simultaneous dual-beam Fe+He ion implantation (650°C, ~50 dpa, ~15 appm He/dpa), simulating fusion-reactor conditions. Examination using scanning/transmission electron microscopy (STEM) revealed high-number-density helium bubbles of ~8 nm, $\sim 10^{21} \text{ m}^{-3}$ (CNA), and of ~3 nm, 10^{23} m^{-3} (NFAs). STEM combined with multivariate statistical analysis datamining suggests that the precipitate-matrix interfaces in all alloys survived ~50 dpa at 650°C and serve as effective helium trapping sites. All alloys appear viable structural material candidates for fusion or advanced fission energy systems. Among these developmental alloys the NFAs appear to sequester the helium into smaller bubbles and away from the grain boundaries more effectively than the early-generation CNA.

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1. Introduction

The viability of structural alloys for fusion and advanced fast-fission applications is dominated in a large part by the alloys' ability to withstand and mitigate high levels of transmutation helium build-up [1-3]. Particularly, void swelling and grain boundary helium embrittlement will be significant challenges to the long-term survival of materials in fusion first-wall/blanket structures. At present, the main design strategies for fusion and fission system structural materials are to use ferritic alloys (which are intrinsically more swelling resistant than austenitic alloys)[4] and to utilize high densities of very small sinks, such as oxide nanoprecipitates, to collect the helium into a subcritical bubble population more resistant to swelling and embrittlement [5].

Oxide dispersion-strengthened (ODS) steels and nanostructured ferritic alloys (NFAs) are ferritic steels containing 9-20 wt% Cr, along with solid solution strengthening elements (e.g., W) and oxide-forming elements (e.g., Ti, Y) [6]. NFAs typically contain $\sim 10^{22}$ - 10^{24} m⁻³ of small (~ 2 nm) oxide particles [7, 8]. Because of the insolubility of Y in the ferritic matrix, the NFAs are produced via mechanical alloying [9-11]. Major examples of NFAs are the 14Cr, W+Y+Ti+O added "14YWT" [e.g., 12, 13-15]; the Al-added MA956 [16, 17]; and the 9Cr, W+Y+Ti+V+O+C added "9YWTV" [18]. Because the high-Cr alloys' fracture toughness is lower than desirable, the 9 wt% Cr variants have been developed, and the C addition to 9YWTV allows intercritical (α + γ -phase field) hot-working for improvement of the microstructure and fracture toughness [19].

In aggressive corrosion environments, such as Pb-Li in fusion systems or a severe accident scenario in a light water fission reactor, corrosive attack on the Fe-Cr system is anticipated so Al-alloyed "FeCrAl" grades have been and continue to be developed to improve corrosion behavior [20]. The Al-addition into the Fe-Cr system improves corrosion/oxidation behavior working in synergy with the Cr. While very high Cr levels (e.g., 20 wt%) would also mitigate corrosion, simply over-alloying with Cr would lead to the irradiation-enhanced formation of the embrittling α' phase. The Al-added, lower-Cr alloys are expected to have a better compromise between corrosion and mechanical properties, both in the non-irradiated and irradiated state, than the Cr-only grades [21, 22]. In order to improve creep and irradiation properties, the higher-Al, lower-Cr FeCrAl grades prepared with oxide-forming elements (Y, Hf, Zr, etc.) via mechanical alloying are under development, becoming ODS- or NFA-FeCrAl. (Hf, Zr, etc., are under consideration because Ti is expected to bind with the Al content and produce undesirable oxides [23-25].)

Because of the expense of mechanically alloyed material, and the difficulty of making large structures via this powder metallurgy route, conventionally processed alloys (i.e., cast and thermomechanically worked) are also under development with the goal of producing high densities of very small precipitates (i.e. several nanometers or less in diameter), to achieve high sink strength and good creep resistance, similar to the mechanically alloyed oxide-particle-containing NFAs. The first generations of so-called cast nanostructured alloys (CNAs) contain a high density ($\sim 10^{21}$ m⁻³) of TaC or other MX-type particles and preliminary investigations have shown excellent resistance to heavy-ion irradiation [26-28].

Helium sequestration is the major concern for fusion-spectrum structural materials, and is also a significant concern for fast-spectrum fission concepts. Helium will exacerbate the growth of

cavities and in particular grain boundary voids, with concomitant embrittlement and loss of mechanical toughness. Therefore, many groups are studying the impact of microstructural engineering methods, such as introduction of nano-oxides, on the suppression of helium-related degradation in structural materials [29, 30]. ODS and ferritic/martensitic (F/M) materials have been extensively studied by dual-beam heavy-ion + helium ion irradiation, using methods such as nanohardness [31-35], positron annihilation [33], and observed effects of dislocation density or other microstructural features and pre-irradiation processing [32-36], as well as changes in phase in Al-rich precipitates in FeCrAl ODS [32]. Similarly, a very comprehensive study comparing F/M to NFA alloys showed excellent helium management in the NFAs (PM2000 and MA957) [37].

These three classes of materials – Cr-based NFA, FeCrAl NFA, and CNA – are all presently considered viable advanced candidate fusion structural materials and in many cases also for advanced fission reactor materials. A key feasibility issue is how well each material mitigates the copious transmutation helium produced in the fusion neutron or fast reactor neutron spectrum. Because radiation tolerance and helium mitigation are complex phenomenon and there is currently no readily available facility to produce high levels of simultaneous neutron damage and transmutation helium we have proposed a target experiment answering a specific question: *do the engineered nanoprecipitates collect injected helium atoms into small bubbles away from the grain boundaries?* To address this question we use a dual-beam simultaneous He+Fe irradiation facility coupled with advanced electron microscopy methods [38, 39], to determine the disposition of He in these steels near the upper range of fusion-relevant temperatures (650°C, where atomic diffusion is high) and at fusion-relevant appm He/dpa ratios (~10-20). In particular, this work is unique in the attempt to relate directly bubbles/cavities to engineered precipitates at high resolution in advanced candidate Fe-based alloys.

2. Experiment

The fabrication process for the 9YWTV (heat PM2) NFA is described elsewhere [18]. Similarly, Y-Zr and Y-Hf 12Cr-5Al FeCrAl alloys were produced as described elsewhere [23]. These NFAs used standard powder metallurgy methods: powder production, mixing with oxide powder, mechanical alloying, canning, and hot consolidation. CNA was produced by arc-melting and drop casting followed by controlled hot working and standard normalization (1120°C) and tempering (750°C) heat treatments [40]. Samples are summarized in Table I.

Samples were prepared for ion irradiation by cutting to ~1 mm × 0.5 mm × 5 mm, ground to the same thickness, and then polished to a colloidal silica finish. Samples were irradiated at 650°C to $\sim 5.2 \times 10^{20}$ Fe³⁺/m² with 6.4 MeV Fe³⁺ (implantation ion depth ~1500 nm) at the DuET facility, Institute of Advanced Energy, Kyoto University, Japan [41]. Simultaneous He injection through a rotating degrader foil provided ~450 to 750 appm He at midrange depths of 400 to 1200 nm (~15 appm He/dpa). A SRIM [42] simulation, using Stoller et al.'s recommended method [43], of damage (in displacements per atom, dpa) and helium injection (in appm) is shown in Figure 1, using a sub-lattice average displacement energy $E_D=40$ eV [44]. Figure 1 is calculated for 91Fe-9Cr; differences between this composition and the other alloys (i.e., 83Fe-12Cr-5Al) are neglected. Subsequent microstructural analysis avoided the irradiation depths corresponding to the implanted ion region

(and peak displacement damage region) due to potential artifacts (suppressed cavity nucleation) associated with injected ions [45-47].

Following irradiation, cross-section specimens (to enable examination of depth-dependent microstructural changes over the entire ion damaged region) were milled via focused ion beam (FIB) with Ga⁺ ions at an initial energy of 30 kV and a finishing energy of 5 kV. All samples were further thinned (removing the surface FIB damage and surface oxide layers) using Ar⁺ ions at 900 eV in a Fischione Nanomill 1040 system, and then immediately (with a delay <2 min) plasma cleaned in a Fischione 1020 Plasma Cleaner followed immediately (<30 sec) by insertion into the TEM vacuum. TEM examination was performed in an FEI Talos F200X scanning/transmission electron microscope (S/TEM) (200 keV, Schottky-emission, non-aberration-corrected [48]), using a SuperX four-detector X-ray energy dispersive spectroscopy (EDS) system [49]. EDS mapping was performed using a small condenser aperture (convergence semiangle ~8 mrad) to minimize beam spread in the thin foils [50].

Imaging was performed using conventional Fresnel contrast for helium bubbles [51]. X-ray EDS spectrum images were evaluated via multivariate statistical analysis (MVSA) [52] using the AXSIA code of Sandia National Laboratories [53], along with data file format conversion and post-processing codes written in MATLAB in-house. Details of MVSA are available elsewhere [53-56], but essentially, the high-rank, noisy, sparse X-ray data is reduced to a set of low-rank, low-noise image and spectra vectors that provide a compact description of the specimen. Specifically, data is subjected to optimal-scaling for Poisson noise, analyzed via principal component analysis (PCA), then subjected to multivariate curve resolution by alternating least squares under non-negativity constraints, with proper descaling from Poisson to physical space [53-56].

The ion-incidence direction is approximately vertical from top-to-bottom in all micrographs. Any data processing or smoothing will be explicitly noted, other than histogram stretch, brightness/contrast, or gamma correction.

3. Results

3.1 Bubble distributions

We found precipitates and He bubbles are easily differentiated in the CNA material, but are far more difficult to discern in the three NFA-type materials. Fresnel-defocused bright field (BF) TEM images of the irradiated midrange (500-1000 nm depth) helium-bearing zones of the four materials are shown in Figure 2, and of the control (nonirradiated, >2000 nm depth) zones of the materials in Figure 3 (roughly 20 dpa, 600 ppm He, ~30 ppm/dpa). In the CNA (Figure 2a and 3a), the bubbles are visible in the He-implanted region, with sharp Fresnel contrast, and little Fresnel contrast is seen in the deep (>2000 nm) nonirradiated region. The NFA-type materials, conversely, show less differentiation between the irradiated and nonirradiated regions. The similar appearance of the background contrast in 9YWTV, for instance, is shown in Figure 4 for the irradiated- and non-irradiated region. The high Cr (and Al) contents of these alloys result in an adherent surface oxide on the top and bottom surfaces of the foils, which will provide a certain amount of amorphous

contrast that, under defocused (Fresnel) conditions will result in contrast similar to small nano-scale helium bubbles. Similarly, the low average atomic number of the oxygen-rich NFA particles may also provide bubble-like contrast under Fresnel defocus. It is therefore important to caution that quantification of very small bubbles in these materials systems must not be taken to be quantitatively accurate, due to unavoidable cross-talk between the different contrast mechanisms. Future work using other methods (atom probe [57-60], etc.) is planned, in order to provide confirmation of the TEM data.

Regardless, comparisons, if somewhat qualitative, of the four materials can be made. The CNA shows comparatively large He bubbles with an average diameter of 8.4 ± 2.9 nm (error here is based on one standard deviation of the mean). The NFA alloys all show smaller bubbles, with mean matrix bubble diameters of 3.0 ± 0.6 nm (9YWTV), 3.3 ± 0.5 nm (FeCrAl-YZ), and 2.4 ± 0.5 nm (FeCrAl-YH). Although the exact TEM foil thickness is unknown, an estimate of 100 nm (obtained from the FIB procedure) leads to number densities, N , calculated in Table II, and rounded off to the nearest 5×10^x , due to inherent imprecision in such a measurement. Fresnel-feature sizes, rough number densities (all assuming ~ 100 nm thick foils), and volume fractions are presented in Table II. Because Fresnel contrast is an unreliable method for sizing features $< \sim 2$ nm in size [61], the samples with smaller bubbles (i.e., the NFA-alloys) may show mean diameters skewed toward slightly higher than "true" values.

Bubbles are often apparently present on precipitates, especially in the CNA where the precipitates are more easy to discern in TEM than in the NFA alloys, where the nanoprecipitates are difficult to observe in conventional TEM [62, 63].

In broad summary, the CNA alloy shows ~ 8 nm diameter bubbles, whereas the three mechanical-alloyed NFAs had ~ 3 nm bubbles. The derived bubble number densities for the NFA alloys are $\sim 20\times$ higher than the CNA, and the volume fraction of detected bubbles is roughly the same in the CNA and the NFA alloys. Anomalous contrast makes highly accurate bubbles sizes difficult to derive, so numbers should not be considered to show high precision. However, even with the difficulty in performing quantitative assessments, the NFA alloys shows the helium is dispersed into a finer bubble sizes.

3.2 Relation of bubbles to nanoprecipitates

In ODS steels and NFAs, it is very difficult to directly relate bubbles to nanoprecipitates [38, 57-60, 64-68], because the nanoscale precipitates show little contrast under most imaging modes (i.e., BF-TEM, BF-STEM) and bubbles and low-atomic-number precipitates (i.e., oxides) show similar contrast under HAADF-STEM and Fe-M-edge EFTEM, the two most common imaging modes that do show nanoprecipitates.

We previously established that X-ray spectrum imaging (SI) in a high-efficiency STEM, usually followed by MVSA data mining, is a robust method to separate the nanoprecipitates from the bubbles [38]. However, the present samples – with far lower appm He levels, and far higher dpa

level, than the past experiments, resulting in the small, high-density bubbles described in Section 3.1, above, provided an interesting challenge to this technique.

3.2.1 Cast-nanostructured alloy

X-ray mapping of the irradiated CNA shows large (~50+ nm) precipitates, Figure 5, which indicate separate Ti-Ta-C and Cr-W-O-C precipitates near the center of the map. Additionally, small (<10 nm) Ti-rich regions are also seen. These appear to come in two varieties: first, Ti-rich rings that coincide with dark (bubble) features in the HAADF image, and second, Ti-Ta(-C) rich regions that are apparently nanoprecipitates.

MVSA data mining of the spectrum image (SI) provides a more cogent and compact view of the data (Figure 6). To reiterate, MVSA bilinear factor-model methods, as used here, reduce the high-rank, noisy SI into a small set of score image / loading spectrum pairs, which allow improved qualitative interpretation of the underlying chemical makeup of the interrogated specimen region [53, 54]. The first two components show Fe-K/Fe-L lines (in different ratios), and describe the matrix. The matrix is broken into two components due to absorption of the soft Fe-L X-rays in the finite foil thickness (consistent with the estimated 100 nm sample thickness). MVSA component #3 shows a large (~170 nm) Cr-rich precipitate, and Cr-rich small precipitates, and a background level of Cr present across the region. MVSA #4 describes Cr-W-carbide nature of the large precipitates. MVSA #5 shows Ti-Ta-W-oxycarbide nature of the small, dispersed precipitates. The precipitate distribution is more easily seen in a color overlay of MVSA components 3-4-5 and matched to the HAADF-STEM image, Figure 7a-b. Presenting MVSA#3 (Fe-Cr) as blue and MVSA#4 (Cr-W-C) as yellow, the large 170 nm precipitate is white (blue+yellow) and indicated to be a complex Cr-W-Fe carbide (or possibly oxycarbide); the second largest precipitate is yellow, and shows a more Cr-W-carbide nature, possibly $M_{23}C_6$. Blue and red (red: MVSA#5, Ti-W-Ta-oxycarbide) precipitates are scattered throughout the region imaged. Features are marked 1-6 in Figure 7c-d; features like '1' are most likely bubbles, and show enhancement of the Cr component MVSA#3 around the edge of the bubble, perhaps indicating segregation of these elements to the bubble surface. (Cr-segregation to voids has previously been reported, e.g., [69].) Feature '2' shows dark HAADF contrast but strong Cr-O-component contrast, and may be either a smaller bubble or a precipitate. Features '5' and '6' are clearly the Ti-Ta-W-oxycarbide precipitates, and show a large number of small, dark-in-HAADF features that are likely bubbles, indicating that helium is preferentially precipitating next to the particles.

An important consideration is that Fe counts are present, at least in small levels, in all of the components. This does not necessarily mean that Fe is present in all of the precipitates; rather, because the particles are embedded in an Fe-Cr matrix, no "pure" precipitate pixels are ever found, and the Fe counts could be present due to ambiguity inherent to the bilinear factor model, and would require additional constraints to remove [52, 70-75]. For the present purposes, it is sufficient to take the spectra as qualitative rather than exact.

By comparing the HAADF, BF, and MVSA images, an approximate count of the precipitate-associated cavities as a fraction of total cavities can be made. Table III shows these results for the four alloys; we will discuss the CNA here and the other alloys below. The CNA showed ~32% affiliations of the cavities (bubbles) with MVSA-EDS-identified precipitates. This is somewhat surprising, given the appearance of a large number density of cavities apparently free in the matrix or on dislocation lines. Figure 8 shows images from a region of the CNA in BF-TEM mode, HAADF-STEM mode, Fresnel BF-STEM [38], and an MVSA decomposition score image showing the precipitates. Apparently, in the CNA, a large number of small bubbles appear (e.g., red arrow, Figure 8) on some of the precipitates, skewing the fraction of precipitate affiliated cavities to a relatively high value. Most of the bubbles on the surfaces of these precipitates are very small and will likely contain a small fraction of the aggregate He and overall cavity volume. Discussion of possible artifacts in these measurements and materials performance implications will be deferred to Section 4.2

3.2.2 Fe-Cr Nanostructured ferritic alloy

In the 9YWTV NFA alloy, very fine Y-Ti-oxide clusters are found, with inhomogeneous distribution, including a denuded zone around grain boundaries, and also larger complex ceramic precipitates; Figure 9. Similar to Figure 6, two components describe the matrix (high- and low-Fe-K/Fe-L ratio), and several components describe the various precipitate chemistries. Specifically, a high-Cr-W content (MVSA #3) surrounds the large precipitate, Strong Y-O content is found in the nanoclusters (#4), V-Cr-W-C is found in the shell of the large precipitate, and Ti is found in the core of the large precipitate and in the NCs. In other words, the large precipitate is a three-layer Cr-W-shell, V-Cr-W-carbide middle, and Ti-Cr-V-W-carbide core, and the nanoclusters are Y-Ti-O rich; Figure 10.

Many of the helium bubbles are directly connected to nanoclusters; roughly 30% of the bubbles were touching a nanocluster when the TEM and MVSA images were compared, Table III. This can be illustrated through careful comparison of the Fresnel BF-TEM and STEM data. The Fresnel BF-TEM image shows the bubbles, and is repeated in Figure 11a. The HAADF data acquired simultaneously with the X-ray SI was resized, rotated, and shifted to match exactly the BF-TEM data, and is overlaid in Figure 11b. (This was performed using PhotoShop software "Free Transform" command, with only 'scale' and 'rotate' functions, and the X and Y scaling was identical, i.e., aspect ratio 1.) Then, the locations of the nanoclusters, in the form of the MVSA#4 (Y-Ti-O) component score image, was subjected to the exact same transformation as the HAADF data, so that this elemental information is now properly aligned to the TEM data. (Precise alignment of the STEM system's nanoprobe pivot points prior to STEM data collection allowed an accurate overlay without applying different X and Y resizing, nor trapezoidal skewing of the STEM data.) This nanocluster map was overlaid to the BF-TEM data with 67% opacity in "Overlay" blend mode in PhotoShop, and is presented in Figure 11c-10d. Several arrows in Figure 11d mark bright X-ray features (e.g., nanoclusters) that coincide closely with Fresnel-contrast features (e.g., bubbles). Not all bubbles

are associated with nanoclusters, and most nanoclusters are associated with 2-4 bubbles. Obviously, because (S)TEM is a two-dimensional projection of the three-dimensional specimen, it is not proven that the nanoclusters associated with bubbles in these images are in fact in intimate contact, but the inference is very likely based on the clustering of bubble and nanocluster contrast near each other.

3.2.3 FeCrAl alloys

Similarly, in the FeCrAl-NFA alloys, the oxide precipitates and the Fresnel-contrast of the bubbles are closely associated.

Zr, Y-Al, and Ar precipitates are seen in the FeCrAl-YZ alloy (Figure 12). The Ar features are presumably bubbles resulting from introduction of Ar gas into the powders during mechanical alloying (Figure 12, MVSA#3). Y and Al are present in small (~several nm) precipitates, densely populated in the matrix (Figure 12, MVSA#2). Zr is present in two larger precipitates, and ringing the larger Ar feature (Figure 12, MVSA#4). Again, like the 9YWTV NFA material, Fresnel-contrast features (likely He bubbles) are seen to associate strongly with the Y-Zr-O nanoclusters when the MVSA component is overlaid to the Fresnel-contrast TEM image using the method discussed above; Figure 13. Roughly 40% of the bubbles were affiliated with a precipitate, Table III.

The FeCrAl-YH material shows essentially the same behavior. Figure 14 shows the MVSA decomposed X-ray maps, with matrix (MVSA#1), Y-Al-rich (MVSA#2), and Hf-rich (MVSA#3) components. The Y-Al and Hf components are mostly co-located for the small (~several nm) precipitates, but Hf is present independent of Y-Al in the larger precipitates (likely Hf-carbide), which is why the Y-Al and Hf were segregated to separate MVSA components by the rank reduction. Again, the nanoclusters are seen to be mostly co-located with He-bubbles in the Fresnel TEM / MVSA STEM overlay (Figure 15); Roughly 40% of the bubbles were affiliated with a precipitate, Table III.

4. Discussion

4.1 Overall bubble behavior

Broadly speaking, all four of the presently examined alloys – CNA, 9YWTV, FeCrAl-YZ, and FeCrAl-YH – are seen to capture helium atoms in form of bubbles at the engineered nanoprecipitates. The CNA material shows slightly larger bubbles (~8 nm vs. ~3 nm) in comparison to the three ODS/NFA alloys. This may be indicative of superior capture of the helium into smaller bubbles by a higher density of nanoprecipitates in the ODS/NFA materials with respect to the CNA. However, the CNA paradigm is new [26-28], and further optimization may allow for improved dispersion and increased number density of the precipitates. Conceptually, whether carbides or oxides will provide better capture of helium is still an unknown, and would probably require first-principles studies of the matrix / precipitate interface as well as significant experimental work.

The question "how effective is the helium sequestration?" is complex, with no simple answer. To precisely address the effects of helium embrittlement, it would be necessary to irradiate tensile and fracture-toughness specimens in a fusion-neutron relevant spectrum under applied stress, and study which materials suffer the least helium embrittlement. For the present purposes, the observed favorable disposition of the bubbles within the specimen grain interiors is a promising but incomplete initial step to resolve the broader question of radiation tolerance and helium mitigation of nanostructured steels.

Based on the known injected He appm, then the amount of helium in the bubbles can be estimated from the bubble mean size and number density, if they are assumed uniform and that visible bubbles contain all the He (i.e., no He remains in the matrix outside of the visible cavities). This should be a reasonable assumption given the relatively high irradiation temperature (650°C, slightly above 50% of the absolute melting temperature). The injected He levels are ~750 appm, based on the ion beam parameters. Table IV shows the calculated He/bubble and He/nm³ values, calculated assuming 750 ppm and monodisperse bubbles of diameter $\langle d \rangle$ and number density N_v . Upper equilibrium pressure P_{eq} for a given bubble size was calculated assuming diameter $\langle d \rangle$ and 1.5 J/m² surface energy. The pressure P_{trin} was calculated assuming all helium is in visible monodisperse bubbles, using the Trinkaus equation of state [76], as given by Walsh et al. [77] for the gas atoms at 650°C. Obviously, all values are very approximate, due to the experimental uncertainties of radius and number density measurements. Values should only be taken as near order-of-magnitude, not exact.

The equilibrium bubble model fits reasonably well, in that the equilibrium and Trinkaus pressures are within factors of ~2-3 $\times$. Given the large numbers of approximations, this is surprisingly good agreement. In other words, if the Fresnel contrast features are He-filled bubbles, they are close to equilibrium in all four irradiated alloys. Further, these complex alloys likely show deviations in surface energy from the approximate 1.5 J/m² assumed for iron. For example, the CNA alloy X-ray maps indicated Ti might have been moving to the cavity surfaces.

Based on the higher density of smaller bubbles in the ODS/NFA materials, it is likely that they will provide superior helium mitigation compared to the CNA. However, the CNA materials will be more easily manufacturable, and have significant room for future alloy and processing optimization, so there is no reason as yet to assume that CNA materials will not also be able to provide good helium mitigation in further-term fusion-spectrum systems such as DEMO or FNSF. (Fast fission systems, such as GenIV concepts, will also require improved helium mitigation in comparison to thermal LWR concepts, although not to the same degree as fusion.) Moreover, we stress that the CNA alloys are in an early stage of development and it can be assumed that the initial microstructure will continue to be optimized.

A maximum heavy ion displacement damage of ~25 dpa (at peak He content) was delivered in the midrange region simultaneously to the helium injection. All four materials showed excellent survival of their nanoprecipitate populations under this displacement damage at the studied temperature of 650°C; this is likely indicative of a self-healing mechanism [78]. Also, limited black-spot or dislocation-loop damage was observed, probably due to rapid self-annealing at the relatively high temperature of 650°C. This indicates all four materials are likely to have little impact on their overall mechanical properties due purely to displacement damage but other degradation

modes could still limit their overall service life. Quantitative analysis of the nanoprecipitates' evolution under displacement damage will be the subject of a follow-on publication. Qualitatively, the densities and diameters of the nanoclusters were nearly unchanged by the irradiation.

Helium bubble characterization, particularly very fine high-density bubbles, is a difficult experimental challenge, especially when the matrix materials show significant amorphous contrast due to Cr or Al-Cr-rich oxides on the foil surfaces. High-efficiency X-ray mapping using an advanced STEM system is very helpful to image the precipitate populations and relate them to the bubbles [39, 64], and these determinations are made easier, faster, and more statistically robust by MVSA rank-reduction of the X-ray spectrum images [52, 53].

4.2 Bubble – precipitate affiliations

As seen in Table III, roughly 30-40% of the visible bubbles are suggested to be associated with a visible precipitate or nanocluster in these experiments. Conversely, and perhaps surprisingly, it appears that few if any of the precipitates visible in the X-ray mapping or MVAS maps are not associated with bubbles. In the CNA, with coarser precipitates, the bubbles on the precipitates appear noticeably smaller than those in the matrix. In the 9YWTV and two FeCrAl alloys, the bubbles are all sufficiently small that limitations in TEM image resolution would prevent a meaningful comparison of precipitate-associated vs. non-associated bubbles.

It is difficult to explain why the 60-70% of bubbles that do not appear associated with the precipitates, and will require further work. The most likely possibility is that some precipitates below the resolution limit in the X-ray maps are present and helping disperse the helium. Another possibility is that bubbles have initially nucleated on precipitates, but because energetic displacement cascades may dissolve or partially dissolve nanoclusters (with subsequent renucleation at the same or an adjacent location [78], there may be a slight spatial rearrangement of the precipitates during prolonged irradiation. It is also possible that other, yet unidentified, mechanisms are at play.

Exact values for precipitate number density and dislocation density are difficult to determine due to precipitate sizes approaching practical resolution limits but for the three ODS-type materials our experimental measurements are generally consistent with previous work on similar alloys [79], i.e., $\sim 10^{23}$ precipitates/m³, most oxide precipitates ~ 2 -4 nm in size, and high dislocation densities $\sim 10^{14}$ /m² [62]. Grain sizes were in the hundreds-of-nanometers range for the ODS alloys [24, 25], and consisted of a martensitic lath structure in the CNA. The CNA showed $\sim 10^{21}$ - 10^{22} /m³ density of the small (3-20 nm) precipitates [40], which is 10-100 $\times$ lower than the ODS alloys; CNA's dislocation density was similar, $\sim 10^{14}$ /m² [40]. However, we estimate that sample-to-sample differences between our three NFAs are not dominating the behavior, especially considering the roughly similar bubble-disposition behavior between the three alloys.

Because of the 3D nature of TEM samples, and the 2D nature of the TEM images, it is possible that some bubbles were apparently affiliated with precipitates but were actually well separate in the foil-thickness direction: this would lead to a higher-than-real value for associated fraction. Similarly, it is possible that some precipitates or nanoclusters associated with visible bubbles were not visible in the X-ray and MVSA analyses, and would lead to a lower-than-real measurement. Another group [67], using similar (but distinct) alloys and neutron irradiation with in-situ helium injection, found a bubble / nanocluster association closer to 100% rather than the present 30~40%. These differences – around 40% vs. around 100% -- will probably be due to a combination of different alloy design, different irradiation conditions ($\sim 1000\times$ lower damage rate in ref. [67]), and different analytical methods. A previously-

published X-ray mapping simulation method [29] estimated the visibility of different-sized nanoclusters under different STEM conditions and established it is generally unlikely that a sizeable fraction of nanoclusters might have been missed in the present experiments.

Regardless of the exact values, the important point is that all of the alloys show significant capture of helium into precipitate- or nanocluster-associated cavities, with the potentially beneficial effects discussed by previous authors. It is encouraging that the CNA showed such a high capture fraction, but as noted in Section 3.2.1, many of the precipitate-associated bubbles are very small and likely contain little of the helium fraction or cavity aggregate volume. Further experiments (particularly neutron irradiations) will be needed to fully explore the behavior of the precipitate/nanocluster-bubble interactions, but it is promising that such a large fraction of the bubbles are clearly associated with the engineered microstructural features, even in the present unoptimized alloys.

Returning to the question posed in Section 1, do the engineered nanoprecipitates collect injected helium atoms into small bubbles away from the grain boundaries, the present results indicate copious nanoscale cavity nucleation within the grain matrix and at the precipitate/matrix interfaces. This sequestration of helium at grain interior features will beneficially reduce the grain boundary precipitation of the helium in these materials under fusion or fast-reactor service. The carbides in the CNA appear to collect helium in a similar fashion to the nanoscale oxides in the ODS/NFA alloys. The NFAs captured large numbers of helium bubbles onto the matrix/particle interfaces, with comparatively small differences between the three different alloys.

5. Conclusions

Four developmental nano-featured ferritic alloys, which are fusion-reactor candidates, were subjected to simultaneous heavy-ion and helium bombardment at 650°C, to determine their response to a simulated fusion reactor irradiation condition and provide insight on their applicability in advanced fission reactor designs. A 9Cr NFA and two Fe-12Cr-5Al NFAs, and a 9Cr CNA, were chosen. The three NFAs showed fine grains and high-density, sub-5 nm nano-oxide dispersions prior to irradiation. The CNA showed a lath microstructure and tens of nm carbide dispersion prior to irradiation. After dual-beam Fe+He ion irradiation to 50 dpa, ~15 appm/dpa, 650°C, the dispersions in the NFAs and CNA all survived and a dense population of helium bubbles formed. Bubbles were larger (~8 nm) in the CNA than the NFAs (~3 nm), with lower density of bubbles in the CNA ($\sim 5 \times 10^{21} / \text{m}^3$) compared to the NFAs ($\sim 10^{23} / \text{m}^3$). The CNA showed a higher concentration of cavities along grain boundaries than the NFAs. In all four alloys, roughly 30-40% of the bubbles were in close association with precipitates, indicating the success of the engineered nanostructures in sequestering helium. The relative constant value for efficiency in sequestering He bubbles in the four alloys is remarkable considering the $\sim 20\times$ variation in nanoprecipitate densities. All four alloy designs appear promising for future fusion or fast-fission applications.

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Figure Captions

Figure 1: SRIM estimates of dpa and He appm. Red line: dpa level. Black lines: He content.

Figure 2: Fresnel-contrast TEM images of the midrange irradiated zone in the four alloys. In Fig. 2b, "DZ," denotes cavity denuded zone near a grain boundary; and "PPT" denotes precipitate. Depths ~500-1000 nm corresponding to a nominal average damage of ~20 dpa.

Figure 3: Fresnel-contrast TEM images far beyond irradiated region (>2000 nm depth) in the four alloys.

Figure 4: Enlarged regions of (a) Figure 2b and (b) Figure 3b, showing the (a) helium-implanted and (b) non-irradiated regions of the 9YWTV specimen. Note the still-significant Fresnel contrast in (b).

Figure 5: X-ray maps derived from a spectrum image, CNA sample. Conditions: 1024×1024 pixel, ~4.9 nA probe, 31 min integration time, ~1.8 msec/pixel, ~140,000 cps. Note that Si-K α is likely spurious, due to the overlapping W-M and Ta-M lines at 1.7-1.8 keV.

Figure 6: Multivariate statistical analysis decomposition of the X-ray data in Figure 5, CNA sample. Binned to 256×256 pixel for analysis. Binned 2× in energy, truncated to 0.17-16.15 keV. Color bar is used for all subsequent figures.

Figure 7: (a) HAADF and (b) color-overlay MVSA of the data in figures 4-5. (c) and (d) are details of the boxed region. CNA sample.

Figure 8: Matched images from one region of the CNA material. BF-TEM, HAADF-STEM, Fresnel BF-STEM, and MVSA score image #2 from an X-ray spectrum image. Bubbles are visible in (a)-(c) and precipitates in (b) and (d). Red arrow denotes a large precipitate, and green arrow a small precipitate.

Figure 9: Multivariate statistical analysis decomposition of the X-ray data SI, 9YWTV sample. 600×600 pixel, binned to 300×300 pixel for analysis, then upsampled to original resolution. Binned 3× in energy, truncated to 0.17-17.17 keV. ~3.7 nA probe, ~33 min integration, ~5.5 msec/pixel. Note large contrast adjustment in #6 component image, to emphasize the nanoclusters.

Figure 10: HAADF-STEM, false-color overlay MVSA, and Fresnel BF-TEM images of the region in Figures 2b and 9. 9YWTV sample.

Figure 11: (a) Fresnel BF-TEM of 9YWTV, He-region. (b) Overlaid with STEM-HAADF image. (c-d) Overlaid with semitransparent MVSA #4 score image, showing nanoclusters associated with bubbles (arrows).

Figure 12: Multivariate statistical analysis decomposition of the X-ray SI data for the FeCrAl-YZ sample. 1024×1024 pixel, binned to 256×256 pixel for analysis, then upsampled to original

resolution. Binned $2\times$ in energy, truncated to 0.17-16.16 keV. ~ 4.8 nA probe, ~ 23 min integration, ~ 1.3 msec/pixel. ~ 130 kcps. Cu lines are from secondary fluorescence of sample holder. Note large histogram stretch on component #4 image to make small precipitates visible.

Figure 13: Overlay of Fresnel BF-TEM and MVSA component #2 (from Figure 12) for the FeCrAl-YZ specimen.

Figure 14: Multivariate statistical analysis decomposition of the X-ray data for FeCrAl-YH specimen. 1024×1024 pixel, binned to 256×256 pixel for analysis, then upsampled to original resolution. Binned $2\times$ in energy, truncated to 0.17-16.16 keV. ~ 4.8 nA probe, ~ 5.5 min integration, ~ 0.3 msec/pixel. ~ 130 kcps. Cu lines are from secondary fluorescence of sample holder.

Figure 15: Overlay of Fresnel BF-TEM and MVSA component #2 (from Figure 14) for the FeCrAl-YH specimen.

Tables

Table I: Samples used in this study. All were produced at ORNL.

Alloy	Reference
9YWTv	[18]
Y-Hf 12Cr-5Al FeCrAl	[23]
Y-Zr 12Cr-5Al FeCrAl	[23]
9Cr CNA	[40]

Table II: Quantifications of bubbles in the four materials. "He-bearing" refers to data taken near the peak of the helium range (~500-1000 nm); "Non-He" refers to data taken well beyond the helium and iron ion ranges (>2000 nm), and indicates spurious contrast due to Fresnel-like contrast arising from the surface oxide on the TEM foil or low-Z precipitates. $\langle d \rangle$ and σ_d are the mean and 1 standard deviation of the diameter, in nm; n_b is number of bubbles (or bubble-appearing contrast features) counted. N is number density, rounded off to nearest 1×10^x or 5×10^x . Vol% is volume percent estimated from N_v and $\langle d \rangle$. $\langle d \rangle$ and σ_d are in nm. N is in m^{-3} .

	Matrix					Grain boundary			Precipitates		
	$\langle d \rangle$	σ_d	n_b	N	vol%	$\langle d \rangle$	σ_d	N	$\langle d \rangle$	σ_d	N
CNA											
He-bearing	8.4	2.9	140	$\sim 5 \times 10^{21}$ *	~ 0.16	8.0	2.2	165	4.6	1.8	143
Non-He	3.1	0.4	6	$\sim 10^{20}$	0						
9YWTv											
He-bearing	3.0	0.6	200	$\sim 10^{23}$	~ 0.14	4.0	1.0	13	2.7	0.3	7
Non-He	3.0	0.6	35								
FeCrAl-YZ											
He-bearing	3.3	0.5	200	$\sim 10^{23}$	~ 0.19	3.3	0.6	48			
Non-He	2.9	0.5	31								
FeCrAl-YH											
He-bearing	2.4	0.5	200	$\sim 10^{23}$	~ 0.07	2.7	0.6	25	2.3	0.4	12
Non-He	3.6	0.8	20								

*: N_v in the CNA, He-bearing data is calculated for all bubbles (matrix, grain boundary, and precipitate). All other N_v calculated for matrix only.

Table III: Bubbles or cavities associated with a precipitate.

Alloy	Bubbles (cavities) counted	Bubbles (cavities) associated with a precipitate	Precipitate-associated fraction
CNA	109	35	32%
9YWTV	337	103	31%
FeCrAl-YZ	165	65	39%
FeCrAl-YH	88	35	40%

Table IV: Calculated equilibrium-bubble model helium present in visible bubbles. Mean diameter, $\langle d \rangle$; Number density, N_v ; volume fraction, vol% (as in Table I); Ω , atomic volume(~ 84.7 atoms/nm³); P_{eq} , equilibrium bubble pressure from $P=2\gamma/R$; P_{trin} , pressure from Trinkaus equation of state [77].

	$\langle d \rangle$ (nm)	N_v (nm ⁻³)	vol%	He atoms/bubble	He/nm ³ (in bubbles)	He/ Ω	P_{eq} (GPa)	P_{trin} (GPa)
CNA	8.4	0.000005	0.16%	12705	41	0.5	0.7	1.1
9YWTV	3.0	0.0001	0.14%	635	45	0.5	2.0	1.3
FeCrAl-YZ	3.3	0.0001	0.19%	635	34	0.4	1.8	0.8
FeCrAl-YH	2.4	0.0001	0.07%	635	88	1.0	2.5	5.6

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HAADF

100 nm

MVSA#3 MVSA#4
MVSA#5 MVSA#6

Fresnel BF-TEM

Figure 1

Figure 2

Midrange irradiated zone

100 nm

50 nm

50 nm

50 nm

Figure 3

Below irradiated zone

Figure 4

9YWTV

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Fresnel BF-TEM

**Fresnel BF-TEM +
HAADF-STEM**

**Fresnel BF-TEM +
MVSA #3 component**

**Fresnel BF-TEM +
MVSA #3 component**

Figure 12

Figure 13

Figure 14

Figure 15