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Temperature dependent dispersoid stability in ion-irradiated ferritic-martensitic dual-phase oxide-dispersion-strengthened alloy: coherent interfaces vs. incoherent interfaces

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Abstract: In this study, the microstructure of a 12Cr ferritic-martensitic oxide-dispersion-strengthened (ODS) alloy is studied before and after Fe ion irradiations up to 200 peak displacements per atom (dpa). Irradiation temperature ranges 325 to 625 °C. Before irradiation, both coherent and incoherent dispersoids exist in the matrix. In response to irradiation, the mean sizes of dispersoids in both the ferrite and tempered martensite phases change to equilibrium values that increase with irradiation temperature. The evolution of dispersoids under irradiation is explained by a competition between athermal-radiation-driven shrinkage and thermal-diffusion-driven growth, with interface coherency affecting the growth mechanism. However, each coherency type exhibits different evolution behavior under irradiation. Coherent dispersoids, regardless of their initial size, change toward an equilibrium size at each temperature tested. On the other hand, incoherent dispersoids are destroyed at lower test temperatures but survive while shrinking in size at higher temperatures. This difference in behavior can be explained by the lower interfacial energy of coherent dispersoids in comparison with incoherent dispersoids. This study sheds lights on the roles of interface configurations in maintaining dispersoid integrity under irradiation.

Keywords: ferritic-martensitic, coherency, interface energy, nano-particle, dispersoid integrity

1. Introduction

Ferritic/martensitic (F/M) steels are being considered as candidates for cladding materials in fast reactors. F/M steels are preferred rather than austenitic steels not only because of their lower thermal expansion and higher thermal conductivity, but also because they are known to have overall higher radiation tolerance to some forms of radiation damage [1–7]. In particular, the swelling resistance of F/M steels is much better in general than austenitic steels, having longer incubation regimes for void nucleation, and a steady-state swelling rate of approximately one-fifth of austenitic steels [6, 8].

Swelling resistance of both austenitic and ferritic alloys is known to be further enhanced by introducing a high density of stable defect sinks, such as grain/sub-grain boundaries and precipitate-matrix interfaces [6–13]. Among F/M alloys, oxide-dispersion-strengthened (ODS) variants are also attractive for nuclear applications due to their strong contribution to creep resistance, especially at higher temperatures where ferritic alloys are much weaker than austenitic alloys [5, 14–16]. The dispersoids pin and stabilize the grain boundaries against recrystallization and grain growth and may act as sinks for both point defects and transmutant helium atoms [13–18]. Trapping of defects and helium at the dispersoid/matrix interphase was evidenced by comparing irradiation-induced microstructure changes of ODS and non-ODS alloys [18]. Such trapping effect was believed to suppress helium bubble growth and enhance the resistance against helium embrittlement of the material [15,16,18].

Ukai et al. have developed a series of ODS alloys combining mesoscopic optimization of dual phase ferrite/tempered martensite with nano-scale optimization of ultra-fine oxide particles to strongly enhance high temperature creep resistance and void swelling [19–22]. Among these alloys, a 12Cr ODS alloy was fabricated to have a very stable dual-phase microstructure by increasing the nickel content which is traditionally low in most F/M alloys [13, 22]. This alloy, when compared to other 9Cr ODS alloys, also has greatly improved resistance to high temperature oxidation and corrosion. The combined roles of the tempered martensite phase at a large volume percentage and the fine-sized dispersoids in both phases make this alloy a promising material for nuclear applications, especially in terms of swelling and creep

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4 resistance [7, 9, 13].
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9 The maintenance of the structural integrity of nano-sized dispersoids during irradiation is very
10 critical to maintain the strength of an ODS alloy, especially at high temperatures. First,
11 dispersoids stabilize the grain/sub-grain structures; second, they pin dislocations and restrain
12 thermal creep; and third, they have been proposed to serve as defect-trapping sites, all of which
13 may work to reduce void swelling. Thus, it is of great importance to understand the evolution of
14 nano-sized dispersoids under various irradiation conditions. Previous studies on various ODS
15 alloys under neutron and ion irradiations have observed a range of behaviors, showing that
16 dispersoids can shrink and/or dissolve [13, 20, 23, 24], coarsen and/or grow [25–27], undergo
17 amorphization [28–30] or be preserved with essentially no changes [31–33]. An excellent review
18 on current understanding of radiation effects on ODS alloys can be found in Refs. 18, 20 and 34.
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28 However, there is still a lack of knowledge on all factors governing dispersoid integrity during
29 irradiation, especially concerning the wide range of dispersoid phases and interface
30 configurations that combine to determine dispersoid stability. In the present study, we select the
31 12Cr dual-phase ODS due to the presence of distinct dispersoid distributions in both the ferrite
32 and tempered martensite phases. Our particular interest is to compare not only the dispersoid
33 stability under irradiation in both phases, but also the changes in their stability as a function of
34 irradiation temperature, a factor we will show to be related to the dispersoid-matrix interface
35 configuration.
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46 **2. Experimental procedures**

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49 The 12Cr ODS dual-phase alloy was supplied by Ukai of Hokkaido University, Japan [22]. The
50 sample had been normalized at 1050°C for 60 minutes and tempered at 800°C for 60 minutes.
51 The resultant two phases, tempered martensite and ferrite, have a ratio of ~4:1 [13], a ratio which
52 is controlled by the nickel content [22]. Y-Ti-O dispersoids were previously observed in both
53 phases, but with distinctly different distributions [13]. The chemical composition of this alloy
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can be found in Table 1.

Irradiation was carried out using a 1.7 MV Ionex Tandetron accelerator located at Texas A&M University. Three temperatures, 325, 475 and 625 °C, were chosen for irradiation. The temperature was monitored throughout the irradiation using a thermocouple attached to the hot stage surface. Temperature fluctuation during irradiation was less than 5 °C. At each irradiation temperature, samples were irradiated with 3.5 MeV Fe ions to 100 and 200 peak dpa. A double charged Fe beam of 200 nA was defocused to irradiate a 6 × 6 mm area on the stage. Use of a defocused beam has been recommended as a better surrogate technique to simulate steady-state neutron damage than use of a rastered beams [35-37].

Fig. 1 shows the displacement and injected Fe distribution profiles caused by 3.5 MeV Fe ion irradiation in pure Fe, calculated using SRIM [38]. The displacement threshold energy for the Fe matrix was set to 40 eV; and the Kinchin-Pease option was used due to recent findings of overestimation of dpa using the full damage cascade mode [39, 40]. The per-ion dpa profile peaks at a depth of ~1000 nm. The injected Fe distribution peaks at ~1200 nm.

Prior to irradiation, specimens were cut into 5 × 5 × 0.7 mm plates and polished mechanically. The surface damage layer resulting from mechanical polishing was removed using electropolishing with a perchloric acid solution. In order to reveal the microstructure in the whole irradiation projected region as well as irradiation-free region, we prepared TEM specimens using focused-ion-beam (FIB) technique with a Tescan LYRA-3. TEM specimens ~10 µm wide by ~ 7 µm deep were lifted out and thinned to ~200 nm using 30 keV Ga beam. Next, a 5 keV Ga beam was used to polish the sample to a thickness of ~100 nm. To complete preparation, a 2 keV Ga beam was used to remove damage caused by higher energy Ga bombardment. Microstructure characterization was performed using a 200 kV Technai F20 Supertwin transmission electron microscope (TEM) and a JOEL 2100F 200 kV TEM; bright field (BF) and weak beam dark field (WBDF) imaging techniques were used to show nano-dispersoid distributions; energy dispersive X-ray spectroscopy (EDX) and energy-filtered transmission electron microscopy (EFTEM) were used for chemical composition studies; high

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4 resolution transmission electron microscopy (HRTEM) was used to reveal some details of the
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6 microstructure.
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9 10 **3. Results**

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12 As shown in Fig. 2a, the two phases of ferrite and tempered martensite have different grain sizes.
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14 The tempered martensite grains are formed by transformation from γ phase and thus have smaller
15 grain sizes, whereas the δ ferrite phase has a much larger grain size [13, 22, 41]. Figs. 2b and 2c
16 are conventional bright field TEM images showing nano-sized dispersoids in both phases. Prior
17 to imaging, we tilt the TEM foil systematically until a maximum number of dispersoids appear as
18 gray spots. A corresponding electron diffraction pattern to illustrate the diffraction condition of
19 BF imaging is shown in Fig. 2d. Comparison between Fig. 2b and 2c shows that dispersoids in
20 the ferrite phase are finer with higher density than dispersoids in the tempered martensite phase.
21 The coarsening of dispersoids in the tempered martensite phase is thought to be the result of
22 coherency loss during phase transformation [41].
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33 The chemical compositions of the dispersoids are carefully studied using EFTEM and EDX
34 techniques. Fig. 3a shows several dispersoids having diameters of 3 nm to 10 nm. The jump-ratio
35 images of iron (Fe) $M_{2,3}$ and titanium (Ti) $M_{2,3}$ are shown in Figs. 3b and c, respectively. The
36 jump-ratio images were obtained over a typical exposure time of 8 seconds using a slit centered
37 at the energy losses of 47 eV and 56 eV for Fe-M, and 31 eV and 38 eV for Ti-M, with a size of
38 6 eV. Yttrium distribution was not studied using EFTEM due to the difficulties as described by
39 Certain et al.[42]. On the other hand, the composition of dispersoids is confirmed by the EDX
40 spectroscopies. Most of the EDX data collected among dispersoids of diameters ranging from 3-
41 30 nm show Ti/Y atomic ratio close to 1.5. Figs. 3d and 3e show spectroscopies collected from
42 dispersoids of diameters of ~20 nm and ~3 nm, respectively. The contributions from the nano-
43 sized dispersoids to EDX can be easily submerged by the signal from the matrix (as shown in
44 Fig. 3e), because of the ultra fine dispersoid sizes in this study (typically 2-20 nm) compared to
45 the thickness of TEM foil (~100 nm). The sample drifting makes long-time data collecting not
46 practical. Hence, in this study, BF and WBDF techniques are primarily used to statistically
47 analyze dispersoid size and density. It is worth noting that in BF images, some dispersoids
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appear to be darker than others. The difference in contrast is likely attributed to the difference in orientation-matrix orientations. Fig. 3b-c show that, regardless of their contrasts difference in the BF images, dispersoids are composed of in Y and Ti.

Fig. 4 shows HRTEM images of two dispersoids of different sizes and orientations relative to the matrix. Images of both dispersoids are taken at the [001] zone axis of the matrix of the unirradiated sample. Fig. 4a presents a coherent dispersoid of ~2.5 nm in diameter. The FFT spots of the dispersoid in Fig. 4b are indexed as (200) and (020) of the orthorhombic YTiO_3 , suggesting a coherent relationship of $[001]_{\text{D}}/[001]_{\text{M}}$ and $(220)_{\text{D}}/(110)_{\text{M}}$ between the dispersoid and the matrix. The circled spots in Fig. 4b are used to generate Fig. 4c, which highlights the dispersoid from the background. On the other hand, Fig. 4d-f present a larger dispersoid showing no coherent relationship to the matrix. The presence of incoherent interphase can be observed from Fig. 4d. The dashed arrow in Fig. 4e points to the FFT spot of the dispersoid. Other spots correspond to either the matrix or Moiré fringes. Some of the spots of the Moiré fringes are labeled with “MF” in Fig. 4e. The d-spacing of the dispersoid is 0.56 nm, which is in good agreement with the (002) of Y_2TiO_5 or (111) of $\text{Y}_2\text{Ti}_2\text{O}_7$.

Dispersoid size changes due to irradiation are shown in Fig. 5, with Fig. 5a showing dispersoids in the tempered martensite phase and Fig. 5b showing dispersoids in the ferrite phase. The local doses received by the regions shown in Fig. 5 are ~100 dpa. Because micrographs in Fig. 5 are captured from a depth of ~500 nm from the surface, the local dose is half of the peak values of 200 dpa. Compared with the as-received condition, as shown in Fig. 2c, dispersoids in the tempered martensite phase have reduced-sizes due to radiation damage. In addition, Fig. 5a shows systematically that the dispersoid size is smaller at lower irradiation temperatures. The changes of dispersoid size in the ferrite phase are not as obvious, although it will be shown later that a similar size variation with temperature also exists for dispersoids in the ferrite phase.

Dislocations and some “black spots” are also observed in Fig 5, especially in samples irradiated at 325 °C. Although it is possible that the sample preparation using FIB might introduce small defect clusters, the fact that much less “black spot” damages are observed in the irradiation-free sample (Fig. 2bc) compared to irradiated samples suggests that the “black spot” damages is primarily introduced by Fe^{2+} irradiation, instead of FIB processing.

Our previous publication showed that after irradiation at 475 °C, the distribution of dispersoids in the tempered martensite phase became identical to the distribution of dispersoids in the ferrite phase, with the coarse dispersoids originally in the tempered martensite phase being removed by the irradiation [13]. In this study, radiation response of dispersoids in both phases at higher temperature exhibits additional complexity. Fig. 6 compares dispersoid diameter distributions in ferrite (black) and tempered martensite (white) grains before (Fig. 6a) and after irradiation at 625 °C (Fig. 6b) and at 475 °C (Fig. 6c). After reviewing Fig. 2b and Fig. 5b, it is not surprising to find that very small dispersoids observed in the unirradiated ferrite phase underwent only limited changes during irradiation. However, in Fig. 6, it can be seen that irradiation at 625 °C shifts the ferrite distribution to be slightly coarser and irradiation at 475 °C shifts the distribution to be slightly finer in size. In contrast, dispersoids in the tempered martensite phase, originally containing both fine (≤ 5 nm) and coarse dispersoids (≥ 5 nm), show more significant changes due to irradiation. Fine dispersoids in the tempered martensite phase evolve to a distribution that is nearly identical as that of dispersoids in ferrite; however, nearly all coarse dispersoids are removed after irradiation at 475 °C and some of the coarse dispersoids remain after irradiation at 625 °C.

Due to further reduced dispersoid sizes after irradiation at the lowest irradiation temperature of 325°C, TEM imaging of dispersoids becomes challenging. The finer and denser features in Figs. 5(a3) and 5(b3) can be a combination of dispersoids and so called black spot damage from ion irradiation. Such features are frequently observed in F/M steels and ODS alloys irradiated under similar conditions [20,41-46]. It is unlikely that these features are FIB induced artifacts due to the reason that such features are not observed in the deep region beyond Fe ion penetration. We analyze the size distribution of these fine features and treat them as dispersoids. Since we cannot exclude the possibility that they are defect clusters, the obtained size distribution for irradiation temperature 325°C represents the upper limit of possible dispersoid sizes. As to be discussed, keeping this size statistics is helpful to show the overall size trend as a function of irradiation temperature, and our conclusion is consistent even the dispersoids at this temperature actually are smaller than these observed features.

Dispersoid density changes can be found in Table 2. Notably, the increase of number density of the dispersoids in the tempered martensite phase after irradiation at 475 °C suggests that, during

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4 irradiation, coarse dispersoids may dissolve and/or break into fine dispersoids, on the other hand,
5 nucleation of dispersoids may occur as well [43, 44].
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12 martensite phase, this phase needs to be more closely examined. Fig. 7 shows the size change of
13 dispersoids in the tempered martensite phase as a function of the depth from the sample surface.
14 As shown in Fig. 7, higher irradiation temperatures result in larger dispersoids on average.
15 However, for a given temperature, different damage levels yield the same dispersoid size after
16 irradiation. Beyond ~1000 nm from the surface, the dispersoid size begins to increase. This depth
17 coincides with the peak damage region calculated by SRIM shown in Fig. 1. Over the range
18 ~1000-1600 nm from the surface, as the dpa quickly approaches zero, the mean dispersoid size
19 increases back to that of the unirradiated condition.
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31 Fig. 8 plots the mean dispersoid size in the tempered martensite phase as a function of local dpa,
32 where dispersoid size data is taken 400-700 nm from the sample surface. At any given
33 temperature, dispersoids quickly shrink during the first ~60 dpa. Additional ion irradiation
34 beyond 60 dpa does not cause any statistically significant additional size change. However, the
35 equilibrium sizes are temperature-dependent. Mean dispersoid sizes change from 5.5 ± 1.6 nm to
36 2.8 ± 0.6 nm, 2.2 ± 0.5 nm and 1.3 ± 0.3 nm after ion bombardment to ~ 120 local dpa at 625,
37 475 and 325 °C, respectively.
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45 In order to differentiate radiation responses of coherent and incoherent dispersoids, which is the
46 key interest of this study, a near two-beam condition and (g, 3g) condition are used to get BF and
47 WBDF images. Fig. 9 shows WBDF and BF micrographs obtained from randomly chosen
48 tempered-martensite grains within regions receiving damage levels of ~50-70 dpa at each
49 temperature, as compared with the unirradiated sample. With g_{110} excited, dispersoids coherent
50 to (110) of the matrix, as well as dislocations with burger's vectors not perpendicular to g_{110} , are
51 highlighted as bright features. At a near two-beam condition, dispersoids are also more
52 prominent in BF micrographs as the diffraction contrast is enhanced. Before irradiation, as
53 shown in Fig. 9(a1-2), both coherent dispersoids (some of which are highlighted with dashed
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circles) and incoherent dispersoids (highlighted by the arrow) exist. Coherent dispersoids are still observed after irradiations at both 475 °C and 625 °C while incoherent dispersoids were only observed in the samples irradiated at 625 °C, but not in the samples irradiated at either 475 °C or 325 °C. One example of surviving incoherent dispersoid observed at 625 °C is highlighted with the arrow in Fig. 9(b2), and more examples of higher magnifications will be shown in Figs. 10 and 11. In addition, the remaining coherent dispersoids are larger after irradiation at 625 °C, in comparison with 475 °C. The above difference is caused by irradiation, which clearly shows the radiation stability of dispersoids is relevant to interface coherency.

Fig. 10 and Fig. 11 provide insights into the semi-coherency and incoherency of dispersoids, which are observed after irradiation at 625 °C but not seen after irradiation at 475 °C or 325 °C. BF and WBDF micrographs in Fig. 10 are obtained near a two-beam condition with the diffraction pattern inserted to the top-left corner of Fig. 10b. The features in Fig. 10 are taken from the depth of ~500 nm from the 200 peak dpa sample, where the dose is ~100 dpa. In this region, some dispersoids of diameters up to 8 nm are observed after irradiation at 625 °C, whereas no dispersoids of comparable sizes were observed in irradiated regions of samples irradiated at lower temperatures. In Fig. 10a, dispersoids with different orientation relationships to the matrix were marked with numbers. The small dispersoid 1 has bright, spot-like contrast in Fig. 10b when g_{110} was excited, indicating that this dispersoid, of diameter of 2.5 nm, is coherent to the matrix. Dispersoid 2 in Fig. 10a also shows the Moiré fringes perpendicular to the g vector, suggesting the alignment of the dispersoid to $(110)_M$ with misfit. Dispersoid 3 has a weak contrast in Fig. 10a but a bright contrast in Fig. 10b. The fringes of dispersoid 3 are not perpendicular to the g_{110} direction and thus the dispersoid should not be considered as coherent to (110) of the matrix. Dispersoid 3 has a bright feature in Fig. 10b most likely because it reflects electron beam to a direction that happens to fall inside of the objective aperture near the $(110)_M$ reflection when the WBDF micrograph is imaged. Dispersoid 4 and 5 have contrast in the BF image but show no contrast in the WBDF image, indicating that neither of them is coherent to $(110)_M$.

HR images in Fig. 11 show dispersoids after receiving ~100 dpa irradiations at 625 °C. Fig. 11a-c correspond to a semi-coherent dispersoid aligned to $(110)_M$. As shown in Fig. 11a, this dispersoid of 7.5 nm in diameter shows Moiré fringes parallel to (110) lattice plane of the matrix.

The FFT pattern in Fig. 11b indicates that the Moiré fringes come from the superimposition of the $(110)_M$ and the lattice plane of the dispersoid marked with the dashed arrow. The d-spacing of the lattice plane of the dispersoid is ~ 0.23 nm, which is in agreement to the (112) of $YTiO_3$, the (331) of $Y_2Ti_2O_7$ or the (312) of Y_2TiO_5 . Inversed FFT image generated using $(110)_M$ and the FFT spot of the dispersoid is shown Fig. 11c. Semi-coherent interphase decorated with plane misfits is shown with arrows pointing to some of the plane dislocations at the interphase.

Fig. 11d, which is obtained at the $[331]$ zone axis of the matrix, shows a dispersoid of ~ 10 nm in diameter after receiving ~ 100 dpa irradiations at 625°C . The incoherent interphase between the dispersoid and the matrix was observed in Fig. 11d. A careful investigation of the FFT pattern of Fig. 11d shows that the “alignment of atoms” in the as-shown dispersoid is the result of Moiré fringe. The FFT pattern in Fig. 11e indicates incoherency between the dispersoid and the matrix. In Fig. 11f, the inversed FFT image, generated using the circled spots in Fig. 11e, illustrates the incoherent interphase as the dark contour surrounding the particle.

Number densities of coherent dispersoids can be obtained using WBDF images. The density of dispersoids coherent to $(110)_M$ in tempered-martensite grains before irradiation is measured to be $6.6 \pm 1.2 \times 10^{16} \text{ cm}^{-3}$. As listed in Table 2, the density appears to slightly increase after irradiation at 475°C and decrease after irradiation at 625°C . Total dispersoid densities, regardless of their coherency, are estimated for samples before and after irradiation, by using BF micrographs. Samples irradiated at 325°C are not included in Table 2, due to the high density of defects, to be shown later. The fraction of $(110)_M$ coherent to total dispersoids is lower in the sample irradiated at 625°C when compared to either the untreated sample or the sample irradiated at 475°C .

Fig. 12 plots size distributions of dispersoids before and after receiving irradiation at different temperatures, obtained from BF and WBDF micrographs of multiple randomly chosen tempered-martensite grains in the irradiated regions, using at least 100 particles for each category. In accordance with observations from conventional BF micrographs, dispersoids in the tempered martensite grains are found to shrink in size after irradiation. Comparing coherent and total distributions in Fig. 12a, it is evident that coarse dispersoids tend to be incoherent while most of the fine dispersoids are coherent. After irradiation at 475°C , the incoherent dispersoids seem to

disappear as shown in Fig. 12c; however, in Fig. 12b, more incoherent dispersoids are found as coarse dispersoids after irradiation at 625 °C.

Radiation-induced void swelling is observed in the matrix of the samples irradiated at 475 °C, with ferrite grains showing a much higher level of swelling than tempered martensite grains. In the 50 local dpa (500 nm depth) region of the 100 peak dpa sample, voids with diameter larger than 30 nm are observed in the ferrite grains, whereas no voids of diameter larger than 2 nm is observed in the tempered martensite phase. The maximum swelling at 50 dpa is 0.3 % in the ferrite phase and 0.003 % in the tempered martensite phase. More details of void formation at 475 °C as a result of damage levels up to 800 peak dpa was reported in our earlier work [13].

A few voids are observed in the samples irradiated at 625 °C, particularly in the ferrite grains. It is interesting that some of the voids observed after irradiation at 625 °C appear be attached to the interface of dispersoid and matrix, and formed inside of the dispersoids. The observation is consistent with the previous studies, which shows the trapping of bubbles by the dispersoid/matrix interface at elevated temperatures [15,16,18].

It is worth noticing that no voids form at the peak dpa region in any of the samples irradiated in this study. The absence of voids at the peak damage region reflects the effect of the defect imbalance caused by ion irradiation with injected interstitials heavily distributed near the peak dpa region [51, 52]. On the other hand, more voids are observed in the samples irradiated at 475 °C than the samples irradiated at 325 °C or 625 °C. This agrees with previous determinations of peak swelling temperatures of F/M steels [4, 6, 7, 53].

4. Discussion

ODS alloys with finer dispersoids have been experimentally observed to have higher creep rupture strength by pinning dislocations and stabilizing grain boundaries [54–59]. Finer dispersoids with a higher number density have a stronger pinning effect on dislocations as suggested by the resultant hardness enhancement [19, 55]. The pinning of grain boundaries, known as Zener pinning, has also been found to be inversely proportional to particle size. Besides size effects, dispersoid-matrix coherency is also important. For grain boundary

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4 stabilization, coherent dispersoids are more effective than incoherent dispersoids [60, 61]. For
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6 dislocation pinning, incoherent $\text{Y}_2\text{Ti}_2\text{O}_7$ dispersoids can be less attractive to dislocations due to a
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8 repulsive contribution caused by the oxide's large elastic modulus when compared to the Fe-Cr
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10 matrix [57, 58, 62, 63].

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14 Size and coherency of a dispersoid are thought to be correlated. As observed in Fig. 12a, in
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16 tempered martensite grains, fine dispersoids tend to be coherent while coarse dispersoids tend to
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18 be incoherent. The size-coherency correlation has been observed in different types of ODS
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20 alloys [13, 64–67]. In general, small dispersoids tend to be coherent with the matrix phase
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22 [13, 64], and lose coherency as they become larger [13, 64, 65]. From a thermodynamics
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24 interpretation, this correlation is a result of the minimization of free energy [64].

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27 The free energy of a particle can be described as a sum of interfacial energy and elastic energy.
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29 The interfacial energy of a particle is positively related to its surface area. For a spherical particle
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31 having radius of r , the interfacial energy, G_I , is given as $4\pi r^2 \gamma_I$, where γ_I is the unit-area
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33 interfacial energy. Elastic energy, on the other hand, is positively related to the volume of the
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35 particle. Compared to an incoherent dispersoid, a coherent dispersoid has more elastic energy
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37 introduced due to the addition of the lattice misfit parameter δ . The elastic energy is given to be:
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39 $4\pi r^3/3(4\delta^2\mu)$ [68].

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41 Fine particles tend to take coherency to minimize surface energy, given that $\gamma_{I,c}$ of coherent
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43 particles is smaller than $\gamma_{I,i}$ of incoherent particles [69, 70]. As particles grow in size, elastic
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45 energy becomes dominate over interfacial energy, explaining why coarse particles prefer to be
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47 incoherent to the matrix. Semi-coherency is an intermediate state, in which dislocations form at
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49 the particle-matrix interface to partially release the stress energy [69, 70].

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53 In the tempered martensite phase of the 12Cr ODS alloy, the dispersoid distribution as shown in
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55 Fig. 12a results from a kinetic process during sample fabrication [18, 22, 71, 72]. In the tempered
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57 martensite phase, a portion of dispersoids lose coherency with the matrix and gain additional
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59 interfacial energy during the α/γ transformation. As a result, they coarsen through Ostwald
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ripening [19, 70, 71]. The remaining dispersoids that retain coherency, on the other hand, have an almost identical distribution to the dispersoid distribution in the ferrite phase.

Kinetics also govern the changes in dispersoid distribution during irradiation [13, 20, 23–27, 73]. A number of researchers have reported that irradiation at relatively low temperatures shrink and/or destroy dispersoids [13, 20, 23, 73] and the dispersoid distributions after irradiation are temperature-dependent [20, 23, 73]. However, to the best of the authors' knowledge, no attention has been paid to the differences in radiation response of coherent and incoherent particles, which was observed in this study as is clearly illustrated by Fig. 9-12. To associate radiation response of dispersoids with their interfacial configurations, the Gibbs Thomson effect can be taken into account in the diffusion model, which is appropriate in this study given that the nano-sized dispersoids have high curvatures. The change in dispersoid radius, r , is driven by thermal diffusion and can be approximated by [74]:

$$\frac{dr}{dt} = \frac{D}{r} \cdot \frac{c - c_r}{c_p - c_r}, \quad c_r = c_\infty \exp\left(\frac{2\gamma_i v_{at}}{kTr}\right) \quad (1)$$

where the radius change rate dr/dt is a function of the solute diffusion coefficient D , solute concentration c in the matrix, the solute concentration c_r at the dispersoid-matrix interface, the solute concentration c_p in the dispersoid, the solubility limit at a flat interface of the two phases c_∞ , the unit interfacial energy at the dispersoid-matrix interface γ_i , the averaged atomic volume in dispersoid v_{at} and environment temperature T , with k being the Boltzmann constant.

In the absence of irradiation, the Gibbs Thomson effect is able to explain the nucleation, growth and coarsening of the particles in ODS alloys and other precipitate systems [43, 75–78]. In this study, however, the thermal diffusion effect needs to be coupled with the athermal irradiation effect, which is described by [78]:

$$\frac{dr}{dt} = -K\psi \quad (2)$$

where K is the dpa rate, ψ is a parameter to describe the efficiency of damage cascades to dissolve dispersoids.

Equation 2 predicts dispersoid shrinkage and/or destruction due to irradiation, which enhances c , the solute concentration in the matrix, as observed in this and previous studies [16, 20, 23, 24, 73]. With a larger concentration of solutes in the, the positive growth rate, as shown by Equation 1, will also be enhanced. Eventually thermal diffusion recovery, as governed by Equation 1, will counterbalance the athermal radiation removal of dispersoids, as governed by Equation 2, leading to an equilibrium state where dispersoid size will not change with increasing dpa levels [78, 79]. This effect has been observed in this study, as shown in Fig. 8, and by others [16, 20]. This equilibrium state can be described as:

$$\frac{dr}{dt} = \frac{D}{r} \cdot \frac{c - c_r}{c_p - c_r} - K\psi = 0 \quad (3)$$

Fig. 13 plots numerical solutions of Equation 3 with different $D/(K\psi)$ and c values, using unit interfacial energy γ_I and dispersoid radius r as variables, with c_p/c_∞ set as 10^3 . Both parameters are given in the formats of reduced units to simplify the discussion. The solution curve $r_e(\gamma_I)$ defines a closed region, within which dispersoids will grow and outside of which dispersoids will shrink. In the small r region the r_e increases with γ_I . Once a maximum γ_I is reached, the trend becomes opposite. Starting dispersoid sizes may be scattered over a large size region. Upon irradiation, those large dispersoids will eventually diminish if their r - γ_I changing trajectories do not span over the $r_e(\gamma_I)$ curve.

Before steady state is reached, radiation dissolution of dispersoids leads to an increase in c , which in return enhances diffusion-driven dispersoid recovery, as shown by the dotted curve (blue colored) in Fig. 13. When an equilibrium state is reached through the competition of radiation-removal and diffusion-recovery, c would come to an equilibrium value, which is

decided by the temperature and solute diffusion coefficients in the system as well as the irradiation conditions including dpa rate and injected particle energy, etc.

When the value of c/c_∞ and the dpa rate, K , are kept constant, and the solute diffusion coefficient, D , is increased, for instance, by a factor of 2, the numerical solution to Equation 3 changes from the solid line (black colored) to the dashed line (red colored) as shown in Fig. 13. Knowing that diffusion coefficients are higher at elevated temperatures, these curves in Fig. 13 predict that some semi/incoherent dispersoids, which do not survive at lower irradiation temperatures due to a relatively higher γ_i , will survive at a higher temperature given the same irradiation conditions. Such a phenomenon was observed in this study.

The range of γ_i in the remaining dispersoids after irradiation at 475 and 625 °C can be estimated using Eq. 3, given that $K\psi$ has a positive value:

$$\frac{D}{r} \cdot \frac{c - c_r}{c_p - c_r} = K\psi > 0 \quad (4)$$

Assuming a composition of $\text{Y}_2\text{Ti}_2\text{O}_7$ for the dispersoids, the atomic volume of Y is $\approx 0.1 \text{ nm}^3$. c_∞ was approximated by the solubility of Y in $\alpha\text{-Fe}$, which is 0.02 at.% for 625 °C and 0.013 at.% for 475 °C [80]. The value of c is ~ 0.1 at.% after 475 °C and 625 °C irradiation, estimated from the dispersoid dissolution determined through TEM investigations. The critical interfacial energy for a coherent particle ($\gamma_{i,cc}$), at 475 °C, satisfying the inequality in Equation 4, is calculated to be 0.32 J/m^2 , providing that 90% of sustained dispersoids after 475 °C irradiation were found to be below 3 nm in diameter. The critical interfacial energy of a semi-coherent dispersoid ($\gamma_{i,sc}$) after irradiation at 625 °C is calculated to be 0.60 J/m^2 , using the experimentally observed dispersoid diameters of ~ 6 nm. The critical interfacial energy $\gamma_{i,ic}$ of the largest incoherent dispersoid observed (11 nm in diameter) after irradiation at 625 °C was 1.10 J/m^2 . Thus, coherent dispersoids should have an interfacial energy $\gamma_{i,c} < 0.32 \text{ J/m}^2$. On the other hand, the interfacial energy $\gamma_{i,s}$ and $\gamma_{i,i}$ of semi-coherent and incoherent dispersoids, respectively, should satisfy $0.32 \text{ J/m}^2 < \gamma_{i,s} < 0.60 \text{ J/m}^2$ and $0.60 \text{ J/m}^2 < \gamma_{i,i} < 1.10 \text{ J/m}^2$. These estimations are in agreement with

the 0.26 - 0.29 J/m^2 interface energy of coherent $Y_2Ti_2O_7$ reported by Ribis et al. [67, 77] and the 0.3-2.5 J/m^2 energy range of incoherent and semi-coherent interfaces reported by Howe [69].

The model presented here not only explains dispersoid shrinkage as observed in this work and others [13, 20, 23], but also predicts dispersoid destruction at low temperatures [73] and stable or coarsened dispersoids at elevated temperatures and/or low radiation damage level (i.e., low dpa rates and/or lower bombardment energies) [25–27, 31–33, 73]. At a low irradiation temperature, the $D/(K\psi)$ ratio decrease so the $dr/dt > 0$ area reduces towards a lower γ_I . At some stage, even the precipitate with lowest interfacial energy falls into the $dr/dt < 0$ region and will be destroyed by irradiation. On the other hand, when the temperature is very high or the radiation damage level is low, the $D/(K\psi)$ ratio becomes very large. Diffusion, under these conditions, is rapid enough to recover most damage caused by radiation so dispersoids remain stable. Thus, the rise in solute concentration in the matrix, c , will be less significant. A possible resultant scenario is shown in Fig. 13 by the dash-dot curve (purple colored). In this case, the Gibbs Thomson effect favors dispersoids with larger size above the curve, leading to the growth of coarse dispersoids in expense of the destruction of fine dispersoids below the curve, in an Ostwald ripening process that has also been observed in samples thermally annealed at 1300 °C without irradiation [27].

5. Conclusions

To understand radiation response of coherent and incoherent dispersoids in a 12 Cr F/M ODS alloy with both ferrite and tempered-martensite structures, microstructure characterizations before and after irradiation by 3.5 MeV Fe^{2+} irradiations at 625, 475 and 325 °C are carried out. Particular focus is given to the effects of coherency on the radiation response of dispersoids. After irradiation, dispersoids in tempered martensite and ferrite are found to approach an equilibrium size that is positively correlated to irradiation temperatures. Dislocations pinned by dispersoids are observed after irradiations, revealing the creep strengthening mechanisms of dispersoids at elevated temperatures. Evidence of the influence of dispersoid-matrix coherency on dispersoid stability were observed in this study. Fine and coherent dispersoids undergo modest size changes under ion irradiations, whereas semi-coherent and incoherent dispersoids

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4 shrink in size and are only observed to remain after higher temperature irradiations. A model
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6 coupling diffusion recovery, governed by the Gibbs-Thomson-effect, and radiation damage is
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8 proposed to explain the observations in this study.
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20 21 **References**

- 22
23 [1] S.J. Zinkle, G.S. Was, Materials challenges in nuclear energy, *Acta Materialia* 61 (2013)
24
25 735–758.
26
27 [2] S.J. Zinkle, J.T. Busby, Structural materials for fission and fusion energy, *Materials Today*
28
29 12 (2009).
30
31 [3] R.L. Klueh, A.T. Nelson, Ferritic/martensitic steels for next-generation reactors, *Journal of*
32
33 *Nuclear Materials* 371 (2007) 37–52.
34
35 [4] F.A. Garner, "Irradiation performance of cladding and structural steels in liquid metal
36
37 reactors", in: volume 10A, *Materials Science and Technology: A Comprehensive Treatment*,
38
39 VCH Publishers, 1994, pp. 419–543.
40
41 [5] L.K. Mansur, A.F. Rowcliffe, R.K. Nanstad, S.J. Zinkle, W.R. Corwin, R.E. Stoller,
42
43 *Materials needs for fusion, Generation IV fission reactors and spallation neutron sources --*
44
45 *similarities and differences*, *Journal of Nuclear Materials* 329-333 (2004) 166–172.
46
47 [6] F.A. Garner, M.B. Toloczko, B.H. Sencer, Comparison of swelling and irradiation creep
48
49 behavior of fcc-austenitic and bcc-ferritic/martensitic alloys at high neutron exposure, *Journal of*
50
51 *Nuclear Materials* 276 (2000) 123–142.
52
53 [7] F.A. Garner, L. Shao, M.B. Toloczko, S.A. Maloy, V.N. Voyevodin, Use of self-ion
54
55 bombardment to study void swelling in advanced radiation-resistant alloys, in: *17th International*
56
57 *conference on environmental degradation of materials in nuclear power systems - water reactors*,
58
59 Ottawa, 2015.
60
61
62
63
64
65

- [8] B.H. Sencer, F.A. Garner, Compositional and temperature dependence of void swelling in model Fe-Cr base alloys irradiated in the EBR-II fast reactor, *Journal of Nuclear Materials* 283-287 (2000) 164–168.
- [9] P. Dubuisson, D. Gilbon, J.L. Séran, Microstructural evolution of ferritic-martensitic steels irradiated in the fast breeder reactor Phénix, *Journal of Nuclear Materials* 205 (1993) 178–189.
- [10] M. Song, Y. Wu, D. Chen, X. Wang, C. Sun, K.Y. Yu, Y. Chen, L. Shao, Y. Yang, K.T. Hartwig, X. Zhang, Response of equal channel angular extrusion processed ultrafine-grained T91 steel subjected to high temperature heavy ion irradiation, *Acta Materialia* 74 (2014) 285–295.
- [11] D. Chen, J. Wang, T. Chen, L. Shao, Defect annihilation at grain boundaries in alpha-Fe, *Scientific Reports* 3 (2013).
- [12] M.B. Toloczko, F.A. Garner, V.N. Voyevodin, V.V. Bryk, O.V. Borodin, V.V. Mel'nychenko, A.S. Kalchenko, Ion-induced swelling of ODS ferritic alloy MA957 tubing to 500 dpa, *Journal of Nuclear Materials* 453 (2014) 323–333.
- [13] T. Chen, E. Aydogan, J.G. Gigax, D. Chen, J. Wang, X. Wang, S. Ukai, F.A. Garner, L. Shao, Microstructural changes and void swelling of a 12Cr ODS ferritic-martensitic alloy after high-dpa self-ion irradiation, *Journal of Nuclear Materials* 467 (2015) 42–49.
- [14] G.R. Odette, M.J. Alinger, B.D. Wirth, Recent developments in irradiation-resistant steels, *Annu. Rev. Mater. Res.* 38 (2008) 471–503.
- [15] J. Chen, P. Jung, T. Rebac, F. Duval, T. Sauvage, Y. de Carlan, M.F. Barthe, Helium effects on creep properties of Fe-14CrWTi ODS steel at 650 °C, *Journal of Nuclear Materials* 453 (2014) 253–258.
- [16] J. Chen, P. Jung, W. Höffelner, H. Ullmaier, Dislocation loops and bubbles in oxide dispersion strengthened ferritic steel after helium implantation under stress, *Acta Materialia* 56 (2008) 250–258.
- [17] G.R. Odette, Recent progress in developing and qualifying nanostructured ferritic alloys for advanced fission and fusion applications, *JOM* 66 (2014) 2427–2441.

- [18] C.H. Zhang, Y.T. Yang, Y. Song, J. Chen, L.Q. Zhang, J. Jang, A. Kimura, Irradiation response of ODS ferritic steels to high-energy Ne ions at HIRFL, *Journal of Nuclear Materials* 455 (2014) 61-67.
- [19] S. Ukai, S. Ohtsuka, Nano-mesoscopic structure control in 9Cr-ODS ferritic steels, *Energy Materials* 2 (2007) 26–35.
- [20] T.R. Allen, J. Gan, J.I. Cole, M.K. Miller, J.T. Busby, S. Shutthanandan, S. Thevuthasan, Radiation response of a 9 chromium oxide dispersion strengthened steel to heavy ion irradiation, *Journal of Nuclear Materials* 375 (2008) 26–37.
- [21] J. Gan, T.R. Allen, B.C. Birtcher, S. Shutthanandan, S. Thevuthasan, Radiation effects on the microstructure of a 9Cr-ODS alloy, *JOM* 60 (2008) 24–28.
- [22] S. Ukai, Y. Kudo, X. Wu, N. Oono, S. Hayashi, S. Ohtsuka, T. Kaito, Residual ferrite formation in 12CrODS steels, *Journal of Nuclear Materials* 455 (2014) 700–703.
- [23] J. He, F. Wan, K. Sridharan, T.R. Allen, A. Certain, V. Shutthanandan, Y.Q. Wu, Stability of nanoclusters in 14YWT oxide dispersion strengthened steel under heavy ion-irradiation by atom probe tomography, *Journal of Nuclear Materials* 455 (2014) 41–45.
- [24] I. Monnet, P. Dubuisson, Y. Serruys, M.O. Ruault, O. Kaïtasov, B. Jouffrey, Microstructural investigation of the stability under irradiation of oxide dispersion strengthened ferritic steels, *Journal of Nuclear Materials* 335 (2004) 311–321.
- [25] S. Yamashita, N. Akasaka, S. Ukai, S. Ohnuki, Microstructural development of a heavily neutron-irradiated ODS ferritic steel (MA957) at elevated temperature, *Journal of Nuclear Materials* 367-370 (2007) 202–207.
- [26] S. Yamashita, N. Akasaka, S. Ohnuki, Nano-oxide particle stability of 9-12Cr grain morphology modified ODS steels under neutron irradiation, *Journal of Nuclear Materials* 329-333 (2004) 377–381.
- [27] M.-L. Lescoat, J. Ribis, Y. Chen, E.A. Marquis, E. Bordas, P. Trocellier, Y. Serruys, A. Gentils, O. Kaïtasov, Y. de Carlan, A. Legris, Radiation-induced ostwald ripening in oxide dispersion strengthened ferritic steels irradiated at high ion dose, *Acta Materialia* 78 (2014) 328–340.

- [28] D. Kaoumi, A. Motta, M. Kirk, Characterization and In-Situ Ion-Irradiation of MA957 ODS Steel, in: Transactions of the American Nuclear Society, volume 98, Anaheim, CA, 2008, pp. 1
- [29] M.-L. Lescoat, I. Monnet, J. Ribis, P. Dubuisson, Y. de Carlan, J.-M. Costantini, J. Malaplate, Amorphization of oxides in ODS materials under low and high energy ion irradiations, *Journal of Nuclear Materials* (2011).
- [30] V.A. Skuratov, Radiation stability of the ODS alloys against swift heavy ion impact, *Journal of Nuclear Materials* 442 (2013) 449–457.
- [31] N. Akasaka, S. Yamashita, T. Yoshitake, S. Ukai, A. Kimura, Microstructural changes of neutron irradiated ODS ferritic and martensitic steels, *Journal of Nuclear Materials* 329-333 (2004) 1053–1056.
- [32] H. Kishimoto, K. Yutani, R. Kasada, O. Hashitomi, A. Kimura, Heavy-ion irradiation effects on the morphology of complex oxide particles in oxide dispersion strengthened ferritic steels, *Journal of Nuclear Materials* 367-370 (2007) 179–184.
- [33] H. Kishimoto, R. Kasada, O. Hashitomi, A. Kimura, Stability of Y-Ti complex oxides in Fe-16Cr-0.1Ti ODS ferritic steel before and after heavy-ion irradiation, *Journal of Nuclear Materials* 386-388 (2009) 533–536.
- [34] S. Pasebani, I. Charit, J. Burns, S. Alsagabi, D.P. Butt, J.I. Cole, L.M. Price, L. Shao, Microstructural stability of a self-ion irradiated lanthana-bearing nanostructured ferritic steel, *Journal of Nuclear Materials* 462 (2015) 191–204.
- [35] ASTM E521, Standard Practice for Neutron Radiation Damage Simulation by Charged-particle Irradiation, ASTM International, West Conshohocken, PA, 2009, <http://dx.doi.org/10.1520/E0521-96R09E01>.
- [36] J. Gigax, E. Aydogan, T. Chen, D. Chen, Y. Wu, W.Y. Lo, Y. Yang, F.A. Garner, The influence of beam rastering on the swelling of self-ion irradiated pure iron at 450 °C, *Journal of Nuclear Materials* 465 (2015) 343-348.

- [37] E. Getto, Z. Jiao, A.M. Monterrosa, K. Sun, G.S. Was, Effect of irradiation mode on the microstructure of self-ion irradiated ferritic-martensitic alloys, *Journal of Nuclear Materials* 465 (2015) 116-126.
- [38] J.F. Ziegler, M.D. Ziegler, J.P. Biersack, SRIM - The stopping and range of ions in matter, *Nuclear Instruments and Methods in Physics Research B* 268 (2010) 1818–1823.
- [39] L.R. Greenwood, R.K. Smither, SPECTER: neutron damage calculations for materials irradiations, Technical Report ANL/FPP/TM-197, Argonne National Laboratory, Lemont, IL, 1985.
- [40] R.E. Stoller, M.B. Toloczko, G.S. Was, A.G. Certain, S. Dwaraknath, F.A. Garner, On the use of SRIM for computing radiation damage exposure, *Nuclear Instruments and Methods in Physics Research B* 310 (2013) 75–80.
- [41] M. Yamamoto, S. Ukai, S. Hayashi, T. Kaito, S. Ohtsuka, Reverse phase transformation from alpha to gamma in 9Cr-ODS ferritic steels, *Journal of Nuclear Materials* 417 (2011) 237–240.
- [42] A.G. Cerain, K.G. Field, T.R. Allen, M.K. Miller, J. Bentley, J.T. Busby, Response of nanoclusters in a 9Cr ODS steel to 1dpa, 525 °C proton irradiation, *Journal of Nuclear Materials* 407 (2010) 2-9
- [43] C. Hin, B.D. Wirth, Formation of Y₂O₃ nanoclusters in nano-structured ferritic alloys: modeling of precipitation kinetics and yield strength, *Journal of Nuclear Materials* (2010) 30–37.
- [44] H.J. Ryu, S.H. Hong, Effect of elastic interaction energy on coarsening of γ' precipitates in a mechanically alloyed ODS Ni-base superalloy, *Journal of Materials Science* (1999) 329-336.
- [45] D.S. Gelles, Microstructural examination of commercial ferritic alloys at 200 dpa, *Journal of Nuclear Materials* 233-237 (1996) 293–298.
- [46] R. Schäublin, D.S. Gelles, M. Victoria, Microstructure of irradiated ferritic/martensitic steels in relation to mechanical properties, *Journal of Nuclear Materials* 307-311 (2002) 197–202.

- [47] R. Schäublin, A. Ramar, N. Baluc, V. de Castro, M.A. Monge, T. Leguey, N. Schmid, C. Bonjour, Microstructural development under irradiation in European ODS ferritic/martensitic steels, *Journal of Nuclear Materials* 351 (2006) 247–260.
- [48] P.J. Maziasz, R.L. Klueh, J.M. Vitek, Helium effects on void formation in 9Cr-1MoVNb and 12Cr-1MoVW irradiated in HFIR, *Journal of Nuclear Materials* 141-143 (1986) 929–937.
- [49] O. Anderoglu, J. Van den Bosch, P. Hosemann, E. Stergar, B.H. Sencer, D. Bhattacharyya, R. Dickerson, P. Dickerson, M. Hartl, S.A. Maloy, Phase stability of an HT-9 duct irradiated in FFTF, *Journal of Nuclear Materials* 430 (2012) 194–204.
- [50] J. Ribis, S. Lozano-Perez, Nano-cluster stability following neutron irradiation in MA957 oxide dispersion strengthened material, *Journal of Nuclear Materials* 444 (2014) 314–322.
- [51] L. Shao, C.-C. Wei, J. Gigax, A. Aitkaliyeva, D. Chen, B.H. Sencer, F.A. Garner, Effect of defect imbalance on void swelling distributions produced in pure iron irradiated with 3.5 MeV self-ions, *Journal of Nuclear Materials* 453 (2014) 176–181.
- [52] F.A. Garner, Impact of the injected interstitial on the correlation of charged particle and neutron-induced radiation damage, *Journal of Nuclear Materials* 117 (1983) 177–197.
- [53] G.S. Was, *Fundamentals of radiation materials science: metals and alloys*, Springer, 2007.
- [54] S. Ukai, M. Fujiwara, Perspective of ODS alloys application in nuclear environments, *Journal of Nuclear Materials* 307-311 (2002) 749–757.
- [55] S. Ukai, T. Okuda, M. Fujiwara, T. Kobayashi, S. Mizuta, H. Nakashima, Characterization of High Temperature Creep Properties in Recrystallized 12Cr--ODS Ferritic Steel Claddings, *Journal of Nuclear Science and Technology* 39 (2002) 872–879.
- [56] P. Susila, D. Sturm, M. Heilmaier, B.S. Murty, V. Subramanya Sarma, Effect of yttria particle size on the microstructure and compression creep properties of nanostructured oxide dispersion strengthened ferritic (Fe-12Cr-2W-0.5Y₂O₃) alloy, *Materials Science & Engineering A* 528 (2011) 4597–4584.
- [57] V.C. Nardone, J.K. Tien, Pinning of dislocations on the departure side of strengthening dispersoids, *Scripta METALLURGICA* 17 (1983) 467–470.

- [58] V.C. Nardone, D.E. Matejczyk, J.K. Tien, The threshold stress and departure side pinning of dislocations by dispersoids, *Acta Materialia* 32 (1984) 1509–1517.
- [59] N. Dudova, A. Plotnikova, D. Molodov, A. Belyakov, R. Kaibyshev, Structural changes of tempered martensitic 9%Cr-2%W-3%Co steel during creep at 650 °C, *Materials Science & Engineering A* 534 (2012) 632–639.
- [60] E. Nes, N. Ryum, O. Hunderi, On the Zener drag, *Acta Materialia* 33 (1985) 11–22.
- [61] M. Mujahid, J.W. Martin, The effect of oxide particle coherency on Zener pinning in ODS superalloys, *Journal of Materials Science Letters* 13 (1994) 153–155.
- [62] L. He, I. Ihara, K. Niihara, Mechanical properties of Y₂Ti₂O₇, *Scripta Materialia* 64 (2011) 548–551.
- [63] K. Mo, Z. Zhou, Y. Miao, D. Yun, H.-M. Tung, G. Zhang, W. Chen, J. Almer, J.F. Stubbins, Synchrotron study on load partitioning between ferrite/martensite and nanoparticles of a 9Cr ODS steel, *Journal of Nuclear Materials* 455 (2014) 376–381.
- [64] Y. Miao, K. Mo, B. Cui, W.Y. Chen, M.K. Miller, K.A. Powers, V. McCreary, D. Gross, J. Almer, I.M. Robertson, J.F. Stubbins, The interfacial orientation relationship of oxide nanoparticles in a hafnium-containing oxide dispersion-strengthened austenitic stainless steel, *Materials Characterization* 101 (2015) 136–143.
- [65] P. Dou, A. Kimura, T. Okuda, M. Inoue, S. Ukai, S. Ohnuki, T. Fujisawa, F. Abe, Effects of extrusion temperature on the nano-mesoscopic structure and mechanical properties of an Al-alloyed high-Cr ODS ferritic steel, *Journal of Nuclear Materials* 417 (2011) 166–170.
- [66] X. Mao, K.H. Oh, S.H. Kang, T.K. Kim, J. Jang, On the coherency of Y₂Ti₂O₇ particles with austenitic matrix of oxide dispersion strengthened steel, *Acta Materialia* 89 (2015) 141–152.
- [67] J. Ribis, Y. de Carlan, Interfacial strained structure and orientation relationships of the nanosized oxide particles deduced from elasticity-driven morphology in oxide dispersion strengthened materials, *Acta Materialia* 60 (2012) 238–252.
- [68] D.A. Porter, K.E. Easterling, M.Y. Sherif, Phase transformations in metals and alloys, 3rd ed., CRC Press, 2006.

- [69] J.M. Howe, Interfaces in materials, Wiley-Interscience, 1997.
- [70] R.W. Balluffi, S.M. Allen, W.C. Carter, Kinetics of materials, Wiley-Interscience, 2005.
- [71] S. Ukai, Metal, ceramic and polymeric composites for various uses, ISBN 978-953-307-353-8, InTech, 2011.
- [72] Y. Yazawa, T. Furuhashi, T. Maki, Effect of matrix recrystallization on morphology, crystallography and coarsening behavior of vanadium carbide in austenite, *Acta Materialia* 52 (2004) 3727–3736.
- [73] C.M. Parish, R.M. White, J.M. LeBeau, M.K. Miller, Response of nanostructured ferritic alloys to high-dose heavy ion irradiation, *Journal of Nuclear Materials* 445 (2014) 251–260.
- [74] C. Wagner, Theory of the ageing of precipitates by redissolution (Ostwald maturing), *Z. Elektrochem* 65 (1961) 581–591.
- [75] J.D. Robson, Modelling the overlap of nucleation, growth and coarsening during precipitation, *Acta Materialia* 52 (2004) 4669–4676.
- [76] M. Perez, Gibbs-Thomson effects in phase transformations, *Scripta Materialia* 52 (2005) 709–712.
- [77] J. Ribis, M.-L. Lescoat, S.Y. Zhong, M.-H. Mathon, Y. de Carlan, Influence of the low interfacial density energy on the coarsening resistivity of the nano-oxide particles in Ti-added ODS material, *Journal of Nuclear Materials* 442 (2013) S101–S105.
- [78] R.S. Nelson, J.A. Hudson, D.J. Mazey, The stability of precipitates in an irradiation environment, *Journal of Nuclear Materials* 44 (1972) 318–330.
- [79] K.C. Russell, Phase instability under irradiation, *Progress in Materials Science* 28 (1984) 229–434.
- [80] H. Okamoto, Comment of Fe-Y (Iron-Yttrium), *Journal of Phase Equilibria* 16 (1995) 473–473.

Figure 1: SRIM calculation of 3.5 MeV self-ion irradiation of pure Fe.

Figure 2: Bright field images obtained from the unirradiated sample: (a) low magnification micrograph showing a ferrite grain surrounded by tempered martensite grains; (b-c) high magnification micrographs showing dispersoids in the ferrite and tempered martensite phases, respectively; (d) a typical electron diffraction pattern showing the diffraction condition when BF images were taken.

Figure 3: (a) Zero-loss-filtered image showing nano-sized dispersoids; (b-c) corresponding jump-ratio images of iron and titanium, respectively; (d-e) the EDX spectroscopies collected from dispersoids of diameters of ~20 nm and ~3 nm, respectively, with the obtained atomic concentrations.

Figure 4: (a) HRTEM, (b) FFT pattern, and (c) inversed FFT image of a coherent dispersoid of diameter of ~2.5 nm; (d) HRTEM, (e) FFT pattern, and (f) inversed FFT image of an incoherent dispersoid of diameter larger than 10 nm.

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625 °C

475 °C

325 °C

Temp. mart.

Ferrite

Figure 5: Bright field micrographs of dispersoids in (a) the tempered martensite phase and (b) the ferrite phase, receiving 100 local dpa at 625, 475 and 325 °C.

Figure 6: Comparison of dispersoid diameter distributions of the ferrite and tempered martensite grains in (a) as-received samples, (b) samples irradiated at 625 °C and (c) samples irradiated at 475 °C.

Figure 7: mean dispersoid diameter in the tempered martensite phase as a function of depth, irradiated at different temperatures, with error bars being the standard deviations of experimental measurements. Due to possible interference with irradiation induced defect cluster, the reported data for 325°C represents the upper limit of possible dispersoids sizes.

Figure 8: Mean dispersoid size as a function of local dpa at different irradiation temperatures, generated using data obtained from 400-700 nm depths, with error bars being the standard deviations of experimental measurements. Due to possible interference with irradiation induced defect cluster, the reported data for 325°C represents the upper limit of possible dispersoids sizes.

Figure 9: WBDF and BF micrographs of the tempered martensite grains obtained near g_{110} : (a1-2) untreated samples, (b1-2) samples irradiated to ~65 dpa at 625 °C and (c1-2) samples irradiated to ~65 dpa at 475 °C. The electron diffraction pattern at the two-beam condition was involved in each of the BF images. WBDF images were taken at (g, 3g) condition.

Figure 10: (a) BF image and (b) WBDF image obtained from the 100 local dpa region of the sample irradiated at 625 °C to 200 dpa at the peak. The diffraction pattern in (b) shows the two-beam condition of g_{110} achieved when taking the BF image.

Figure 11: (a) HRTEM, (b) FFT pattern, and (c) inversed FFT image of a semi-coherent dispersoid found coherent to (110) of the matrix from the sample irradiated at 625 °C. (d) HRTEM, (e) FFT pattern, and (c) inversed FFT image of a dispersoid found incoherent to the matrix from the sample irradiated at 625 °C. The FFT spots of the dispersoid and Moiré patterns are pointed out with dashed arrows and solid triangles in (b) and (e). Solid arrows in (c) point to some of the dislocations found at the dispersoid-matrix interphase.

Figure 12: Size distributions of total and (110)_M coherent dispersoid in the tempered martensite phase of (a) untreated samples, (b) samples irradiated at 625 °C and (c) samples irradiated at 475 °C, with error bars being the standard deviations of experimental measurements.

Figure 13: Numerical solutions of Equation 3 at different conditions.

Tables

Table 1: Chemical composition of the 12Cr ODS alloy investigated in this study, with Ex. O standing for excessive oxygen

Component:	Fe	C	Cr	Ni	W	Ti	N	Ar	Y ₂ O ₃	Ex. O
Weight, %:	Bal.	0.16	11.52	0.34	1.44	0.28	0.007	0.006	0.36	0.144

Table 2: Dispersoid densities before and after irradiation of ~50 local dpa

Density ($\times 10^{16} \text{ cm}^{-3}$)		As-received	625 °C irradiated	475 °C irradiated
Ferrite $\rho_{F,t}$		19.6 ± 3.6	10.4 ± 3.6	16.1 ± 1.1
Tempered martensite	Total $\rho_{TM,t}$	7.6 ± 0.6	5.4 ± 1.4	12.4 ± 2.6
	Coherent $\rho_{TM,110}$	6.6 ± 1.2	3.7 ± 1.5	11.4 ± 1.2