In situ study on enhanced heavy ion irradiation tolerance of porous Mg

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Mg is known to be highly vulnerable to irradiation damage. Here we show, via in situ Kr ion irradiation studies inside a transmission electron microscope, that both defect density and size have been reduced substantially in porous Mg compared to dense coarse-grained Mg counterpart. Both prism and basal dislocation loops form at low dose in coarse-grained Mg, but basal loops dominate at a higher dose level. Meanwhile, in irradiated porous Mg, basal loops prevail throughout the entire irradiation process. Mechanisms that lead to enhanced irradiation tolerance of porous Mg are discussed.

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Structural materials in nuclear reactors are subjected to severe radiation and their service lifetime is determined by the extent of irradiation damage in terms of void swelling, hardening, and embrittlement, etc. [1–5]. In general, the significant microstructural evolutions may drastically degrade the mechanical properties of irradiated materials. Next-generation nuclear reactors call for the discovery of advanced structural materials that are resistant to high levels of irradiation, up to hundreds of displacements-per-atom (dpa) while maintaining their mechanical and thermal properties [6,7]. Although it remains a significant challenge to design radiation immune materials, numerous approaches have been taken to design irradiation-resistant materials. Most of these approaches take advantages of different types of defect sinks, such as grain boundary (GB), twin boundary (TB), phase boundary, etc. [8–17]. Free surface is also an important type of defect sinks and nanoporous (NP) materials may exhibit enhanced irradiation tolerance because of the large surface-to-volume ratio [18–20]. Prior studies indicate that free surfaces are ideal defect sinks for irradiation-induced point defects and their clusters [8,18,19]. However, irradiation studies on NP materials remain limited. NP Ag and Au show enhanced irradiation resistance due to the elimination of defects by free surface [20–22]. In addition, an enlightening thought has been proposed regarding the development of naturally porous structural materials in nuclear fuels to alleviate the fuel swelling caused by the accumulation of fission gas [23–27].

Furthermore, the effect of crystal structures (e.g. face-centered cubic (FCC); body-centered cubic (BCC); and hexagonal close-packed (HCP)) on irradiation response have also been extensively studied [28–31]. Point defect production is usually different between cubic systems (FCC/BCC) and HCP systems. In the former cases, point defects, including self-interstitials (SIAs) and vacancies, diffuse isotropically whereas anisotropic diffusion often occurs in the later (HCP) cases due to their crystallographic anisotropy [32–34]. For instance, it has been shown that the ratio of defects on prism plane to basal plane produced by electron irradiation strongly depends on the foil orientation in pure Mg [35]. Additionally, it has been shown that the evolution of irradiation-induced defects has a strong correlation with c/a ratio and impurities [29,36,37]. For high-purity monolithic HCP metals, nucleation of loops on basal planes (basal loops) occurs when c/a ratio is greater than the ideal value, 1.633, while prism loops often form when c/a ratio is < 1.633. When purity is low, the formation of basal loops is dominating even when c/a ratio is < 1.633, such as in Mg (c/a = 1.623) and Zr (c/a = 1.593) [36,38–40]. However, radiation damage in HCP metals is far more complex and exceptions have been frequently reported. For instance, basal loops have been observed in Mg [41], Zr [42], Ti [43], in which the c/a ratio is < 1.633. The situation becomes even more complicated in Zr and Ti, where prismatic loops exhibit both vacancy and interstitial characters [44].

500 nm-thick Mg films were deposited by DC magnetron sputtering from Mg targets with the purity of 99.95%. Depositions were performed onto both SiO\textsubscript{2} as well as HF etched single crystal Si (111) substrates. More details on film fabrication can be found elsewhere [45]. X-ray
Diffraction (XRD) experiments were performed on a PANalytical X'Pert PRO Materials Research Diffractometer (Cu Kα irradiation) at room temperature. Plan-view transmission electron microscopy (TEM) specimens were prepared by grinding, polishing, and ion milling. No water was used during the entire specimen preparation process to minimize chemical reaction between Mg and water. In situ irradiation experiment was performed at the IVEM-TANDEM facility at Argonne National Laboratory. Specimens were then irradiated under 1 MeV Kr2+ ion beam at a dose rate of ~5 × 10−4 dpa/s at room temperature. To avoid oxidation issue, the TEM specimens used in this study were made one night before in situ irradiation studies. The irradiation damage profile in the unit of dpa has been calculated by using the SRIM (Stopping and Range of Ions in Matter) with the Kinchin-Pease method [46]. 99.99% of Kr ions penetrated through the 100 nm-thick TEM specimens during irradiation. The temperature rise of specimens measured by thermocouple during irradiation was <10 °C.

The XRD profiles of the as-deposited 500 nm-thick Mg films on both SiO2 and Si (111) substrates in Fig. 1a show polycrystalline Mg forms on SiO2 substrates, while (0002) Mg grows epitaxially on Si (111) substrates. Plan-view scanning electron microscopy (SEM) micrographs in Fig. 1b–c indicate that Mg films on Si (111) exhibit primarily a dense surface, in contrast to porous Mg with hexagonal grains deposited on SiO2. The average grain size in CG Mg is several microns while it is only ~250 nm for porous Mg. The microstructural evolutions in CG and porous Mg under 1 MeV Kr2+ ion irradiation at room temperature are compared in Fig. 1d–k by using two sets of TEM snapshots obtained from in situ irradiation videos. The imaging direction is perpendicular to specimens' surfaces (or along the film growth direction). Before irradiation, both CG and porous Mg appeared relatively clean with little preexisting defects (Fig. 1d and h). However, defects with elliptical shape (prism loops) increased rapidly by 0.0125 dpa in CG Mg (Fig. 1e). Defects with spherical geometry (mostly basal loops) emerged by 0.1 dpa (Fig. 1f). By 0.5 dpa, basal loops with a large number density became dominant (Fig. 1g). In contrast, a gradual and moderate increase of defect density was observed in irradiated porous Mg (Fig. 1i–k). There is little evidence for the formation of prism loops. Scattered basal loops with a much lower number density were observed by 0.5 dpa (Fig. 1k). Suppl. Video 1 shows the comparison of microstructure evolution between CG and porous Mg from 0 to 0.05 dpa. Note that defects in irradiated CG Mg accumulated rapidly and evolved into complex shape, prohibiting a reliable determination of the true defect density in CG Mg. Yet defect density in CG Mg appears to be at least one order of magnitude greater than that in porous Mg.

Representative defect capture events by the free surface in porous Mg are shown by in situ video snapshots in Fig. 2. A small dislocation loop shown in Fig. 2a formed close to the free surface at 0 s. As shown in Fig. 2b–c, the dislocation loop stayed for ~11 s and finally was absorbed by the adjacent free surface instantly by 12 s (see Suppl. Video 2). Fig. 2d shows four dislocation loops (three smaller loops and a slightly larger one) within the grain, and their positions are indicated by white half circles. These dislocation loops were connected by a large dislocation string as indicated by the white dotted line. After 6 s (Fig. 2e), three smaller loops migrated together toward the adjacent free face. By 7 s (Fig. 2f), the three smaller loops migrated together toward the adjacent free face, and the slightly larger loop remained at a similar location (see Suppl. Video 3). The migration process for the dislocation loops is shown in the schematics embedded in Fig. 2d–f. The complex geometry of defects and an enormous increase in the population of defects in CG Mg render it nearly impossible to obtain a reliable measurement of defect density. Nevertheless, it is obvious that due to the defect-surface interaction, both defect size and density have been reduced substantially in porous Mg. As shown in Fig. 2g, the dimension of defect cluster in CG Mg increases rapidly and reaches a saturation value of ~26 nm by 0.03 dpa. In contrast, the defect dimension reaches a

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**Fig. 1.** (a) XRD profiles and (b, c) SEM images of 500 nm thick Mg films deposited on Si (111) and oxidized Si substrates. (d–k) In situ video snapshots of CG Mg and porous Mg during Kr ion irradiation up to 0.5 dpa.
saturation of ~11 nm after 0.1 dpa in porous Mg. The error bar for porous Mg data is much narrower compared to CG Mg data as defects in porous Mg have a much narrower size distribution. Notice that, limited to 2D images, the longest dimension of each defect cluster is measured and the error bar is a standard deviation based on abundant measurement.

Free surface is typically considered as an unsaturable defect sink, and therefore, porous Mg with a large surface-to-volume ratio would exhibit an improved irradiation tolerance compared to the fully dense CG counterparts as manifested by a significant reduction in both defect size and density in porous Mg as observed in this study. The continuous migration of point defects as well as their clusters toward free surface captured by in situ studies (Fig. 2a–f) leads to the decrease in both defect size and density. Although the defect size in porous Mg (~11 nm) is not significantly less than that in CG Mg (~26 nm), the defect density in CG Mg is much higher than that in porous Mg. Furthermore, compared to CG Mg, the defect clusters in porous Mg have a narrower size distribution as evidenced by smaller error bars for porous Mg in Fig. 2g. Thus the overall point defect concentration in irradiated porous Mg is substantially lower than that in CG Mg. Similar phenomena have been reported previously in NP Ag and NP Au using in situ irradiation technique [20,21].

Radiation responses of both high-purity Mg films (99.9999%) and Mg foils with commercial purity (99.8%) have been studied previously. As mentioned earlier, the evolution of defect clusters can be correlated with both the c/a ratio and impurity concentration in HCP metals. Nucleation of basal loops takes place in HCP metals with c/a ratio ≥1.633 and prism loops form in metals with c/a ratio <1.633 due to the higher packing density of prism (10\overline{1}0) planes. The mechanisms for the formation of basal loops in HCP metals with low purity are complicated and remain unclear. Impurities may reduce the SFE of metals, resulting in the formation of faulted dislocations on basal planes [47]. However, Griffiths et al. [36] contended that impurities may contribute to dislocation bias, lattice strain and anisotropic diffusion, which in turn may affect the loop habit planes. In addition to impurities, other factors, such as stresses in irradiated thin foils [48] and the film texture, also need to be taken into account. For instance, the role of impurities in HCP metals with different textures might be different due to the anisotropy in diffusion. However, Khan et al. have shown that in ion irradiated Mg, prism loops are dominating at early stage in all irradiated Mg foils with different textures (prism, intermediate and basal), whereas basal loops are dominating at a higher dose [38]. Clearly, the loop formation mechanism in HCP metals is an intrinsic issue that requires further studies.

Prior studies show that Mg is particularly sensitive to impurities as its c/a ratio (1.623) is very close to the ideal value, 1.633 [36]. Prism loops with Burgers vector 1/3(1\overline{1}0\overline{2}) form in pure Mg (<1 ppm impurities) and basal loops with Burgers vector 1/6(20\overline{2}3) form in impure Mg (≥100 ppm impurities). Khan et al. have studied irradiation damage in commercial purity Mg (≥100 ppm impurities) by both electron beam and ion beam [38]. They found that the primary type of dislocation loops after electron irradiation is the basal loops with Burgers vector 1/6(20\overline{2}3), and most of these loops are of interstitial type [38]. Xu et al. also found that interstitial loops first nucleate on basal planes, followed by the formation of voids in the vicinity of these interstitial loops in electron irradiated Mg [49]. In ion irradiated Mg, it is interesting to note that the interstitial type prism loops with Burger vector 1/3(11\overline{2}0) are dominating at a low dose level (0.1 dpa), whereas basal loops become the majority when irradiation dose increases to 0.7 dpa [38]. These findings are in good agreement with the prevailing view on the formation of dislocation loops in other HCP metals, except that the formation of prism loops at low doses in Mg with low purity. Since the Mg targets used in this study have the impurity concentration larger than 100 ppm, it is natural to speculate that basal loops may dominate in both CG and porous Mg. However, the current in situ studies show that, in CG Mg, a large number of prism loops form at an early stage and finally basal loops take over at higher doses, in agreement with the results reported by Khan et al. for polycrystalline Mg [38].

A schematic in Fig. 3 illustrates the different irradiation responses between CG Mg and porous Mg at 0.1 and 0.5 dpa. In CG Mg, a large number of prism loops form at 0.1 dpa, while the quantity of basal loops is relatively few. However, basal loops dominate at higher dose level (0.5 dpa) in CG Mg. The types of dislocation loops are conjectured from previous studies (defects with elliptical shape are prism loops and those with spherical geometry are basal loops [29,36,38]) as the Mg films degraded quickly after irradiation, prohibiting the post-irradiation g-b studies for the determination of Burgers vector of dislocation loops. In comparison, the primary dislocation loops in porous Mg are basal loops regardless of the dose level. The possible reason that prism loop density in porous Mg is much lower than that in CG Mg at 0.1 dpa is that prism loops with Burgers vector 1/3(11\overline{1}20) glide over a short distance toward the free surface due to the small grain size in porous Mg. However, in CG Mg with large grain size, only those prism loops that are close to grain boundaries may be absorbed efficiently during irradiation, and the rest of the prism loops accumulate rapidly in the grain. As a result, both the density and size of prism loops in CG Mg increase rapidly at the early stage of irradiation. It is likely that the low density of prism loops in porous Mg may be affected by the existence of impurities as well, whereas the case becomes more complicated in CG Mg. At a high dose level (~0.5 dpa in this study), CG Mg exhibits a low density of prism loops, which is not only due to the impurities but also because of the instability of prism loops as compared to the basal loops at higher doses. Prism loops ((1\overline{1}0)0) planes with Burgers vector 1/3(1\overline{1}0\overline{2}) are perfect loops that are glissile and basal loops (on (0001) plane with

Fig. 2. (a–f) In situ video snapshots showing defect capture events by the free surface in porous Mg. (g) Statistics of defect cluster diameter in CG dense Mg and porous Mg.
Burgers vector \(1/6\langle 2023 \rangle\) are sessile [50] (therefore prism loops could migrate toward the free surface in porous Mg with ultra-fine grains). In CG Mg, since the density of defect sinks (GBs in this case) is much lower than that in porous Mg, the annihilation of prism loops is likely to be caused by the reaction among prism loops with other types of loops rather than the absorption of prism loops by GBs. Two possible reactions would be [51]:

\[
\frac{1}{6}\langle 2023 \rangle + 1/3\langle 2\overline{1}10 \rangle \rightarrow \frac{1}{6}\langle 2\overline{2}03 \rangle, \tag{1}
\]

and

\[
\frac{1}{3}\langle \overline{1}1\overline{2}3 \rangle + 1/3\langle \overline{T}T0 \rangle \rightarrow \langle 0001 \rangle \tag{2}
\]

Although Eq. (1) is rarely proposed, it is highly energetically favorable, and may be responsible for the dissociation of prism loops. Loop reaction via Eq. (2) has already been adopted [52] and is also energetically favorable.

The above equations may explain the high-density of basal loops in CG Mg at higher doses. It remains difficult to interpret the formation of prism loops in CG Mg at lower doses. A legitimate explanation shall focus on the nucleation of dislocation loops. A loop habit planes may be determined at its nucleation stage. Prism loops, basal loops and other types of loops with different habit planes may nucleate simultaneously during irradiation. The population of these different types of loops may be determined by factors that impact the subsequent loop growth process. Hence, it is likely that although prism loops nucleate at lower doses cannot survive during the subsequent loop growth process due to its instability compared to the basal loop.

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