Anti-radiation mechanisms in nanoporous gold studied via molecular dynamics simulations

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The radiation resistance performance of nanoporous (NP) gold is investigated by cascade simulations of a gold nanowire using molecular dynamics. The role of the surface on primary defect production was clarified: the mean size of the vacancy clusters (VCs) near the surface in the nanowire becomes larger compared to that of a single crystal. In the surface region, the reduction of the formation and migration energies of point defects leads to a continuous flux of point defects towards the free surface, which retards the formation and growth of defect clusters, resulting in a good anti-radiation performance. In the cascade region, however, the retained vacancies tend to form larger sessile VCs due to their low migration energies and large attractive forces, resulting in radiation damage. The competition between these two factors determines the anti-radiation behavior of NP gold.

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1. Introduction
The irradiation of metals under energetic particles produces a large population of vacancies and self-interstitial atoms (SIAs) [1] that can form clusters, such as dislocation loops [2,3] and voids [4], directly or indirectly. The evolution of these point defects could further lead to amorphization, hardening, or swelling in materials. Therefore, the fusion reactors of the future will require materials that are resistant to extreme radiation conditions without significant changes to their mechanical and thermal properties. Material interfaces can serve as sinks for absorbing and annihilating radiation-induced defects [5–7]. Many experiments have demonstrated that nanostructured materials, such as nanocrystals [8–10], nanolayers [11] and nanoporous (NP) materials [12,13], have superior radiation tolerance compared to their bulk counterparts. Therefore, nanostructured materials are considered to be one of the most promising candidates for the construction materials of nuclear power plants in the future.

NP materials provide a large surface-to-volume ratio due to their three-dimensional open sponge-like structure of interconnected ligaments. Several investigations have focused on the experimental testing [14,15] and computational modeling [16–18] of the mechanical behaviors of NP materials. In general, when materials are subjected to irradiation conditions, a large number of vacancy clusters (VCs) are observed near the surface [19,20] because of the preferential removal of mobile SIAs by free surface. Limited recent studies have been performed on the behavior of NP materials in response to radiation exposure [12,13,21]. With a model and molecular dynamics (MD) simulations, Bringa et al. predicted that the Au NP materials would be resistant to radiation damage over a large dose-rate range [12]. However, these authors only used the diffusivity of point defects to estimate the behavior of defect clusters and did not consider the interactions among the point defects. By using ex situ Ne ion irradiation, Fu et al. [21] reported the dose-rate-dependent formation of relatively stable stacking fault tetrahedra (SFT) in nanoporous Au. Sun et al. [13] directly observed the free surface-induced frequent removal of various types of defect clusters, including SFT, individual dislocation loops and dislocation segments in NP Ag subjected to in situ Kr ion irradiation. They also indicated that both the global and instantaneous diffusivity of defect clusters in NP Ag are lower compared to those in coarse-grained Ag. Therefore, the behavior of defect clustering is an important factor to understand the enhanced radiation resistance of NP materials. Furthermore, the relation between the numbers of defects generated at the primary damage stage and the distance of the primary knock-on atom (PKA) to the surface is critical to the long-term defect structure evolution.
However, to our knowledge, there is no detailed information regarding the distribution of defect clusters in the adjacent region of the surface in NP materials. Therefore, a detailed study is required on the effects of the surface on defect production at the primary damage stage and on the properties of point defects at the long-term evolution stage. In this paper, cascade simulations with energies of 1.0, 1.5 and 2.0 keV are performed at different PKA distances from the surface at 300 K. From the perspective of the thermal behavior of vacancies, the interactions among the vacancies are also analyzed by comparing the energetic parameters and kinetic properties of vacancies between an Au pristine nanowire (NW) and its corresponding cascade NW. Our results indicate that vacancy production is sensitive to the specific distance between the PKA and the surface and exhibits a maximum value versus the distance. The mean size of the interstitial clusters (ICs) between the PKA and the surface and exhibits a maximum value versus the distance. The mean size of the interstitial clusters (ICs) becomes smaller; meanwhile, the size of VCs becomes larger. A competition between the two effects of the surface absorption of point defects and vacancies agglomerating in the cascade zone dominates the anti-radiation behavior of NP materials.

2. Methods

2.1. Details of the MD simulations

A single Au NW structure is created to model the influence of radiation damage on Au NP materials. The origin of coordinate is located in the center of the Au NW; the x-axis (100) and y-axis (010) are set along the radial direction, and the z-axis (001) is set along the axial direction; the periodic boundary condition is used along the z-axis. The static relaxed structure of the Au NW with the conjugate gradient method is shown in Fig. 1. The Au embedded atom model (EAM) potential [22] combined with a ‘universal’ screening function of ZBL [23] at short distances is implemented in the code LAMMPS [24] for our MD simulations. For the EAM potential, the total energy of a system with N atoms is shown as follows:

$$ E = \sum_i F(\rho_i) + \frac{1}{2} \sum_{i<j}^N \phi(r_{ij}). $$

where $\phi(r_{ij})$ is the pair-interaction term between atoms $i$ and $j$ separated by the distance $r_{ij}$, $\rho_i$ is the host electron density at atom $i$ due to the remaining atoms of the system, and $F(\rho_i)$ is the energy to embed atom into the background electron density $\rho$. $\phi(r_{ij})$ can be written as: $\phi(r_{ij}) = E^0/4\pi\epsilon_0 Z(r_{ij})Z(0)\rho_{ij}$, where $Z(r_{ij})$ is the effective charge of the pair-interaction term; $\epsilon$ and $\epsilon_0$ are elementary charge and vacuum permittivity, respectively. The effective charge $Z(r_{ij})$ is joined as follows:

$$ Z(r_{ij}) = \begin{cases} Z_{\text{ZBL}} & (r_{ij} < r_1) \\ \exp\left(b_0 + b_1 r_{ij}^2 + b_2 r_{ij}^3\right) & (r_1 \leq r_{ij} \leq r_2) \\ Z_{\text{EAM–Foiles}} & (r_{ij} > r_2) \end{cases} $$

When $r_1$ and $r_2$ is determined, $b_0$, $b_1$, $b_2$ and $b_3$ can be determined by controlling $Z(r_{ij})$ and $dZ(r_{ij})/dr_{ij}$ continuous at $r_1$ and $r_2$. This combining potential is named as exp-Foiles, whose parameters are shown in Table 1. EAM potentials are widely used for metals because of their accurate description of point defects and surface properties. Another EAM potential developed by Grochola and co-workers [25] is also adopted for comparison. Four different potentials with different joining methods and parameters are applied to compare the results of cascade simulations with energy of 2.0 keV at different PKA distances away from surface of the Au NW. It is found that the tendency of defect production with the PKA distance is nearly the same, so different potentials do not affect the qualitative estimation of the defect production with surface effects. Therefore, the exp-Foiles potential is applied for all calculations in this paper. The MD simulations include two stages. At stage I, the simulation system is released at 300 K with the NVT ensemble (constant number of atoms, volume and temperature) for 10 ps with a time step of 1 fs. At stage II, the NVE ensemble (constant number of atoms, volume and total energy) is applied for 80 ps. At the beginning of this stage, a PKA with a cascade energy of 0.5 keV, 1.0 keV, or 2.0 keV is set at a certain distance from the NW surface. Only the atoms within a shell of approximately 0.4 nm from the outer margin of the NW along the axial direction are under thermostat by applying the velocity rescaling method at 300 K. For all of the MD calculations, the static relaxed Au NW structure is used as an initial configuration and the velocity of the PKA is set along the positive direction of the x-axis. In the following discussion, ‘surface’ normally refers to the surface region, which is safely defined as 0–0.4 nm from the outer face of the NW according to our defect formation energy analysis. To explore the effects of the initial PKA positions on the defect productions, 11 different PKA distances from the surface are chosen, ranging from 1.27 nm to 9.43 nm, with the same interval of 0.816 nm. To reduce the statistical error, 10 independent cascade simulations are performed at each PKA distance. In addition, for comparison, cascade simulations with energies of up to 30 keV are conducted in a single crystal of Au, and the number of stable defects is obtained, as shown in Fig. A.1. The nudged elastic band method [26] is used to calculate the migration barriers of the point defects for examining the mobility of defects near the surface.

2.2. Defect characteristics

The Wigner–Seitz cells method is used to identify the point defects with reference to the static relaxed Au NW structure.

| Table 1 |
|------------------|------------------|------------------|------------------|------------------|------------------|
| $r_1$(nm) | $r_2$(nm) | $b_0$ | $b_1$ | $b_2$ | $b_3$ |
| 0.046716 | 0.1200 | 2.8519159 | 2.8687407 | –8.00470296 | 3.5073770769 |

Fig. 1. Visualizations (AtomEye [29]) of the static relaxed Au NW (left) and the configuration of the defects (right) produced by a cascade energy of 2.0 keV after 80 ps of annealing. The diameter (D) and length (L) of the NW are 10.7 nm and 20.4 nm, respectively. In the static relaxed structure, atoms are colored according to their potential energies. In the configuration of the defects, SIAs and vacancies are marked by red and blue colors, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
defects are considered to belong to the same cluster if their separation is less than a given cutoff [27]. The cutoff for ICs is set as the distance of the first nearest neighbor (1-nn) and that for VCs is set as the distance of the second nearest neighbor (2-nn) because the vacancy–vacancy interaction is attractive in the range of 2-nn and becomes repulsive or negligible at larger distances.

3. Results and discussion

3.1. Defect formation in the Au NW

In single crystal Au, the defect production is position-independent of the PKA, which can be estimated by the Norgett–Robinson–Torrens (NRT) model or calculated by using the MD method, as described in Appendix A. However, defect production is dependent on the PKA distance in NP Au. The defect production in the bulk region by various cascade energies for different PKA distances from the surface is shown in Fig. 2. For comparison, the defect production in single crystal Au with a cascade energy of 2.0 keV described in Appendix A is represented by a horizontal line. The vacancy production is sensitive to the initial PKA position and, in principle, exhibits three regions. For example, for the cascade energy of 2.0 keV, as shown Fig. 2(a), when the PKA is too far from the surface (e.g., 6.0–9.0 nm) to affect the vacancy production, the number of vacancies approaches the horizontal line, that is, the vacancy production is equal to that in single crystal Au within standard errors (region A). When the PKA is closer to the surface (e.g., 2.0–6.0 nm), the number of vacancies is much greater than that of the single crystal (region B) and exhibits a maximum value at approximately 4.5 nm from the surface of PKA. Following our previous work [28], the cascade region is evaluated as 3.0 nm along the direction of PKA velocity, where the cascade region is visualized by showing the displacement vectors between the atomic positions at 0 ps and 80 ps. Therefore, the distance of 4.5 nm is the distance where the center of the cascade region is far from the surface and where the SIAs can still be absorbed efficiently by the surface, leaving a maximum number of vacancies in the cascade region. When the PKA is closer to the surface (e.g., 1.0–2.0 nm), more vacancies are produced within the surface region. In addition, vacancies can also be absorbed by the surface, due to their lower migration barriers in the region close to the surface, which will be discussed later in Subsection 3.3. As a result, a relatively lower number of vacancies is found near the surface than that in the single crystal (region C). The variation of SIA production with PKA distance is quite different from that of the vacancies. As shown in Fig. 2(b), the number of SIAs is less than that in single crystal Au for all of the distances considered due to their high mobility and efficient absorption by the surface. In particular, when the PKA distance is less than 3.0 nm, no self-interstitial atom remains in the bulk region of the Au NW. The number of atoms sputtered away from the surface is reverse to the SIA production (Fig. 2(b) and (c)). When the PKA distance is beyond 4.0 nm, the number of atoms sputtered is negligible, whereas when the PKA distance is less than 4.0 nm, one-to-five times the number of atoms are sputtered away from the Au NW compared to the defects created in the single crystal.

Fig. 2(a) shows that with the increase of the cascade energy, the maximum number of vacancies retained in the bulk region of NW becomes higher and the location corresponding to the maximum value shifts away from the surface into the interior because of the additional momentum of the displaced atoms towards the surface as well as the shift of the cascade region correlated to the cascade energy, as mentioned above. Fig. 2(b) also shows that the number of SIAs retained in the bulk region of NW is not sensitive to the cascade energy because of their high mobility and efficient absorption by the surface. Fig. 2(c) shows that the region of atoms sputtered also becomes wider when the cascade energy increases.

3.2. Behaviors of defect clustering

To understand the important effects of the surface on defect (SIA and vacancy) clustering, three PKA distances from the surface are selected corresponding to those three regions, as indicated in Fig. 2(a). Because no self-interstitial atom remains when the PKA distance is less than 3 nm for all of the cascade simulations (Fig. 2(a)), the size distribution of ICs obviously vanishes in Fig. 3(a) for a PKA distance of 2 nm. For the 4.5 nm of PKA distance, the size distribution of ICs shifts to smaller sizes (Fig. 3(b)) compared to the case of the single crystal (Fig. 3(d)) because the number of SIAs retained in the bulk region of the Au NW is relatively smaller than that in single crystal Au, as shown in Fig. 2(b). The behavior of vacancy clustering is quite different from that of interstitial clustering. Although vacancies are absorbed efficiently by the surface
when cascades are initiated at distances of approximately 2.0 nm to the surface (Fig. 3(a)), there is a slight shift to greater sizes for the distribution of the VCs formed in the bulk region compared to that of the single crystal (Fig. 3(d)). However, for the cascade simulations at approximately 4.5 nm, the size distribution of the VCs significantly shifts to larger sizes (Fig. 3(b)). In fact, SIAs are trapped by the surface and thus cannot recombine with the vacancies retained in the bulk region. Therefore, the more vacancies that are retained in the bulk region, the larger the clusters that can be formed. When a cascade is initiated at approximately 7.0 nm (Fig. 3(c)), which is far enough away from the surface such that the cascade has no direct interactions with the surface, the size distribution of the VCs is similar to that of the single crystal (Fig. 3(d)).

To emphasize our results, we obtained two characteristics of defect clustering near the surface in NP Au: (1) the size distribution of ICs shifts to smaller sizes due to the efficient absorption of SIAs by the surface and, in contrast, (2) the size distribution of VCs shifts to larger sizes.

3.3. Energetic and kinetic properties of point defects in pristine and cascade Au NW

We now discuss the influence of the surface from the perspective of the thermal behaviors of defects by investigating the formation energy and diffusion barrier. As shown in Fig. 4(a), when point defects approach the surface, the formation energies of point defects are significantly lower than those in the bulk region. Furthermore, the migration barriers of point defects also decrease near the surface (Fig. 4(b)). In particular, point defects even diffuse with nearly zero migration barriers in the surface region, which is favorable for point defects to migrate to the surface and rapidly annihilate. Consequently, NP materials are regarded as promising candidates for materials of high radiation resistance due to the ideally unsaturated sink strength represented by a large volume of free surfaces.

Fig. 2(a) and (b) indicate that many more vacancies are retained in the bulk region of the Au NW by cascade simulations compared to those of the SIAs. Thus, the properties of vacancies in the cascade NW are critical for its long-term structural evolution. We compare the energetic and kinetic properties of the vacancies between a pristine NW and its corresponding cascade NW in Fig. 5. The cascade is simulated with a PKA distance of 7.4 nm and a cascade energy of 5 keV at 300 K. After an annealing time of 80 ps, 46 vacancies and 3 SIAs are retained in the bulk region of the NW. The center of all of the vacancies is 4.5 nm to the surface. A region exists in the range of approximately 3.0–6.0 nm to the surface. A region exists in the range of approximately 3.0–6.0 nm to the surface.
of which is consistent with the center of the vacancies retained in the bulk region of the NW. In this region, the formation energies of the vacancies decrease, indicating that vacancies attract each other. In addition, the vacancy migration barriers in this region are significantly lower than those in the pristine Au NW and increase slightly in the periphery (2.0–3.0 nm and 6.0–7.0 nm) of this region. The overall interactions among vacancies which result in agglomeration of vacancies is named as the attractive force. To analyze the attractive force among vacancies qualitatively, vacancies are scattered randomly under certain concentration in a spherical region with the radius of 1.23 nm in Au single crystal. Then, the formation energy per vacancy at different concentrations is calculated. The relationship between the concentration (C) and the mean distance of vacancies (d) is given by this formula: 4/3(πr^3)/d^3 = Cn, where r and n (459) are the radius of the spherical region and the number of total Au atoms in the spherical region, respectively. The formation energy per vacancy as a function of the mean distance of vacancies is shown in Fig. 6. It is obvious that the formation energy per vacancy decreases with decreasing the mean distance of vacancies. In other words, from the perspective of energetic properties of vacancies, vacancies prefer to agglomerate to decrease the formation energy per vacancy. The attractive force vanishes when d is larger than around 0.6 nm (d_c), with which vacancies are then termed as random walkers.

Fig. 7 shows the schematic illustration on anti-radiation mechanisms of Au nanoporous materials. For d is less than d_c, vacancies attract with each other under the influence of the attractive force and agglomerate in the interior of the NW. For d is larger than d_c, vacancies diffuse randomly and may be absorbed by surfaces. The competition between the attractive force among vacancies in the cascade region and the driving force due to free surfaces will determine the accumulation behavior of vacancies in the interior of the NW. On the one hand, a continuous flux of point defects towards the free surface leads to the drainage of the overall point defect concentration in the interior of NP Au. Hence, the formation and growth of defect clusters internally are significantly retarded. On the other hand, vacancies can migrate relatively more easily in the cascade zones and form larger clusters, such as sessile SFT structures, due to the attractive forces among them. In addition, experiments have revealed that point defects and defect clusters can only be absorbed in several-nanometer wide surface-affected zones [13], whereas SFT structures are stable and cannot diffuse in the interior of the NW [21]. By estimating the diffusion coefficient of VCs to be approximately 1% that of a vacancy, Bringa et al. [12] provided a size window of NP Au materials with radiation endurance that depends on the combined effects of two length scales: a diffusion length (l) for defect annihilation relative to the dose-rate (R_d), i.e., l ~ \sqrt{6 \times 10^{-5} \cdot D_c/R_d}, and a characteristic ligament size compared to the collision cascade size. Within this dimensional window, ligaments are large enough not to be melted by the cascade and are still sufficiently small that the time taken by defects to migrate to the ligament surface is less than the time between cascades. However, the interactions among the vacancies retained in the bulk region of the NW are not considered in Ref. [12], leading to the over evaluation of the diffusion coefficient of the VCs. Accordingly, the upper critical size of NP Au materials with
radiation endurance obtained in Ref. [12] is also over-estimated. This effect has been satisfactorily considered by using the cluster dynamics model, but the discussion is beyond the scope of this paper and will be published in the future.

4. Conclusion

MD cascade simulations of Au NW were conducted for investigating the role of the surface in NP Au in the primary defect production. Cascade simulations with energies of 1.0, 1.5 and 2.0 keV were simulated at different PKA distances from the surface at 300 K, respectively. The results indicate that the vacancy production is sensitive to the specific distance between the PKA and the surface and exhibits a maximum value. In addition, the mean size of ICs becomes smaller due to the efficient absorption of SIAs by the surface. Meanwhile, the size of VCs becomes larger. A competition of two effects, that is, the surface absorption of point defects and vacancies agglomerating in the cascade zone, dominates the anti-radiation behavior of NP materials. The mechanisms described above could provide a better understanding of the radiation resistance performance of a material, which can efficiently guide the design of the anti-radiation materials.

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Appendix A. Defect production in single crystal Au

The NRT model [30] gives the number of Frenkel pairs rescaled by an efficiency factor ($\nu$) as

$$N_d(E) = \nu \cdot 0.8 \cdot E / \left(2 \cdot E^c_d\right)$$

(A.1)

where $E$ is the damage energy, which is equal to the cascade energy, and $E^c_d$ is the average displacement threshold energy. The initial work of Bacon and his coworkers indicated that the number of stable Frenkel pairs at the end of a cascade simulation, $N_d$, exhibits a power-law dependence on the cascade energy [31]. Subsequent work by Stoller [32] indicated that three well-defined regions with different power-law energy dependencies exist. As shown in Fig. A.1, depending on our calculated results, two different types of fitting are applied to obtain the relationship between the number of defects and the cascade energy. When the cascade energy is less than 15 keV, a simple power-law energy dependence exists, i.e., $N_d = 3.31 \times E^{0.49}$. When the energy is greater than 10 keV, a basic number is added to the power-law item, i.e., $N_d = 9.8 + 4.0 \times 10^{-5} \times E^{0.96}$. For comparison, the result of the NRT model ($\nu = 0.1$, $E^c_d = 25$ eV) is also shown by the blue line in Fig. A.1.

References