A molecular dynamics simulation of energetics and diffusion of point defects in a Au–Ag alloy

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Abstract. For revealing an aging mechanism for self-irradiation in a Pu–Ga alloy, we carried out a molecular dynamics (MD) simulation on a substitutional material, i.e., Au–Ag alloy. In this work, we estimate physical and microscopic properties of the Au–Ag alloy containing various point defects using a MD method, in particular, formation energy for point defects, migration energy for point defects diffusion into interstitial sites, and diffusion coefficient for the Au–Ag alloy containing point defects, such as vacancy, He atom and He-vacancy (He–V) cluster. The results indicate that volumetric heat capacity and linear expansion coefficient would decrease due to the various point defects, and He atom has the most remarkable influence on the physical properties of the Au–Ag alloy for point defects considered in this work. The formation energy of Au and Ag self-interstitial atom indicates that Octa1 is the most stable site, and structural stability of octahedral (Octa) interstitial sites for the He atom obeys Octa1 > Octa2 > Octa4 > Octa3. For the He_nV_m cluster, the formation energy of the defect structure is most stable at $n = m$. The diffusion coefficient of the He–V cluster is relatively smaller, showing that vacancy defects would further decrease atomic diffusion. An influence of various point defects on the diffusion velocity in the Au–Ag alloy obeys the He–V cluster > He > vacancy > Ag > Au.

Keywords. Radiation damage; point defects; formation energy; migration energy; molecular dynamics.

1. Introduction

Over past few years, we have witnessed dramatic progress in nucleation and growth mechanisms for He behaviour in Pu-based materials, in particular, pure δ phase Pu and Pu–Ga alloys [1–10]. Being a radioactive nuclide, Pu α decay would produce various defects, such as He interstitial atom, self-interstitial atom (SIA) and vacancy, resulting in collision displacement cascade, and disrupt physical, chemical and mechanical properties of the Pu-based system. Therefore, the self-irradiation effect, in particular, behaviour of He defects, would be useful for revealing aging mechanisms in Pu metal. However, we have not yet completely understood the self-irradiation effect in Pu material, in particular, aggregation of He atom, nucleation and growth of a He-vacancy (He–V) cluster and/or He bubble, which still demands for further investigation [10]. Recently, many research groups [11–14] have reported on collision displacement cascade induced by self-irradiation due to α decay in Pu-based materials using a multi-scale simulation technique, e.g., first principles, molecular dynamics (MD) and kinetic Monte Carlo. In fact, experimental work on the behaviour and properties of He atom in δ -Pu is very difficult to perform due to its chemical activity, toxicity, radioactivity and instability of a lattice structure [11–14]; therefore, experimental observation and/or numerical simulation on a substitution material for

the Pu–Ga alloy might be a feasible approach. In principle, two important material properties for studying radiation damage in irradiated materials due to self-irradiation are crystal structure and mass density. Different distributions and types of radiation-induced defects would be produced for different crystal structures with different crystal structures or compositions. On the other hand, mass density influences the distance that an energetic particle transports through a material due to an interaction cross-section between the incident atom and host atom, and thus, affects the concentration of radiation defects [15]. For these reasons, we take the Au–Ag alloy (face-centred cubic structure) as an opposite surrogate for the Pu–Ga alloy (fcc structure). In this respect, physical properties, point defect properties and He behaviour in the Au–Ag alloy might be useful to understand the He behaviour in the Pu–Ga alloy. Stevens *et al* [15] have used transmission electron microscopy (TEM) to investigate the nucleation and growth of He defects in the Au–Ag alloy, and found that He bubbles are not homogeneously distributed across the crystal lattice, and nucleation of He bubbles might not be related to He irradiation in the Au–Ag alloy. For He behaviour in the Au–Ag alloy, Thomé and Grynszpan [16] have investigated radiation damage in a He implanted Au-based alloy (Au₃Ag₂) using a positron annihilation spectrum (PAS) technique. The results indicate that a fundamental reason for the degradation of

the Au_3Ag_2 alloy is an increase in pressure resulting from nucleation and growth of He bubbles. Zhu [17] has studied typical point defects in the Au–Ag alloy, such as He atom interstitial, vacancy and its cluster, from first principles calculations using density functional theory (DFT), and evaluated formation energies for the He atom in individual defect sites. The results show that relative stability of point defects and formation energies of the He atom in the Au–Ag alloy are in close relationship with an atomic configuration of the host atom in the vicinity of the defect site and mass density. Metallurgically, a fcc δ phase Ga 1.0 wt.% Pu–Ga alloy has a mass-density of 15.8 g cm^{-3} . The Au–Ag system is viewed as a suitable surrogate for the Pu–Ga alloy in terms of its complete miscibility, its fcc crystal structure and mass density of the Au–Ag alloy composed of 60 wt.% Au and 40 wt.% Ag. In this work, therefore, we choose a fcc Au–Ag alloy (60 wt.% Au + 40 wt.% Ag) as a candidate for the δ phase Pu–Ga alloy, thus the atomic ratio of Au/Ag is about 9:11.

To our knowledge, some research groups have adopted the first principles method within the framework of DFT to study the physical properties of the Au–Ag alloy and microscopic behaviour of He defects [17], however, seldom reports have paid attention on MD simulation for He behaviour in the Au–Ag alloy. In this work, we will adopt the MD method to analyse the physical properties and He behaviour in the Au–Ag alloy using an embedded atom method (EAM) potential, which might shed light on understanding the He point defects in the Au–Ag alloy. This paper is organized as follows. In section 2, we present a structure model and computational details. Then, we will analyse the influence of point defects on the physical properties of the Au–Ag alloy in section 3. In section 4, we will evaluate the formation energies for single Au and Ag atoms, He atom in octahedral (Octa) and tetrahedral (Tetra) interstitial sites and He_nV_m (V represents vacancy) cluster. Next, we will discuss migration energies for Au, Ag and He atom diffusion into interstitial sites in section 5. In section 6, we will evaluate the effective diffusion coefficient for various point defects using the MD method, and analyse the influence of these defects on the effective diffusion coefficient. Finally, we will give summary remark and outlook in section 7.

2. Computational details

2.1 Structure model

For the simulation model of an Au–Ag alloy, we construct a $5a_0 \times 1a_0 \times 1a_0$ supercell (20 Ag atoms, a_0 represents the lattice constant of fcc Ag metal), and substitute partial Ag atoms by Au atoms to obtain an atomic ratio of Au/Ag as 9:11. Then, we expand this supercell to a periodic $20a_0 \times 20a_0 \times 10a_0$ simulation cell (including 16,000 atoms in total), as shown in figure 1.

For a monatomic fcc crystal, interstitial defects include only two types, i.e., Tetra and Octa interstitial sites due to equivalence of host atoms [18]. However, Au atom is not equivalent to Ag atom in the Au–Ag alloy, hence, interstitial sites for Au and Ag atoms, respectively. According to the atom type and number of the first nearest neighbours (1NN) for interstitial sites, four Octa and two Tetra interstitial sites are shown in figure 2, and the atom type and number are listed in table 1.

2.2 Methodology

All MD simulations in this work are carried out within the classical MD code in the LAMMPS software package. Periodic boundary conditions are adopted. For the formation energy of the interstitial atom in the Au–Ag alloy, an annealing MD method is used to completely relax the Au–Ag alloy including interstitial atom, and obtain an atomic configuration with the minimum energy; computational details for energetics and diffusion properties are presented below.

In MD simulations, we have used Au, Ag and Au–Ag embedded atom model (EAM) potentials of Zhou *et al* [19,20] and He–He potential of Valone *et al* [21]. For Au–He and Ag–He interatomic potentials, we perform first principles calculations on hypothetical Au_3He and Ag_3He crystals ($L1_2$ lattice structure) within the space group of $Pm\bar{3}m$, and fit to a revised form of the universal equation of state of Rose *et al* [1,22].

$$E(R) = -E_c \left(1 + a^* + \mu a^{*3} \frac{r_e}{R} \right) e^{-a^*}, \quad (1)$$

$$a^* = \alpha \left(\frac{R}{r_e} - 1 \right), \quad (2)$$

Figure 1. A simulation model for the Au–Ag alloy. Yellow and blue spheres represent Au and Ag atoms, respectively.

Figure 2. Atomic configuration for four Octa and two Tetra interstitial sites in the Au–Ag alloy. Yellow, blue and red spheres represent Au, Ag and He/SIA atoms, respectively.

Table 1. Number of the first nearest neighbour (INN) for interstitial sites in the Au–Ag alloy.

Interstitial site	Octa1	Octa2	Octa3	Octa4	Tetra1	Tetra2
Number of Au atom	0	2	3	4	1	2
Number of Ag atom	6	4	3	2	3	2

$$\alpha^2 = \frac{9\Omega B}{E_c}, \quad (3)$$

where E_c , r_e , Ω and B are the cohesive energy, nearest-neighbour distance, atomic volume and bulk modulus at the equilibrium reference structure, respectively. μ is a dimensionless quantity related to the pressure derivative of the bulk modulus.

First principles calculations in this work are implemented by DFT using an all-electron full potential linearized augmented plane wave (FP-LAPW) method within the framework of the WIEN2 K code [23–25]. The exchange–correlation energies are approximated with the Perdew–Burke–Ernzerhof (PBE) [26] form of generalized gradient approximation (GGA). The maximum l values for partial waves used inside muffin-tin (MT) spheres are up to $l_{\max} = 10$. The cut-off parameter is $R_{\text{mt}} \times K_{\max} = 9$. In an interstitial region, the charge density and the potential are expanded as a Fourier series with wave vectors up to $G_{\max} = 12 \text{ a.u.}^{-1}$. The MT radius values are set to be 2.00, 2.00 and 1.60 Bohr for Au, Ag and He atoms, respectively. The optimized lattice constants for Au_3He and Ag_3He are 4.0671019 and 4.1256438 Å. The modified EAM (MEAM) potential parameters for Au–He and Ag–He crystals are shown in table 2.

For the formation energies of interstitial atoms in the Au–Ag alloy, MD simulations are carried out using annealing MD under periodic boundary conditions. For the initial configuration containing 16,000 atoms, temperature slowly increases

Table 2. MEAM potential parameters for Au–He and Ag–He interatomic potentials.

Parameter	Au–He	Ag–He	Meaning
E_c (eV)	0.07752	0.11041	Cohesive energy
R_0 (Å)	2.87629	2.91768	Nearest-neighbour distance
α (dimensionless)	34.4269	21.99064	Definition in equation (3)
δ (dimensionless)	6.06854	5.95779	Definition in equation (1)
B (GPa)	97.23950	54.13636	Bulk modulus
Z (dimensionless)	12	12	Number of nearest-neighbour

The parameters are for a fit to the Rose curve.

from 0.0001 to 300 K during 80,000 steps within the NVT ensemble; time step is set to 5.0 fs. The total simulation time of 400 ps (80,000 steps) is enough for the formation energies of interstitial atoms in the Au–Ag alloy though it might seem inadequate for conventional MD simulation. For the He atom or SIA, they are added to the interstitial site when the temperature reaches 300 K. Then, the system is completely relaxed through isothermal MD simulation during 5000 steps within the NPT ensemble ($P = 1.0 \text{ atm}$). Next, the system is slowly cooled to 0.0001 K during 80,000 steps within the NVT ensemble where the volume V is defined as the average value of the above NPT equilibration. Finally, we will obtain an energetically optimal configuration containing interstitial atom.

For the formation energy of the He_nV_m cluster (V represents vacancy), we delete the metallic atom in the centre site of the simulated cell to model a mono-vacancy defect, and then, fully relax this system to reach a new energy equilibrium

Figure 3. Total energy as a function of temperature for the Au–Ag alloy. **(a)** Au–Ag (pure) represents pure Au–Ag alloy free of any defect, **(b)** Au–Ag (V): Au–Ag alloy containing vacancy, **(c)** Au–Ag (Ag): Au–Ag alloy containing Ag interstitial atom, **(d)** Au–Ag (Au): Au–Ag alloy containing Au interstitial atom, **(e)** Au–Ag (He): Au–Ag alloy containing He interstitial atom and **(f)** Au–Ag (He-V): Au–Ag alloy containing He-V cluster. Filled triangle and red solid line are calculation data and linear fitting curve, respectively.

state. Next, we evaluate potential energy of every atom in this system, delete the atom with the maximum potential energy, obtain di-vacancy defects, and evaluate the formation energy of di-vacancy, and so on. Vacancy number would gradually

increase, and we will obtain a vacancy cluster with different sizes and structures. For the He_nV_m cluster, we introduce a He atom in the above vacancy cluster, and then, the system is fully relaxed to reach a new energy equilibrium state. Next,

Table 3. Volumetric heat capacity of the Au–Ag alloy.

Point defect	Pure	V	Ag	Au	He	He-V
Volume, V (10^{-24} cm $^{-3}$)			273671.716			
$\Delta E/\Delta T$ (eV K $^{-1}$)	4.109	4.099	4.079	4.081	4.065	4.095
Volumetric heat capacity, C_V (J cm $^{-3}$ K $^{-1}$)	2.406	2.400	2.388	2.389	2.380	2.397

Pure, V, Ag, Au, He and He-V represent pure Au–Ag alloy free of any defect, Au–Ag alloy containing vacancy, Au–Ag alloy containing Ag interstitial atom, Au–Ag alloy containing Au interstitial atom, Au–Ag alloy containing He interstitial atom and Au–Ag alloy containing He-V cluster, respectively.

we will obtain an atomic configuration containing He_1V_m cluster, and evaluate the formation energy of this cluster. Then, we add another He atom into this system, and evaluate the formation energy of the corresponding system. The largest He_nV_m cluster includes 12 vacancies and seven He atoms in this work, hence, $n/m \leq 7$.

For evaluation of the migration energy for interstitial atom diffusion in the Au–Ag alloy, a nudged elastic band (NEB) method is adopted, however, we do not evaluate energy evolution for interstitial diffusion into its neighbouring sites, but migration energy for interstitial atom diffusion into another interstitial site. For this reason, we first evaluate the total energy of interstitial atoms occupying individual interstitial sites. Then, the interstitial site with the minimum energy is viewed as the initial state to diffuse into the transition state with higher energy, and the NEB method is used to evaluate energy evolution during the diffusion procedure. Finally, migration energy for individual interstitial sites is given by equation (4), i.e., deduced from total energy of the saddle point on the minimum energy path (MEP) minus total energy of the initial site [27,28]

$$E_m = E_s - E_0, \quad (4)$$

where E_m represents the migration energy of atomic diffusion, E_s the total energy of the interstitial atom located at the saddle point on the MEP and E_0 the total energy of a system when the interstitial atom locates the initial site. The more the transition states for defect diffusion between initial and final sites one sets, the more precise the saddle point will be. We set 18 transition states for migration energy of defect diffusion in total.

For evaluation of atomic diffusion properties, classical MD simulation might be a direct method, however, it is relatively hard to calculate the diffusion of point defects, possible reasons are listed as follows. Firstly, the jump frequency of point defects in the internal lattice is relatively low, hence, the count number is not enough to satisfy statistical requirements. Secondly, a relatively smaller system size results in number of point defects hardly reaching equilibrium concentration. Thirdly, only longer simulation times could mimic statistically meaningful particle displacement if the number of point defects is smaller, however, the

time scale at MD simulation does not satisfy this requirement [8]. For these reasons, introducing excess point defects in a simulation cell might be a feasible way. The atomic jump frequency would be greatly increased when many point defects are introduced into the simulation cell, and create statistical atomic displacement during the simulation procedure. Effective diffusion coefficient D_{eff} is given by

$$D_{\text{eff}} = \frac{D_{\text{sim}}}{X_d}, \quad (5)$$

where D_{sim} is the atomic diffusion coefficient and X_d is the concentration of point defects.

According to the diffusion law of Einstein, D_{sim} is defined as

$$D_{\text{sim}} = \lim_{t \rightarrow \infty} \frac{1}{2Nt} \langle |r(t) - r(0)|^2 \rangle, \quad (6)$$

where $r(t)$ represents the atomic coordinate at t , $r(0)$ the initial atomic coordinate and N the dimension of the simulation system. The system in this work is all cubic structure, hence, $N = 3$.

Atomic mean square displacement (MSD) is given by

$$\text{MSD} = \langle r^2(t) \rangle = \frac{1}{n} \sum_{i=1}^n (|r_i(t) - r_i(0)|^2). \quad (7)$$

Merging equation (6) with equation (4), one could obtain

$$D_{\text{sim}} = \frac{\text{MSD}}{6t}. \quad (8)$$

Substituting equation (8) into equation (5), one could obtain an atomic effective diffusion coefficient

$$D_{\text{eff}} = \frac{\text{MSD}}{6X_d t}. \quad (9)$$

During the simulation procedure, we have introduced point defects into the simulation system, and deduced the effective diffusion coefficient from equation (9) through MSD and the concentration of point defects.

Figure 4. Lattice constant as a function of temperature for the Au–Ag alloy. (a) Au–Ag (pure) represents pure Au–Ag alloy free of any defect, (b) Au–Ag (V): Au–Ag alloy containing vacancy, (c) Au–Ag (Ag): Au–Ag alloy containing Ag interstitial atom, (d) Au–Ag (Au): Au–Ag alloy containing Au interstitial atom, (e) Au–Ag (He): Au–Ag alloy containing He interstitial atom and (f) Au–Ag (He–V): Au–Ag alloy containing He–V cluster. Filled triangles and red solid line are the calculated data and linear fitting curve, respectively.

For the atomic effective diffusion coefficient in the Au–Ag alloy, we construct a $20a_0 \times 20a_0 \times 10a_0$ simulation cell (including 16,000 atoms in total), and introduce point defects, such as vacancy, self-interstitial atom (SIA) and He interstitial atom. For the evaluation of the atomic effective diffusion

coefficient, periodic boundary conditions are adopted, and initial atomic velocity obeys Gaussian distribution. Isothermal MD simulation is performed at six different temperatures from 1500 to 2000 K under the NPT ensemble ($P = 1.0$ atm), simulation time at individual temperature is 5.0 ns, then,

Table 4. Linear expansion coefficient of the Au–Ag alloy.

Point defect	Pure	V	Ag	Au	He	He-V
Lattice constant (Å)				4.090		
$\Delta L/\Delta T$ (10^{-6} nm K $^{-1}$)	7.637	7.748	7.774	7.807	7.878	7.812
α (10^{-6} K $^{-1}$)	18.672	18.943	19.007	19.088	19.262	19.100

Pure, V, Ag, Au, He and He-V represent pure Au–Ag alloy free of any defect, Au–Ag alloy containing vacancy, Au–Ag alloy containing Ag interstitial atom, Au–Ag alloy containing Au interstitial atom, Au–Ag alloy containing He interstitial atom and Au–Ag alloy containing He-V cluster, respectively.

Table 5. Formation energy (in eV) of the interstitial atom in the Au–Ag alloy.

Interstitial atom	E_f^{Octa1}	E_f^{Octa2}	E_f^{Octa3}	E_f^{Octa4}	E_f^{Tetra1}	E_f^{Tetra2}
Au	3.081	2.931	2.758	2.737	3.101	3.216
Ag	3.129	3.088	2.894	2.885	3.261	3.295
He	3.527	3.609	4.013	3.652	3.818	4.090

E_f^{Octai} ($i = 1, 2, 3$ and 4) represents the formation energy of the interstitial atom located at the i th Octa site and $E_f^{\text{Tetra}j}$ ($j = 1$ and 2) is the formation energy of the j th Tetra interstitial site.

we record MSD. Finally, we deduce the atomic effective diffusion coefficient through equation (9) and the concentration of point defects.

3. Influence of point defects on physical properties of Au–Ag alloy

3.1 Volumetric heat capacity of Au–Ag alloy

According to volumetric heat capacity defined in equation (10), volume of the simulation system should be fixed when describing total energy as a function of temperature. For this reason, we choose the NVT ensemble for the simulation system, and adopt a Nosé–Hoover thermostat to control the system temperature.

$$C_V = \frac{\Delta E}{\Delta T \times V}, \quad (10)$$

where C_V is the volumetric heat capacity, ΔE the variation of total energy, ΔT the variation of system temperature and V the system volume. System temperature is increased from 2.5 to 1200 K in a total time of 1200 ps, and we determine the temperature and total energy of the simulation system at every 1.0 ps. Then, we obtain a slope of $\Delta E/\Delta T$ through linear fitting, and evaluate the volumetric heat capacity of the Au–Ag alloy containing various defects.

The E – T curve for the Au–Ag alloy is shown in figure 3, and the corresponding volumetric heat capacity is listed in table 3.

The volumetric heat capacity of the Au–Ag alloy would decrease, which is arising from various point defects (table 3), indicating that endothermic capacity would weaken, which is resulting from point defects. A possible reason is that point defects enhance the activity of host atoms, lattice atoms are more apt to displace from original lattice sites, and accordingly reduce volumetric heat capacity. The reduction amplitude for volumetric heat capacity resulting from the He interstitial atom would be the largest one since the He atom is a filled electronic configuration, not readily bonding with host atoms. However, Au and Ag interstitial atoms might bond with host atoms, thus, partial energy would be spent on destroying the bonding behaviours, and endothermic capacity is relatively stronger at higher temperature. As shown in 6th and 7th columns in table 3, vacancy would combine with the He atom, form a stable He-V cluster, increase volumetric heat capacity and make an Au–Ag alloy more stable.

3.2 Linear expansion coefficient of Au–Ag alloy

According to equation (11), we choose an NPT ensemble and periodic boundary conditions because the system volume is variable during the evaluation of the linear expansion coefficient in the Au–Ag alloy

$$\beta = \frac{\Delta L}{\Delta T \times L}, \quad (11)$$

where β is the linear expansion coefficient, L the lattice constant of the Au–Ag alloy and ΔL the variation for the lattice constant.

For evaluation of the linear expansion coefficient, system temperature is increased from 200 to 1200 K with a step of 50 K, and total simulation time is 5.0 ns. We determine the system temperature (T) and volume (V) after thermodynamic equilibrium in the NVT ensemble, evaluate lattice constants at different temperatures, plot lattice constant (L) vs. temperature (T) curve, and obtain slope for the L – T curve through linear fitting. Finally, the linear expansion coefficient is deduced from the initial lattice constant and

Figure 5. Formation energy of the $\text{He}_n \text{V}_m$ cluster as a function of (a) number of vacancies and (b) number of He atoms in the Au–Ag alloy. Individual labels for every curve are shown in the legend.

Figure 6. Total energy as a function of reaction coordinate for (a) Au SIA and (b) Ag SIA diffusion between Octa interstitial sites. Individual labels for every curve are shown in the legend.

$\Delta L/\Delta T$. The L – T curve for the Au–Ag alloy is shown in figure 4 and the linear expansion coefficient is listed in table 4.

The linear expansion coefficient for the Au–Ag alloy would increase due to various point defects (table 4), showing that the introduction of point defects would expand the Au–Ag lattice (hence, volume/lattice constant changes), and reduce the structural stability of the Au–Ag alloy. As discussed above, interstitial atoms would collide lattice atoms, produce atomic displacement, and enhance the activity of host atoms. For this reason, structural stability of the Au–Ag alloy would be more susceptible to destroy when the system temperature is increased. Analogy to volumetric heat capacity, the He interstitial atom poses the largest influence on the linear expansion coefficient. A possible reason is that the inertial He atom is not readily bonded with other atoms, actively collide lattice atom, produce more displaced atoms, and reduce structural stability of the Au–Ag alloys.

Figure 7. Total energy as a function of reaction coordinate for Tetra interstitial diffusion. Hollow circles and filled triangles represent Au and Ag SIAs, respectively.

Table 6. Migration energy, E_m (in eV) of SIA diffusion between various interstitial sites in the Au–Ag alloy.

Interstitial atom	$O_2 \rightarrow O_1$	$O_3 \rightarrow O_1$	$O_4 \rightarrow O_1$	$O_3 \rightarrow O_2$	$O_4 \rightarrow O_2$	$O_4 \rightarrow O_3$	$T_1 \rightarrow T_2$
Au	0.269	0.545	0.537	0.376	0.351	0.260	0.441
Ag	0.213	0.376	0.365	0.353	0.330	0.234	0.401

O_i ($i = 1, 2, 3$ and 4) represents the i th Octa site and T_j ($j = 1$ and 2) is the j th Tetra site.

Figure 8. Total energy as a function of reaction coordinate for He diffusion between (a) Octa and (b) Tetra interstitial sites, respectively. Individual labels for every curve are shown in the legend.

4. Formation energy of point defects

4.1 SIA and He atom

In this subsection, we adopt the MD method to evaluate the total energies of Au, Ag SIAs and He occupying interstitial sites after annealing at 0 K, and then, deduce the formation energies of Au, Ag and He located at various interstitial sites in the Au–Ag alloy from equations (12) and (13) as listed in table 5.

The formation energy of SIA is given by

$$E_f(\text{SIA}) = E_t(16,001X) - E_t(16,000X) - E_t(X), \quad (12)$$

where X represents the host atom (Au/Ag atom in this work). $E_t(X)$ the total energy of a single host atom. $E_t(16,000X)$ is the total energy of the ideal lattice including 16,000 metallic atoms, while $E_t(16,001X)$ is the total energy of the above system including a SIA.

As shown in table 5, for Au and Ag Octa SIAs, formation energy of the Octa4 interstitial site is the smallest, and the sequence of formation energy is $E_f^{\text{Octa1}} > E_f^{\text{Octa2}} > E_f^{\text{Octa3}} > E_f^{\text{Octa4}}$, indicating that the structure for Octa4 SIA is most stable. However, the formation energy of Octa3 SIA is close to that of Octa4 SIA, namely these two sites have the same structural stability. The formation energy of Octa interstitial defects would decrease with an increase in the

first nearest neighbour (1NN) Au atoms in terms of 1NN for the interstitial site, implying that defect structures of Octa interstitial would increase resulting from an increase in Au atoms, and enhance structural stability. For the Tetra interstitial site, the formation energy of the Tetra1 interstitial atom is relatively smaller, showing that its structural stability is more stable, namely stability of the defect structure would enhance with a decrease in 1NN Au atoms for the interstitial site.

For the Octa defect structure of the He atom in the Au–Ag alloy, the formation energy of the Octa1 site is the smallest, indicating that the Octa defect structure of the He atom occupying this site is most stable. The sequence for the formation energy of Octa defect structures is $E_f^{\text{Octa3}} > E_f^{\text{Octa4}} > E_f^{\text{Octa2}} > E_f^{\text{Octa1}}$, i.e., structural stability of Octa interstitial sites for the He atom obeys Octa1 > Octa2 > Octa4 > Octa3. For the Tetra interstitial defect structure, the formation energy of the Tetra1 site (3.818 eV) is smaller than that of the Tetra2 site (4.090 eV), implying that the Tetra defect structure for the Tetra1 site is more stable.

4.2 He-vacancy cluster

As mentioned above, the Pu material would produce He atom which is insoluble with the material matrix resulting from the spontaneous α decay during long-term storage, and these He atoms are readily combining with vacancy (V) to form

Table 7. Migration energy E_m (in eV) of He atom diffused between various interstitial sites in the Au–Ag alloy.

Interstitial atom	$O_1 \rightarrow O_2$	$O_1 \rightarrow O_3$	$O_1 \rightarrow O_4$	$O_2 \rightarrow O_3$	$O_2 \rightarrow O_4$	$O_4 \rightarrow O_3$	$T_1 \rightarrow T_2$
He	0.469	0.722	0.507	0.678	0.271	0.648	0.622

O_i ($i = 1, 2, 3$ and 4) represents the i th Octa site and T_j ($j = 1$ and 2) is the j th Tetra site.

Figure 9. MSD as a function of simulation time for the Ag atom in the Au–Ag alloy containing (a) Ag SIA and (b) Au SIA. Individual labels for every curve are shown in the legend.**Table 8.** Diffusion coefficient for Ag atom in the Au–Ag alloy.

Simulation system	Diffusion coefficient	1500 K	1600 K	1700 K	1800 K	1900 K	2000 K
Au–Ag (Au)	$D_{sim}^{Ag} (10^{-2} \text{ nm}^2 \text{ ps}^{-1})$	0.7511	0.8772	1.009	1.152	1.295	1.455
	$D_{eff}^{Ag} (\text{nm}^2 \text{ ps}^{-1})$	1.5023	1.7544	2.018	2.305	2.589	2.91
Au–Ag (Ag)	$D_{sim}^{Ag} (10^{-2} \text{ nm}^2 \text{ ps}^{-1})$	0.756	0.8843	1.016	1.125	1.279	1.425
	$D_{eff}^{Ag} (\text{nm}^2 \text{ ps}^{-1})$	1.512	1.7686	2.026	2.25	2.557	2.85

Au–Ag (Au) and Au–Ag (Ag) represent Au–Ag alloy containing Au SIA and Ag SIA, respectively. D_{sim}^{Ag} and D_{eff}^{Ag} are simulated and effective diffusion coefficients for Ag atom in the Au–Ag alloy, respectively.

a He_nV_m cluster, of which formation energy is useful for understanding the He behaviour in the material. We evaluate the formation energy of the He_nV_m cluster in an alternate candidate for the Pu–Ga alloy, i.e., Au–Ag alloy, as shown in figure 5a and b ($n > 30$, not shown here).

As shown in figure 5a, the formation energy of the He_nV_m cluster gradually decreases with an increase in vacancy when the number of He atoms is fixed, and the formation energy reaches the minimum value if number of He atoms is equal to that of vacancies, i.e., $n = m$. The formation energy of the He_nV_m cluster gradually increases with a further increase in He atoms, indicating that the He_nV_m cluster is most stable at $n = m$. One may draw the same conclusion from the formation energy of the He_nV_m cluster as a function of He atom n (figure 5b), namely formation energy would first decrease

and then increase with an increase in the He atoms when the number of vacancies is kept constant. The formation energy would reach the minimum value at $n = m$. One could see from figure 5a and b that the structure of the He_nV_m cluster is most stable when one vacancy is occupied by one He atom in the Au–Ag alloy.

5. Migration energy of point defects

5.1 Migration energy of SIA

As discussed above, we have evaluated formation energies for various interstitial sites, and find that structural stability

Figure 10. MSD for Ag atom in the Au–Ag alloy containing (a) vacancy and (b) He atom. Individual labels for every curve are shown in the legend.

for Octa interstitial defects obeys Octa1 < Octa2 < Octa3 < Octa4, while for Tetra interstitial defect Tetra2 < Tetra1. Then, we choose a relatively stable defect structure for SIA in the Au–Ag alloy as an initial diffusion state, while another relative unstable defect structure as a final state, and describe evolution of total energy between initial and final states using the NEB method. The results for Octa and Tetra SIA diffusion are shown in figures 6 and 7, respectively. Migration energy E_m deduced from equation (4) is listed in table 6.

As shown in table 6, migration energy for Au SIA diffusion from Octa4 to Octa3 is the smallest case, indicating that SIA located at the Octa4 site is the most apt to diffuse into the Octa3 site. However, Au SIA located at the Octa3 site tends to diffuse into the Octa2 site. These observations establish that Au SIA would diffuse between Octa interstitial sites with similar structural stability. Note, however, that migration energy of Ag is smaller than that of the Au atom at the same diffusion sites, indicating that Ag SIA is more apt to diffuse into other interstitial sites as compared to Au SIA. Octa4 → Octa2 and Octa4 → Octa1 diffusion paths are similar to Octa3 → Octa2 and Octa3 → Octa1 (figure 7), respectively. For Octa4 → Octa3 diffusion, total energy for the initial state is close to its final state, implying that total energy of the defect structure for Octa4 SIA is close to that of Octa3 site, which is consistent with formation energies for E_f^{Octa3} and E_f^{Octa4} .

5.2 Migration energy for He atom

In section 4, we have evaluated the formation energies for Octa and Tetra He interstitial atoms. In this section, we will evaluate migration energy for He diffusion from a relatively stable interstitial site to a relatively stable interstitial site using the NEB method, and total energy as a function of reaction coordinate for different He interstitial sites is shown in figure 8a and b. Migration energy E_m deduced from equation (1) is listed in table 7.

As shown in figure 8a, Octa1 → Octa3, Octa2 → Octa3 and Octa4 → Octa3 diffusion paths are similar, indicating that total energies and spatial arrangements for He Octa1, Octa2 and Octa4 interstitial sites are also similar. The formation energy of He Octa3 sites is remarkably larger than those of the other three interstitial sites (table 7), and formation energies of Octa1, Octa2 and Octa4 are close to each other, which verify the above conclusion. In addition, migration energies for Octa1 → Octa3, Octa2 → Octa3 and Octa4 → Octa3 paths are larger than those of other diffusion paths, and total energy of the Octa3 site is obviously larger than those of the other sites, also verifying the above conclusion.

6. Calculation of effective diffusion coefficient

6.1 SIA

To further understand the SIA behaviour in the Au–Ag alloy, we evaluate the effective diffusion coefficient of the Ag atom for the Au–Ag alloy containing 0.5 at.% SIA. For evaluation of the atomic effective diffusion coefficient, 80 Au and 80 Ag atoms are introduced into the Au–Ag alloy, respectively. Periodic boundary conditions and NPT ensemble are adopted. Isothermal MD simulation (total simulation time is 5.0 ns) is performed at six different temperatures from 1500 to 2000 K, and then, we record Ag MSD in the Au–Ag alloy as shown in figure 9a and b. Next, we linearly fit the MSD curve, and obtain a slope of MSD vs. t curve. Finally, we deduced simulated and effective diffusion coefficients for the Ag atom in the Au–Ag alloy containing Au/Ag SIAs through equation (12) in table 8.

As shown in table 8, the effective diffusion coefficient for the Ag atom in the Au–Ag alloy would enhance with an increase in temperature, no matter whether the introduction of the Au or Ag atom. A possible reason is that, as we all know, temperature will increase the average kinetic energy when the

Table 9. Diffusion coefficient for Ag atom in the Au–Ag alloy containing vacancy and He atom.

System	Diffusion coefficient	1500 K	1600 K	1700 K	1800 K	1900 K	2000 K
Au–Ag (V)	$D_{\text{sim}}^{\text{Ag}}$ ($10^{-2} \text{ nm}^2 \text{ ps}^{-1}$)	0.7453	0.8893	1.003	1.147	1.299	1.413
	$D_{\text{eff}}^{\text{Ag}}$ ($\text{nm}^2 \text{ ps}^{-1}$)	1.491	1.777	2.006	2.294	2.598	2.826
Au–Ag (He)	$D_{\text{sim}}^{\text{Ag}}$ ($10^{-2} \text{ nm}^2 \text{ ps}^{-1}$)	0.7198	0.8363	0.988	1.1003	1.2635	1.389
	$D_{\text{eff}}^{\text{Ag}}$ ($\text{nm}^2 \text{ ps}^{-1}$)	1.4396	1.6726	1.976	2.2006	2.527	2.779

Au–Ag (V) and Au–Ag (He) represent Au–Ag alloy containing vacancy and He atom, respectively.

$D_{\text{sim}}^{\text{Ag}}$ and $D_{\text{eff}}^{\text{Ag}}$ are simulated and effective diffusion coefficients for Ag atom in the Au–Ag alloy, respectively.

Figure 11. MSD as a function of simulation time for (a) Ag and (b) Au in the Au–Ag alloy containing He–V cluster. Individual labels for every curve are shown in the legend.

interatomic interaction is fixed. For this reason, it is expected that diffusion, being an activated process, of which effective diffusion coefficient will increase with temperature. Therefore, the Ag atom would move faster, and MSD and effective diffusion coefficients for the Ag atom would be larger. However, the effective diffusion coefficient for the Ag atom in the Au–Ag alloy containing Au SIA would be larger at the same temperature because Au is higher in atomic number and electron number. An interaction between Au and Au/Ag atoms is obviously higher than those of Ag atoms; the introduction of the Au atom would activate lattice atoms and enhance atomic diffusion.

6.2 Vacancy and He atom

For migration energies of vacancy and He atoms, 80 vacancies and He atoms are introduced into the Au–Ag alloy, respectively. Isothermal MD simulation (total simulation time is 5.0 ns) is performed at six different temperatures from 1500 to 2000 K, and then, we record Ag MSD in the Au–Ag alloy as shown in figure 10. Next, we linearly fit the MSD curve, and obtain a slope of MSD vs. t curve. Finally, we deduce simulated and effective diffusion coefficients for vacancy and the He atom in the Au–Ag alloy through equation (12) in table 9.

As shown in table 9, temperature rise would enhance atomic diffusion in the Au–Ag alloy. Compared to the effective diffusion coefficient for the Ag atom in the Au–Ag alloy containing vacancy and He atom at the same temperature, one could see that the He atom is not readily bonding with the Au and/or Ag atom due to its filled shell electron configuration, and has a strong repulsion with the matrix atom, resulting in a decrease of atomic diffusion. However, vacancy is more apt to combine with the matrix atom, and makes atom readily diffusion into vacancy defects. Therefore, the He atom has a stronger suppression on diffusion in the Au–Ag alloy.

6.3 He-vacancy cluster

For the effect of the He–V cluster on atomic diffusion in the Au–Ag alloy, we construct a $20a_0 \times 20a_0 \times 10a_0$ simulation cell (16,000 atoms), and introduce a $\text{He}_{80}\text{V}_{16}$ cluster composed of 80 He atoms and 16 vacancies. For the evaluation of the atomic diffusion coefficient, periodic boundary conditions are adopted, and initial atomic velocity obeys Gaussian distribution. To analyse the influence of temperature on atomic diffusion, isothermal MD simulation is performed at six different temperatures from 1500 to 2000 K under the NPT ensemble, and then we record Ag MSD in the Au–Ag alloy as shown in figure 11a and b. Next, we linearly

Table 10. Diffusion coefficient for Ag/Au atom in the Au–Ag alloy containing He–V cluster.

System	Diffusion coefficient	1500 K	1600 K	1700 K	1800 K	1900 K	2000 K
Au–Ag (He–V)	$D_{\text{sim}}^{\text{Ag}} (10^{-2} \text{ nm}^2 \text{ ps}^{-1})$	0.7311	0.8291	0.9603	1.093	1.249	1.388
	$D_{\text{eff}}^{\text{Ag}} (\text{nm}^2 \text{ ps}^{-1})$	1.4622	1.6582	1.9206	2.186	2.498	2.776
	$D_{\text{sim}}^{\text{Au}} (10^{-2} \text{ nm}^2 \text{ ps}^{-1})$	0.6971	0.8243	0.9466	1.067	1.2165	1.3435
	$D_{\text{eff}}^{\text{Au}} (\text{nm}^2 \text{ ps}^{-1})$	1.3942	1.6486	1.8932	2.134	2.433	2.687

$D_{\text{sim}}^{\text{Ag}}$ ($D_{\text{sim}}^{\text{Au}}$) and $D_{\text{eff}}^{\text{Ag}}$ ($D_{\text{eff}}^{\text{Au}}$) are simulated and effective diffusion coefficients for Ag (Au) atom in the Au–Ag alloy, respectively.

fit the MSD curve, and obtain a slope of MSD vs. t curve. Finally, we deduce simulated and effective diffusion coefficients for the Ag/Au atom in the Au–Ag alloy containing a $\text{He}_{80}\text{V}_{16}$ cluster through equation (12) and are listed in table 10.

As shown in table 10, temperature rise would enhance atomic diffusion in the Au–Ag alloy, and the effective diffusion coefficient for the Ag atom is somewhat larger than that of the Au atom at the same temperature, the Ag atom moves faster, and is more apt to diffuse. A possible reason is that the diffusion velocity of Ag is slower than that of the Au atom due to the atomic weight of Au being larger. Compared to the diffusion coefficient of the Ag atom in the Au–Ag alloy containing He atom in table 8, the diffusion coefficient of the He–V cluster is relatively smaller, indicating that the introduction of vacancy defects would further decrease atomic diffusion, vacancy is readily combined with the He atom to form a stable He–V cluster, enhance structural stability of the Au–Ag alloy, and hinder atomic diffusion, namely the He–V cluster has a remarkable inhibition on atomic diffusion.

7. Summary and outlook

In this work, we have evaluated energetics and diffusion properties of the Au–Ag alloy containing various point defects using a MD method, in particular, formation energy for point defects, migration energy for point defects diffusion into interstitial sites, and diffusion coefficient for the Au–Ag alloy containing point defects, such as vacancy, He atom and He–V cluster. The results show that a melting point, volumetric heat capacity and linear expansion coefficient would decrease resulting from the introduction of various point defects, He atom has the most remarkable influence on the physical properties of the Au–Ag alloy for various point defects considering in this work. For the He_nV_m cluster, the formation energy of the defect structure is most stable at $n = m$. SIA is more apt to diffuse between two Octa interstitial sites with similar structural stability. The diffusion coefficient of the He–V cluster is relatively smaller, indicating that the introduction of vacancy defects would further decrease atomic diffusion, vacancy is readily combining with He atom to form a stable

He–V cluster, enhance structural stability of the Au–Ag alloy and hinder atomic diffusion. The influence of various point defects on diffusion velocity in the Au–Ag alloy obeys He–V cluster > He > vacancy > Ag > Au. This work could be viewed as an analogous work to investigate point defects in the Pu–Ga alloy, in particular, nucleation and growth mechanism for He bubbles in aging the Pu–Ga alloy. In future works, we plan to adopt the MD method and/or the mesoscopic technique to simulate the properties of point defects, such as SIA, He–V cluster and He bubbles in Pu–Ga alloys, and compare the theoretical result with available experimental data, such as TEM, SEM and PAS examination of He–implanted and/or aging samples.

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