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Determination of thermal and nucleation rate properties of Pd-Au, Pd-Au and Ag-Au metallic systems: A molecular dynamic study

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Molecular dynamics (MD) simulation employing Sutton-Chen (SC) based on embedded atom method was used to investigate the effect of Au addition to Pt, Pd and Ag metallic systems on the thermal properties, lattice parameters and nucleation rates at nano-scale. The potential energies, melting temperatures and heat of fusions of systems were determined by using MD calculations. The nucleation rates for systems were examined with classical nucleation theory (CNT) during the solidification at a slow cooling rate. The structural characteristics from melt to solid were analyzed with radial distribution function (RDF) curves during the phase transitions. The crystal-type bonded pairs described by indexes of Honeycutt-Andersen (HA) method were considered as embryos in the systems. As a result, the simulation results were in good agreement with the experimental and other simulation studies based on CNT.

Keywords: Molecular dynamics, classical nucleation theory, metallic alloys, Honeycutt-Andersen method.

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1. Introduction

Recently, the binary metallic alloys have been known as functional materials because they exhibit a specific role in thermal and mechanical characterizations [1-3]. Hence, the understanding of their different properties of these alloys have a powerful interest in materials science [4]. Specially, the nucleation and crystallization mechanism effect on the functional properties of materials due to the character of phase equilibria [5, 6]. Au-doped Ag, Pt and Pd binary alloys exhibit the important physical properties, but there are still several shortcomings in homogeneous nucleation mechanisms of these systems during solidification process at the atomic level.

Although many studies on the nucleation and crystallization process have been monitored as many experimental studies or microscopic methods for years [4, 7-9], there are several experimental difficulties in nucleation mechanism, such as nucleation rate. Hence, there is not much knowledge about the details of the nucleation rate on the microscopic level [10, 11]. On the other hand, alternative investigations for understanding the phenomena of nucleation rate have been applied by using computational methods based on classical nucleation theory (CNT) [12-14]. Molecular dynamics (MD) simulation method enables to understand the different physical properties of materials.

In this study, we employed MD simulation method utilizing the SC-EAM potential function for $Ag_{50}Au_{50}$, $Pd_{50}Au_{50}$ and $Pd_{50}Au_{50}$ binary alloy systems. We also provided the details of the melting points, volumes, heat of fusions and potential energies at 300 K. The nucleation rates of systems from melt to solid are estimated by using MD method. We analyzed the structural development of the system using RDF analysis and the total energies at given temperatures. Specially, we indicated that the effect of pressure on nucleation rate which important for nucleation was investigated by using computational method.

2. Material and Methods

2.1. Simulation details

In our study, the potential function is employed as the interatomic interactions developed by SC version of EAM [15]. The SC potential consists of two contributions to the total energy (E_{tot}) for entire system with N atoms. The total energy can be expressed as [16]

$$\sum_i ((F\overline{(\rho_i)} + \frac{1}{2}\sum_{j\neq i}(\phi(rij)) \qquad (1)$$

where F_i is the embedding energy as a function of electron density. ϕ_{ij} is the pair potential and r_{ij} is the distance between atoms. More knowledge for EAM parameters of systems have been detailed by previously studies [17, 18]. The probability of finding of an atom in the circle with the radius of r around a given center atom enable to probe the structural evolution of a system [19]. This structural development can be defined with radial distribution function (RDF). The RDF, g(r), is defined as

$$g(r) = \frac{V}{N^2}\langle\frac{\sum_i n_i(r)}{4\pi r^2 \Delta r}\rangle \qquad (2)$$

where V is volume the MD box, N is the number of atoms and n(r) represents the number of atoms around a central atom within the circle [19].

MD simulation of alloy systems is performed using Parrinello-Rahman based on classical calculations [20]. The present simulation is formed with periodic boundary conditions under the NPT ensemble with 4.000 atoms. Firstly, the alloy systems are heated from 300 K to melting temperature as known experimental. Then, the system runs at liquid phase at 500.000 MD steps for isothermal relaxation. In the end, the liquid systems are cooled from melting points to 300 K at a slow cooling rate of 9.0×10^{10} K/s.

2.2. Nucleation rate

CNT is used as an important tool for understanding the homogenous nucleation kinetics [4]. According to CNT, the number of unfrozen clusters (Nn) and nucleation rate can be written as

$$ln\left(\frac{N_n}{N_0}\right) = -JV_c(t - t_0) \qquad (3)$$

Where N_0 is the number of cluster and Vc effective volume of cluster [10, 11].

1. Results and Discussion

Fig. 2 shows the changes in total energy with temperature during heating process of Pt-Au, Pd-Au and Ag-Au systems. As seen from figure that the total energy of systems increases with increases temperature. When a discontinuous change in the total potential energy at a certain temperature occurs, this temperature value is known as melting point of system. We obtain the melting temperatures of Pd-Au, Pt-Au and Ag-Au as 1600±10 K, 1500±10 K and 1400±10 K, respectively. The highest melting temperature is determined in Pd-Au system

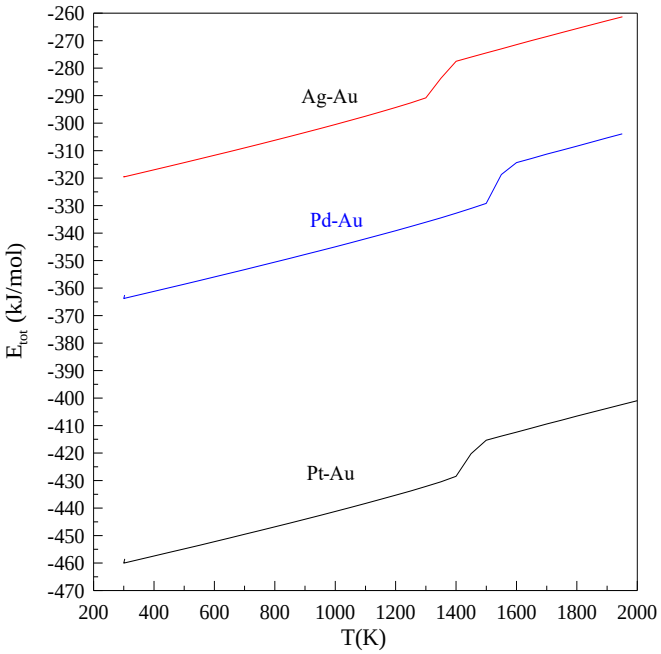

Fig. 2. The variation of total energy of systems with temperatures during the heating.

The structural characteristics of a system during the phase transitions can be analyzed by RDF curves. Hence, The RDF is a useful tool to describe the structural changes of a system [32]. Fig. 3. shows the RDF curve peaks at defined atomic distances at 300 K temperature in the final heating process. As seen from figure that all systems are close to fcc crystal structure because RDF peaks at atomic distances define the fcc lattice properties. When RDF curves are analyzed, the lattice parameters are obtained as 4.09 Å for Ag-Au, 4.0067 Å for Pd-Au and 3.99 Å for Pt-Au at 300 K. These physical parameters are listed in Table 1.

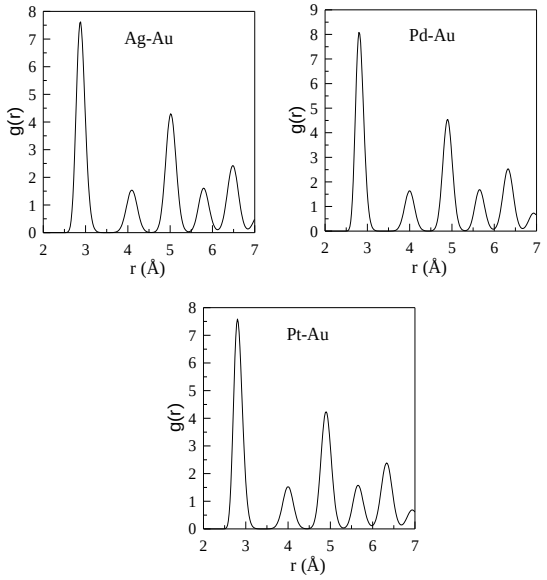

Fig. 3. The variation of RDF curves of systems at 300 K temperature in the final heating process.

The estimation of nucleation rate is a central subject to understand the nucleation mechanism of a system [4, 18, 19]. For modelling systems, the nucleation rates obtained by MD calculations according to Eq. (3) are plotted in Fig. 4 and summarized in Table 1. The nucleation rates derive from the slopes of curves in the figure. Here, N_{cry} represents the total number of crystal-type bonded pairs and N_0 is the number of total clusters of systems. While the highest nucleation rate obtains for Pd-Au system, the lowest nucleation rate obtains for Pt-Au during the solidification. This result indicated that the adding of Pd to Au increase the nucleation rate. Hence, Pd-doped to Au system favors for easily crystallization compared to Pt/Ag doped.

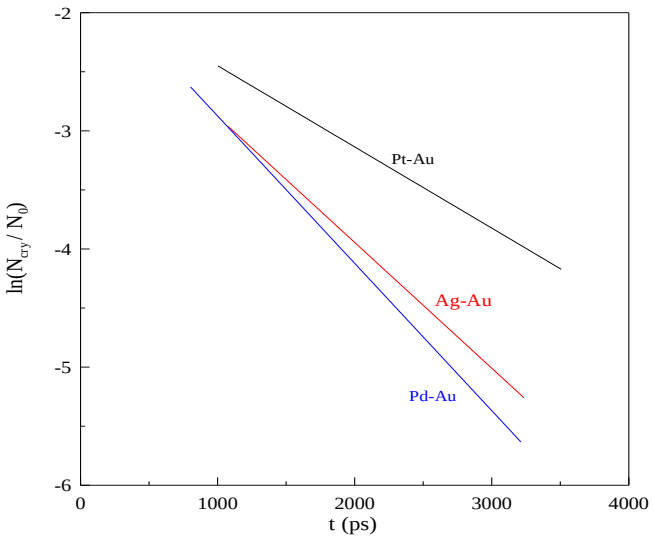

Fig. 4. The plots ln (N_{cry}/N_0) versus time for systems.

Table 1. The physical parameters and nucleation rates of systems.

T = 300 K					
	V (Å^3/atom)	Ep (eV/atom)	Tm (K)	Lattice paramaters (Å)	J (×10^{-35}, m^{-3}s^{-1})
Ag-Au	17.33	-3.35	1400	4.09	1.06
Pt-Au	16.19	-4.80	1500	3.99	0.69
Pd-Au	16.16	-3.80	1600	4.0067	1.24

3.Conclusion

In this study, we have calculated some thermal and structural properties of $Cu_{50}Ag_{50}$, Pt_{50}-Au_{50}, Pd_{50}-Au_{50} binary alloy systems by using MD calculations. The potential energy is used to Sutton-Chen version of EAM. The nucleation rates during the cooling process are estimated by computational method based on CNT. On the other hand, the structural analysis was analyzed with RDF. This result indicated that the adding of Pd to Au increase the nucleation rate. Hence, Pd-doped to Au system favors for easily crystallization compared to Pt/Ag doped.

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