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The concentration effect of Pd and Pt-doped Cu on short range order formation in the rapid cooling process with molecular-dynamics simulation

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ABSTRACT

In this study, the formation of bonded pairs which represent amorphous and crystalline structures of Cu-Pd and Cu-Pt ordered alloy systems for different composition of copper was determined with molecular dynamic simulation method during the fast cooling process. The structural properties and phase transformation of systems at different temperatures were investigated with radial distribution functions. The structural formation of bonded pairs was obtained by using Honeycutt-Andersen (HA) method. Physical interactions among atoms were modelled using Sutton-Chen (SC) type of the Embedded Atom Method (EAM) based on many-body interactions. During the rapid cooling process, an amorphous phase conversion was observed at 300K and an increase in the number of bound pairs representing the amorphous phase was detected.

1. Introduction

The field of use of platinum, palladium group metals has increasingly expanded with developing technology and changing environmental regulations [1]. Platinum is a heavy, malleable element with the symbol Pt which has grayish white color and is very important in terms of technology. In recent years, it has increasingly concentrated on the studies on platinum and palladium alloys [2-4]. Platinum (Pt) is commonly used in industrial applications due to its superior properties including high abrasion resistance, high catalytic properties, corrosion resistance and excellent workability [5]. Palladium (Pd) is a very similar metal to platinum. It is used as raw material in many products due to its interesting properties. Palladium is among valuable metals in both economic and chemical aspects [6]. It is the building block of white gold and sometimes referred to as “white gold”. it is obvious that experimental studies on platinum and palladium alloys are not sufficient. One of the most important reason of this is the fact that these metals are very expensive substances [7,8].

In parallel with developments in nanotechnology, it is understood that many physical properties of materials are determined by nanostructured atomic groups within the material. However, such groups or clusters can structurally change in a very short time or transform into differently atomic groups [9]. Such different groups usually occur during thermal processes and phase transitions such as amorphous phase during the cooling process [10]. Since they are nano-sized, it is very difficult to examine structural changes experimentally and properties of the different types of in a material in some physical processes. But, molecular dynamic simulations (MDS) is a highly efficient method designed for understanding the physical properties of such atomic arrangements in a material in different phase such as amorphous phase [11]. Amorphous solids are thermodynamically unstable and have a tendency to revert to a more stable form under suitable conditions [12].

In this study, two important metallic systems -Pt and Pd- was combined with copper (Cu) having important physical properties to form an alloy, and the structural formation and many physical parameters of atomically bonded pairs in the alloy systems during rapid solidification process based on the composition of copper were determined by MD method

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2. Material and Method

2.1. Molecular Dynamic (MD) Simulations

The Molecular dynamic (MD) simulation method provides information on the microscopic or macroscopic structure of system after a series of computer-based calculation based on conventional interactions [13]. The conventional MD method is applied to the systems with constant volume (V), constant particle number (N) and constant energy (E). This method is based on the computation of forces exerted on each other by atoms placed into a cubic computation cell (MD cell - MDH) with the help of potential energy functions and the numerical analysis of motion equations of the system. In the PR MD method, edge vectors of the computation cell are represented by three time-dependent vectors; A(t), B(t) and C(t). A cell matrix as h(t)=(ABC) is defined and the Lagrange function of the cell which can change in volume and form is obtained [13].

$$\mathrm{L}_{\mathrm{PR}} = \frac{1}{2}\sum_{i=1}^{N} m_i(\dot{\mathrm{s}}_i^{\mathrm{t}}\mathbf{G}\dot{\mathrm{s}}_i) - \Phi(\mathrm{r}) + \frac{1}{2}W\,\mathrm{Tr}(\dot{\mathbf{h}}^{\mathrm{t}}\dot{\mathbf{h}}) - p_{\mathrm{dıı}}\Omega \tag{1}$$

The motion equations of system

$$\ddot{\mathbf{s}}_i = -\sum_{j\neq i}^{N} m_i^{-1}\frac{\mathrm{d}\phi(r_{ij})}{r_{ij}\mathrm{d}r_{ij}}(\mathbf{s}_i - \mathbf{s}_j) - \mathbf{G}^{-1}\dot{\mathbf{G}}\dot{\mathbf{s}}_i \tag{2}$$

In present work, we have carried out MD method proposed by Parrinello and Rahman [14] based on changeable in shape of MD cell. Embedded Atom Method (EAM) [15] is used as potential energy function for thermostat in an isothermal–isobaric (NPT) ensemble. The total energy of a system in the Sutton-Chen SC-EAM approach is given by [16]

$$\begin{aligned} E_T^{SC} = &\left\{\frac{1}{2}\sum_{i^a,j^a}^{N^a}\varepsilon_a\left(\frac{A_a}{r_{ij}}\right)^{n_a} - \sum_{i^a}^{N^a}\varepsilon_a c_a\left[\sum_j\left(\frac{A_a}{r_{ij}}\right)^{m_a}\right]^{1/2}\right\} + \\ &\left\{\frac{1}{2}\sum_{i^b,j^b}^{N^b}\varepsilon_b\left(\frac{A_b}{r_{ij}}\right)^{n_b} - \sum_{i^b}^{N^b}\varepsilon_b c_b\left[\sum_j\left(\frac{A_b}{r_{ij}}\right)^{m_b}\right]^{1/2}\right\} + \\ &\frac{1}{2}\sum_{i^a,j^b}^{N^{ab}}\varepsilon_{ab}\left(\frac{A_{ab}}{r_{ij}}\right)^{n_{ab}} + \frac{1}{2}\sum_{i^b,j^a}^{N^{ba}}\varepsilon_{ba}\left(\frac{A_{ba}}{r_{ij}}\right)^{n_{ba}} \end{aligned} \tag{3}$$

Structural characteristics of a crystal, liquid or a glass during the phase transformations are investigated using the radial distribution function (RDF) at every temperature.

2.2. Honeycutt-Andersen (HA) Method

Honeycutt-Andersen put forward a method to detect some structural properties of atomic clusters at nano-scale [17]. This method has displayed that four basic indices (*ijkl*) represent the bonding with neighbour atoms of root pair atoms in a cluster as seen in Fig. 1 [18]. This method indicates that while the 1551 bonded pairs represent a non-defected (ideal) icosahedral (ICOS) structure, 1541 and 1431 bonded pairs represent the defected ICOS structures. The bonded pairs which represent crystalline-type structures (FCC and HCP) are indicated by 1421 and 1422, respectively. 1661 and 1441 are basic pairs of BCC lattice structure [17].

3. Findings and Discussion

In this study, the atoms comprising Cu-Pd and Cu-Pt alloy systems were placed into $L1_2$ super lattice points with FCC unit cell according to different copper concentration ($Cu_{90}Pt_{10}$, $Cu_{80}Pt_{20}$, $Cu_{70}Pt_{30}$, $Cu_{60}Pt_{40}$ ve $Cu_{90}Pd_{10}$, $Cu_{80}Pd_{20}$, $Cu_{70}Pd_{30}$, $Cu_{60}Pd_{40}$) with periodic boundary conditions. Maxwell-Boltzman distribution was used at all temperature values to determine the initial speed values of the systems. The motion equations of the systems were solved using the fifth order Gear predictor-corrector algorithm. The molecular dynamic computation time was determined to be 4.85 fs. Potential energy function parameters for the alloy systems are entered in the program and the potential energy function was defined. The potential energy parameters suitable for the systems were obtained from previous studies [19]. The modeled structures were heated from 300K to 2000K at 50K intervals with 1000 MD steps per temperature interval. In the rapid cooling process, the structures were cooled down from the melting points determined by MD method by 100K temperature value and 300K temperature value was reached with 1000 MD steps per each temperature interval and a cooling rate of 10^3 K/s.

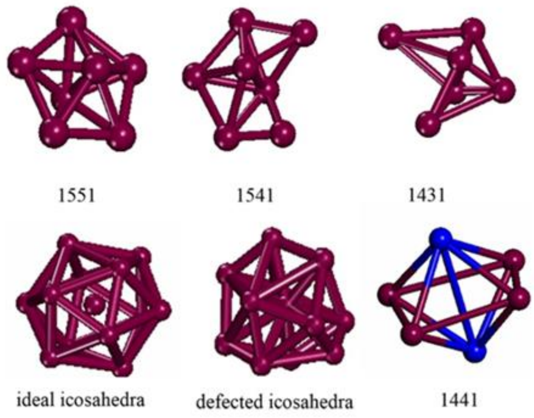

Figure 1. The systematic drawing of the related different bonded pairs [18].

In the rapid cooling process, the RDF curves of the Cu-Pd and Cu-Pt systems obtained at different temperature values for different concentration values of copper are shown in Figure 2. Where, the structures were cooled down from the determined melting points to 300K temperature value with a cooling rate of 10^3 K/s. It was determined that the atoms for which there is sufficient time to settle crystal lattice points during the rapid cooling process have remained stable in amorphous phase without forming ordered crystal structure.

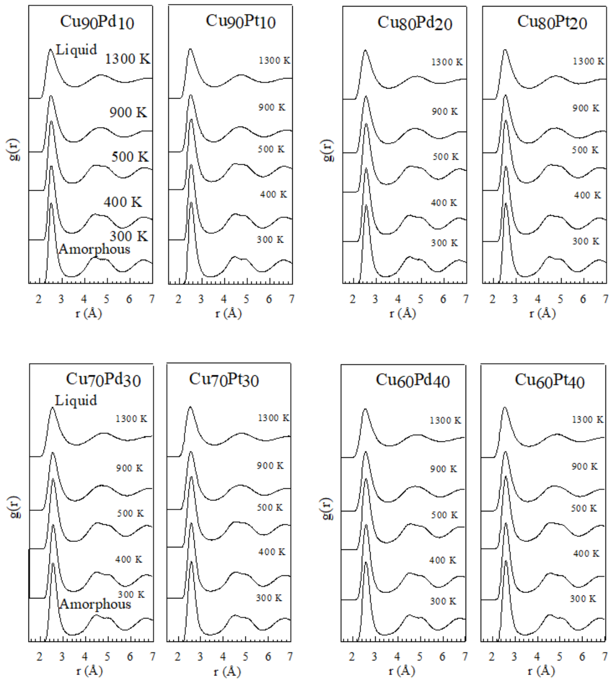

Figure 2. RDF curves of Cu-Pd ve Cu-Pt systems for different copper composition values at different temperatures during the cooling process.

The change of the number of bonded pairs representing the crystal structures for different types of copper by temperature for Cu-Pd system is given in Figure 3. As can be seen in the figure, the number of 1441 and 1661 crystalline type bonded pairs decreases for all concentration values after a certain temperature value as temperature decreases, while the number of 1421 and 1422 crystalline type bonded pairs increased. This phenomenon may be considered as an indicator of the fact that BCC crystalline lattices transform into FCC structures. The number of 1422 bonded pairs generally increased after 700K temperature value in all cases. However, it reached to the maximum value of 10% by rapidly increasing at $Cu_{60}Pd_{40}$ concentration.

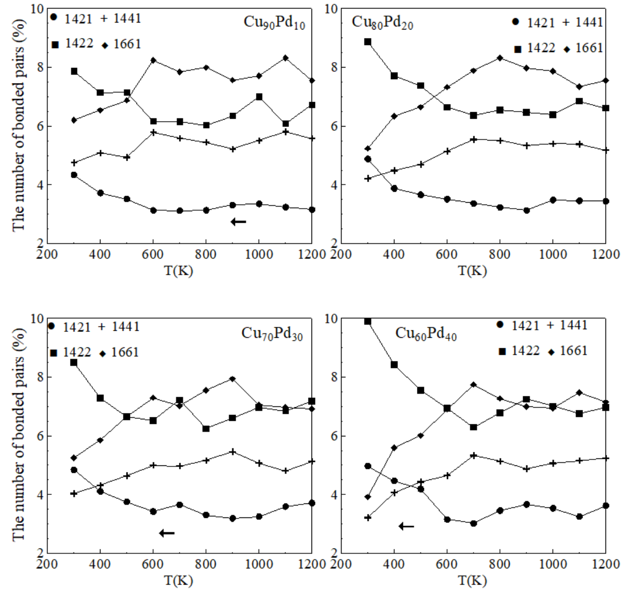

Figure 3. The number of crystalline-type bonded pairs of Cu-Pd for different copper concentration values at different temperatures during the cooling process.

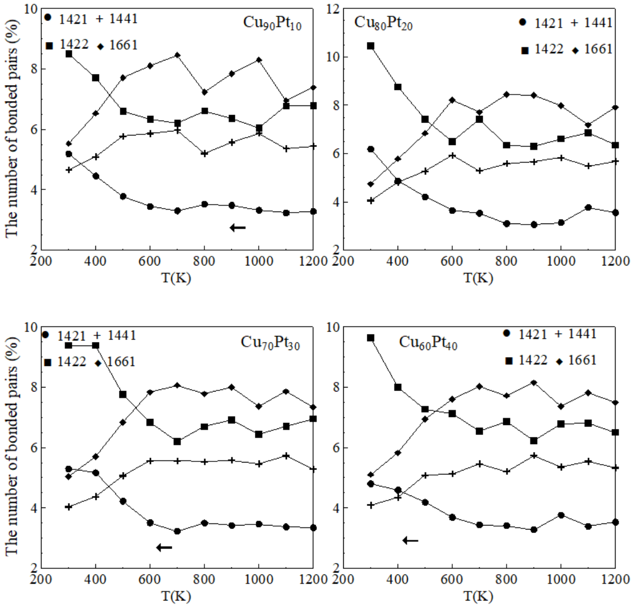

Figure 4. The number of crystalline-type bonded pairs of Cu-Pt for different copper concentration values at different temperatures during the cooling process.

The change of the number of bonded pairs representing the crystal structures for Cu-Pt alloy by temperature is given in Figure 4. The numerical change of crystalline bonded pairs for Cu-Pt alloy was similar to as is the case with Cu-Pd structure. The number of 1422 bonded pairs reached its maximum value at $Cu_{60}Pd_{40}$ and $Cu_{80}Pt_{20}$. The presence of 1422 bonded pairs in amorphous phase shows that the number of hexagonal crystal lattices is higher than the number of cubic crystal lattices.

The change of bonded pairs representing amorphous structure for Cu-Pt alloy by temperature at different copper concentration values during the rapid cooling process is shown in Figure 5 and Figure 6. The number of amorphous bonded pairs (1551, 1541, 1431) rapidly increased after the rapid cooling process. The 1551 amorphous bonded pair ratio rapidly increased to about 700K and then rapidly decreased at all concentration values. It has the maximum value (20%) at the value with the highest platinum concentration ($Cu_{60}Pt_{40}$). The 1431 bonded pair ratio generally was about 20%-30%. The 1541 amorphous bonded pair ratio rapidly increased at 1200K-200K, reaching above 20%. For $Cu_{90}Pt_{10}$; the 1551 ratio decreased by 4% from 21% to 17%. Similarly, $Cu_{80}Pt_{20}$ decreased by 5%. The 1551 ratio decreased by 2% in $Cu_{70}Pt_{30}$ structure while it decreased by 1% in $Cu_{60}Pt_{40}$ structure. When the change of the number of amorphous type bonded pairs by temperature was examined in both system, it was determined that it had minimum value at liquid phase and high temperatures. The number of 1541 and 1431 bonded pairs reached to maximum values at low temperature values. This suggested that defected icosahedral (ICOS) type clusters are more dominant in amorphous phase. The change of 1551 bonded pairs is more different. The number of 1551 bonded pairs reached to its minimum value at 300K temperature at all copper concentration values for Cu-Pt structure. But this is not the case for Cu-Pd alloy. The 1551 bonded pair reached its maximum value at $Cu_{90}Pd_{10}$ alloy system. This suggested that copper concentration plays an important role in the formation of ideal ICOS type aggregates for Cu-Pd alloy.

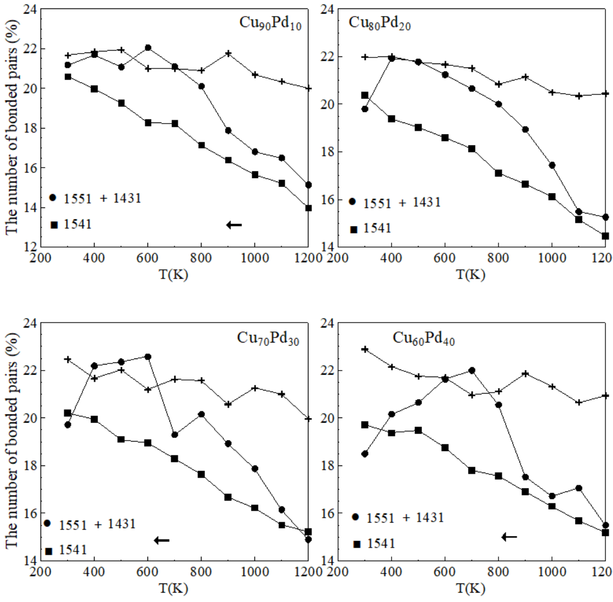

Figure 5. The number of amorphous -type bonded pairs of Cu-Pt for different copper concentration values at different temperatures during the cooling process

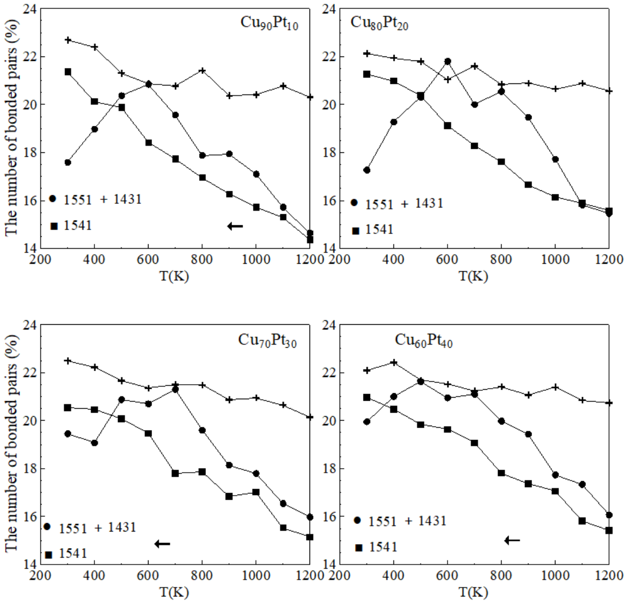

Figure 6. The number of amorphous -type bonded pairs of Cu-Pt for different copper concentration values at different temperatures during the cooling process.

The 3D image of atomic distributions of Cu-Pd and Cu-Pt structures for different copper concentration (60 and 90) values at 300K temperature during the rapid cooling process was created by Ovito [20] program and shown in Figure 7. The temperature was rapidly decreased from the melting points to 300K temperature value. In the rapid cooling process, the structures did not place into crystal lattice points to form crystal planes and remained stable in amorphous phase.

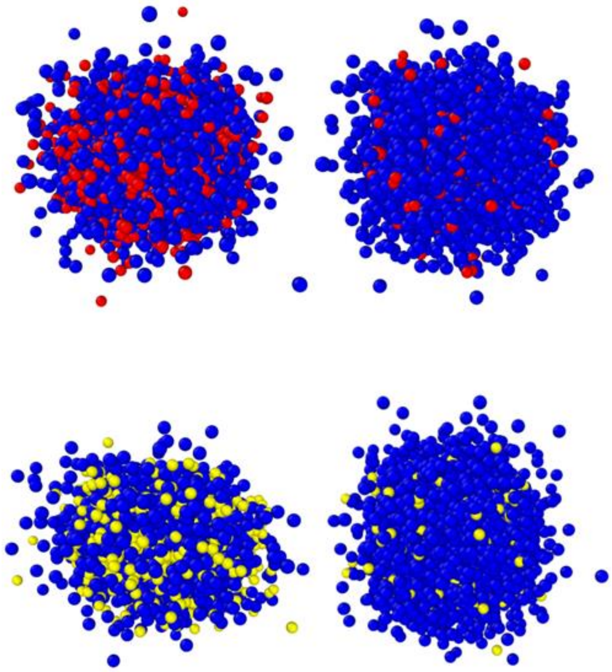

Figure 7. Representative atomic structures Cu-Pd and Cu Pt systems at 300 K for Pt for 60 and 90 copper concentration values. (blue atoms represent Cu, red atoms represent Pd and blue atoms represent Pt)

4. Conclusions

The local short range order formation of Cu-Pd and Cu-Pt alloys systems for diffrerent Cu concentration has been analysed by using molecular dynamics simulation with EAM interatomic potential. Structural development has been RDF functions shown that the model systems have remained in amorphous phase during the rapid cooling process. According to the HA method, it has been found that while crystalline-type bonded pairs are little, disordered-type bonded pairs composed of ICOS-type (1551, 1541, and 1431) are large in the amorphous phase. The 1551 bonded pair reached its maximum value at $Cu_{90}Pd_{10}$ alloy system. This suggested that copper concentration plays an important role in the formation of ideal ICOS type aggregates for Cu-Pd and Cu-Pt alloys.

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