**Temperature effect on the characteristic quantities of microstructure and phase transition of the alloy Ag$_{0.25}$Au$_{0.75}$**

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**Abstract:** In this research, Molecular Dynamics (MD) simulations were conducted to explore the temperature effect on the microstructure and phase transition of the Ag$_{0.25}$Au$_{0.75}$ alloy. The findings reveal that as the temperature rises, the material's phase transition switches from crystalline to liquid and vice versa. Notably, during the phase transition, significant changes occur in the link length ($r$), the total energy of the system ($E_{\text{tot}}$), and the number of structural units FCC, HCP, BCC, and Amor. The microstructural features of the models were analyzed using the radial distribution function (RDF), a number of structural units, shape, size ($l$), and total energy of the system ($E_{\text{tot}}$). In addition, the length of the link Ag-Ag, Ag-Au, Au-Au, the size of the material has a very small change value and is considered almost constant, and the height of the radial distribution function (RDF) decreases. The number of structural units FCC, HCP decreased, BCC, Amor increased, and the total energy of the system increased, thereby confirming that the influence of temperature on the microstructure and phase transition of the Ag$_{0.25}$Au$_{0.75}$ alloy is very large. Besides, the micro-structural characteristics of the Ag$_{0.25}$Au$_{0.75}$ alloy can be applied as a basis for future experimental studies.

**Keywords:** Ag$_{0.25}$Au$_{0.75}$ alloy, microstructure, molecular dynamics, phase transition, temperature.

1. INTRODUCTION

Gold and silver alloy (AuAg) is an alloy of two precious metals including gold and silver. Both metals are materials with very good electrical and thermal conductivity and are widely used in fields such as photocatalysis, sensors [1], optics [2], electronics [3], medical research [4], sensing [5], and energy storage and conversion [6]. Studies on this alloy have been carried out since about 1920, concerning corrosion and stress cracking [7]. After that, studies of mechanical properties began to work on structural evolution [8]. To study and fabricate this alloy, researchers have applied a lot of methods. Based on the experimental methods, researchers have successfully studied the formation and growth of nanostructures during processing [9]. With the metal reduction method, the doping ratio from 25% to 55% has been successfully determined in the AgAu alloy [10]. In different studies, researchers have proposed and discovered to improve the electrocatalytic performance of
metals by modifying the composition, size [11], morphology [12], and arrangement of surface atoms [13].

The probabilistic simulation method for investigating physical quantities using molecular dynamics is a commonly used approach for approximate simulations that involves treating physical parameters as random variables or classical random processes, and then performing numerical simulations using classical equations. This probabilistic simulation method was frequently employed in Molecular Dynamics (MD), a microscopic analysis [14] technique developed in the 1920s. In MD simulations, Newton's equations of motion are used with randomly generated initial conditions. An early precursor of MD is the classical ionization model for two-electron atoms in a high-intensity laser beam, which was analyzed and detailed in a paper (referenced as [16]) and mentioned in [15]. This paper delves into the classical ionization model and highlights its significance in developing the MD method.

In this paper, we apply the MD simulation method, but some aspects need to be considered carefully, such as the stability of the computational code, the accuracy of the integral method, the sensitivity dependence sensitivity of the initial conditions and the appropriate selection of the pairwise interactions between the components involved [17]. We use phenomenological criteria to evaluate the validity of the results obtained. Recent studies have succeeded in studying the electronic structure, phase transition, and crystallization of alloys such as AuCu [18], and NiAu [18]. The obtained results show that when increases the temperature and heating rate, the bond length decreases, and when the number of atoms increases, and the annealing time increases, the bond length, and g(r) function increase. From there, it raises the question of whether when changing the temperature, there is a phenomenon that the length of the link AgAu changes. To answer the question, we continue to study the temperature effect on the microstructure of the Ag$_{0.25}$Au$_{0.75}$ alloy. The reason for choosing AgAu alloy with the doping rate of 25% Ag, and 75% Au is because previously, by the experimental method, successfully mixed Au doping ratio from 25% to 50% obtained results quite positive. At the same time, we will answer why researchers do not perform with Au doping concentration with a doping rate higher than 50% with the experimental method.

Significant Changes in Physical Parameters during Phase Transition of AgAu Material. The study reveals that numerous physical parameters undergo significant changes during the phase transition of AgAu materials. These include bond length, total energy, size, and the number of FCC, HCP, and Amor structural units. These findings are essential for advancing research and fabrication of AgAu materials for future photocatalytic applications.

2. METHOD OF CALCULATION

First, we randomly seed a material system consisting of Ag$_{0.25}$Au$_{0.75}$ 4000 atoms with an Ag:Au ratio of 1:3, equivalent to 1000 Ag atoms and 3000 Au atoms. These atoms have been initialized in a cube with the size (l) calculated by the following formula (1)

\[
l = \sqrt{\frac{(m_{Ag} \cdot n_{Ag} + m_{Au} \cdot n_{Au})}{\rho}}
\]

where: \( \rho \) is density; \( m \) is the atomic molar mass, \( n \) is the atomic number of the metal Ag and is similar to Au.

All simulations were performed using LAMMPS code [21, 22] using the potential Embedded Atomic Method (EAM) [23]. To study microstructural characteristics and phase transitions by using molecular dynamics (MD) simulation with Sutton-Chen (SC) embedded interaction potential (2) [20, 24-27], under periodic boundary conditions.

In that, the values of the coefficient of the bulk Ag$_{0.25}$Au$_{0.75}$ materials are shown in Table 1 [21, 22]. Set of the MEAM potential parameters for
single elements. The reference structures for Ag, Au are FCC. $E_i$ is the cohesive energy, $a$ is the equilibrium lattice parameter, $A_i$ is the scaling factor for the embedding energy, $\alpha_i$ is the exponential decay factor for the universal energy, $\beta_i(0−3)$ are the exponential decay factors for the atomic densities, $t_i(0−3)$ are the weighting factors for the atomic densities.

$$E_{\text{tot}} = \frac{1}{2} \sum_{i<j} V_{ij}(r_{ij}) + \sum_i F_i(\bar{\rho}_i), \quad F_i(\rho) = A_i E_i^{\rho} \rho \ln \rho, \quad V(r_{ij}) = E_i \left( \frac{a}{r_{ij}} \right)^n,$$

$$(\bar{\rho}_i)^2 = \sum_{i=0}^3 t_i^{(0)} (\rho_i^{(0)})^2, \quad \rho_i^{(0)}(R) = e^{-b_i} b_i = \beta_i^{(0)} \left( \frac{R}{R_i^{(0)} - 1} \right).$$

**Table 1.** The parameters of the bulk AgAu material

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th></th>
<th>Au</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient</td>
<td>$E_i^0$ (eV)</td>
<td>$R_i^0$ (Å)</td>
<td>$\alpha_i$</td>
<td>$A_i$</td>
</tr>
<tr>
<td></td>
<td>2.850</td>
<td>3.000</td>
<td>5.892</td>
<td>0.940</td>
</tr>
<tr>
<td>Coefficient</td>
<td>$\beta_i^{(2)}$</td>
<td>$\beta_i^{(4)}$</td>
<td>$t_i^{(0)}$</td>
<td>$t_i^{(1)}$</td>
</tr>
<tr>
<td></td>
<td>2.000</td>
<td>6.000</td>
<td>1.000</td>
<td>3.400</td>
</tr>
<tr>
<td>Coefficient</td>
<td>$E_i^0$ (eV)</td>
<td>$R_i^0$ (Å)</td>
<td>$\alpha_i$</td>
<td>$A_i$</td>
</tr>
<tr>
<td></td>
<td>3.930</td>
<td>1.640</td>
<td>6.341</td>
<td>1.000</td>
</tr>
<tr>
<td>Coefficient</td>
<td>$\beta_i^{(2)}$</td>
<td>$\beta_i^{(4)}$</td>
<td>$t_i^{(0)}$</td>
<td>$t_i^{(1)}$</td>
</tr>
<tr>
<td></td>
<td>2.000</td>
<td>6.000</td>
<td>1.000</td>
<td>2.900</td>
</tr>
</tbody>
</table>

After creating the alloy model Ag$_{0.25}$Au$_{0.75}$, we run all samples for recovery statistics with 2×10$^4$ steps of molecular dynamics (MD) simulation to prevent applied between atoms. Then, increase the temperature from 300 K to 4500 K by running 42×10$^4$ MD steps to convert the material from the initial crystalline state to the liquid state with a heating step of 1fs. The temperature is then reduced from the liquid state at $T = 4500$ K to $T = 1200, 1100, 1000, 900, 800, 700, 600, 500, 400$, and 300 K to convert the material from the liquid state to the condensed state, new crystal. Then, all the sample values are determined using the Velet algorithm [28]. To study the characteristic quantities of microstructure through material shape, size ($l$), energy, and radial distribution function (RDF), calculated according to formula (3):

$$g(r) = \frac{V}{N^2} \left( \frac{\sum n(r)}{4\pi r^2 \Delta r} \right).$$

3. RESULTS AND DISCUSSION

3.1. Structural characteristics

Figure 1 illustrates the characteristic quantities of the microstructure and phase transition of Ag$_{0.25}$Au$_{0.75}$ alloy at $T = 300$ K with a heating rate of 4×1012 K/s and a time step of 1fs. Figure 1a shows a particular shape of the alloy Ag$_{0.25}$Au$_{0.75}$ at 300 K temperature. The structural shape (Figure 1b) is determined by the number of structural units 1234 FCC, 1640 HCP, 317 BCC, 809 Amor (Figure 1c), the radial distribution function (RDF) has the lengths of link...
Ag-Ag, Ag-Au, Au-Au is r = 2.83, 2.78, 2.83 Å with the function height, respectively, radial distribution g(r) = 4.73, 5.00, 4.99 (Figure 1d). The obtained results are in complete agreement with the simulation results of Ag-Ag is 2.78 Å [18], Au-Au is 3.17 Å [19].

The obtained results show that the lengths of the link Ag-Ag and Au-Au have equal values, but with g(r) of Au being larger than g(r) of Ag, it is confirmed with the ratio. The high doping ratio of Au leads to a higher probability density of the Au atom than that of the Ag atom. This is the initial result as well as the basis for us to continue to study the influence of temperature on the microstructure and phase transition of Ag0.25Au0.75 alloy.

Figure 1. Alloy shape Ag0.25Au0.75 (a), structure shape (b), number of structural units (c), radial distribution function (d) of Ag0.25Au0.75 alloy at 300 K temperature

3.2. Effect of temperature
This page contains a series of diagrams labeled as \(c1\), \(c2\), \(c3\), \(d1\), \(d2\), \(d3\), \(e1\), \(e2\), \(e3\), \(f1\), \(f2\), \(f3\), \(g1\), \(g2\), and \(g3\). Each diagram appears to represent structural units and their distribution at different temperatures, indicated by the colors FCC, HCP, BCC, and Amor. The diagrams suggest a study on the structural changes in materials with varying temperatures, as indicated by the peaks and distributions in the graphs.

The diagrams are accompanied by bar charts showing the number of structural units at different temperatures, with colors corresponding to FCC, HCP, BCC, and Amor phases. The graphs on the right side of each diagram likely represent the structural distribution or some related property as a function of distance.

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Figure 2. Structure shape (a1, b1, .., k1), number of structural units (a2, b2, .., k2), RDF radial distribution function (a3, b3, .., k3) of alloy Ag_{0.25}Au_{0.75} at different temperatures

Table 2. Energy of system, size of alloy Ag_{0.25}Au_{0.75} at different temperatures

<table>
<thead>
<tr>
<th>T(K)</th>
<th>E_{tot} (eV)</th>
<th>l (nm)</th>
<th>T (K)</th>
<th>E_{tot} (eV)</th>
<th>l (nm)</th>
</tr>
</thead>
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<td>300</td>
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<td>800</td>
<td>-11732</td>
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</tr>
<tr>
<td>400</td>
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<td>40.851</td>
<td>900</td>
<td>-11654</td>
<td>40.856</td>
</tr>
<tr>
<td>500</td>
<td>-11932</td>
<td>40.852</td>
<td>1000</td>
<td>-11579</td>
<td>40.857</td>
</tr>
<tr>
<td>600</td>
<td>-11864</td>
<td>40.853</td>
<td>1100</td>
<td>-11485</td>
<td>40.858</td>
</tr>
<tr>
<td>700</td>
<td>-11798</td>
<td>40.854</td>
<td>1200</td>
<td>-11419</td>
<td>40.859</td>
</tr>
</tbody>
</table>

Observation in Figure 2 shows, the alloy Ag_{0.25}Au_{0.75} at 300 K temperature has a structural shape (Figure 2a1) determined by the number of structural units 1234 FCC, 1640 HCP, 317 BCC, 809 Amor (Figure 2a2), the radial distribution function (RDF) has the lengths of the link Ag-Ag, Ag-Au, Au-Au respectively r = 2.83, 2.78, 2.83 Å with the height of the radial distribution function g(r) = 4.73, 5.00, 4.99 (Figure 2a3). When increasing the temperature from T = 300 K to T = 400, 500, 600, 700, 800, 900, 1000, 1100, 1200 K, the structure shape changes (Figure 2a1, 2b1, 2c1, .., 2k1), number of structural units FCC, HCP, Amor architecture changes. FCC decreased...
from 1234 FCC to 109 FCC, HCP decreased from 1640 HCP to 1211 HCP, BCC increased from 317 BCC to 767 BCC, Amor increased from 809 Amor to 2004 Amor (Figure 2a2, 2b2, 2c2, .., 2k2), and the radial distribution function changed as the Ag bond lengths increased. Au has a constant value \( r = 2.78 \) Å, and the height of the radial distribution function from \( g(r) = 5.0 \) to \( g(r) = 3.1 \) (Figure 2a3, 2b3, 2c3, .., 2k3). Through the obtained results, when the temperature is increased, the number of structural units FCC, HCP decreases, then BCC, Amor increases, which shows that when the alloy changes from solid state to liquid state. In addition, the Ag-Au bond length is almost constant, with \( r = 2.78 \) Å, the RDF height decreases. These obtained results can be applied for future application research and fabrication of \( \text{Ag}_{0.25}\text{Au}_{0.75} \) alloy.

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Data Availability Statement: The data that supports the findings of this study are available within the article.

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