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Kinetic Study of the Effect of Cu Content on the Structure of CuZr Alloys

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Abstract

Copper-zirconium alloys are industrial materials with significant application value. Their mechanical and thermal stability properties are determined by their microstructure and dynamic characteristics. To gain a deeper comprehension of the characteristics of copper-zirconium alloys, they have been subjected to investigation through the utilization of molecular dynamics simulations. The simulations were conducted using the Materials Studio software, with the EAM potential function employed to describe the interatomic interactions. The microcanonical system synthesis (N, V, E) was selected as the method of system generation. The atomic structure, radial distribution function, and kinetic properties of three distinct ratios of copper-zirconium alloys, namely $Cu_{300}Zr_{700}$, $Cu_{400}Zr_{600}$, and $Cu_{500}Zr_{500}$, at varying temperatures were examined through the utilization of molecular dynamics simulations. The findings indicate that the mutual free energy of CuZr alloys rises in conjunction with elevated Cu atomic content, yet exerts minimal influence on their atomic diffusion state. An escalation in temperature results in a surge in the mutual free energy of the alloys and a pronounced impact on the extent of atom diffusion within the alloy system. The results are of significant value in optimizing the properties and material design of CuZr alloys.

Keywords

Kinetic Properties; CuZr Alloys; Molecular Dynamics Simulations; Elemental Content; Temperature.

1. Introduction

Copper-zirconium alloy is an important engineering alloy [1], which is mainly composed of two metals, copper and zirconium. Copper-zirconium alloys have excellent physical and chemical properties such as good corrosion resistance, high strength, high hardness, high toughness, etc [2]., and are widely used in a variety of occasions where high strength and high corrosion resistance materials are required [3]. Mainly used in aerospace, military, nuclear, and chemical industries and other fields, such as aircraft engine parts, missiles, and nuclear reactor components. Factors such as the composition, structure, and method of production of copper-zirconium alloys affect their properties. Common copper-zirconium alloys include CuZr, CuZrAl, CuZrTi, and other alloys [4-7] in which the main element is copper with a high zirconium content and a low zirconium content, usually around 1% [8].

From 1960 to 1980, copper-zirconium alloys were mainly produced by traditional metallurgical methods [9], such as powder metallurgy, electric arc melting, and vacuum induction melting [10], The working process was to first carry out powder preparation and mix the copper and zirconium powders, and then to place the mixed copper-zirconium powder into molds and carry out unidirectional press forming[11]. The copper-zirconium alloy billet is placed in the furnace and sintered into a dense copper-zirconium alloy material[12]. The sintered copper-zirconium alloy material must be heat-treated and cold-worked to achieve higher material properties[13]. The final metallurgical preparation of copper-zirconium alloys has the advantages of high purity, uniform organization, better low-temperature toughness, and high quality, but it has the problems of high manufacturing cost, difficulty in controlling the process, unstable preparation, higher cost, and high gas content[14-18]. With the development of advanced preparation methods advanced experimental instruments and analytical methods, the preparation and properties of copper-zirconium alloys have entered a completely new stage of research [19].In 1990, copper-zirconium alloys prepared by new preparation methods such as co-precipitation method and chemical reduction method have more excellent properties[20]. The co-precipitation method produces a copper-zirconium mixture with a homogeneous particle size, while the chemical reduction method allows the rapid production of powdered copper-zirconium mixtures[20]. The combination of co-precipitation and chemical reduction eliminates the weaknesses of using the two methods separately, and in the production of high-quality copper-zirconium alloys, the resulting alloys are better performing and more pure. However, there are some drawbacks. By mixing the co-precipitation method and the chemical reduction method, the alloy powder obtained may contain a certain amount of impurities, which may have a certain negative impact on the performance of copper-zirconium alloys[21]. The chemicals used in the preparation process may cause some environmental pollution.

After 2000, the demand for high-temperature alloys gradually increased, and copper-zirconium alloys, as a kind of high-temperature alloy material with better thermal stability and corrosion resistance [22], have received wide attention and have been extensively studied and applied. Therefore, the focus of research on the preparation of copper-zirconium alloys has gradually shifted from the alloy composition and preparation process to the high-temperature resistance, corrosion resistance, high-temperature mechanical properties, and other properties of the alloy. At the same time, the development of copper-zirconium alloy technology also faces new challenges and opportunities, such as new material technology, advanced preparation process, new surface treatment technology, etc. [23], in view of which computer simulation methods can be used to study the formation process of CuZr alloys to reduce the research cost. The simulation study of CuZr alloys is mainly through the computer simulation means of material microstructure, energy band structure, etc. From the 1990s to the beginning of the 21st century, the study of CuZr alloys is mainly used in the simulation of some simple potential functions, such as the Lennard-Jones potential function, etc. [24]. This method is suitable for studying the basic physical properties of CuZr alloys, such as crystal structure, defects, and oxidation states [25]. From the beginning of the 21st century to the present, with the development of computer technology and first-principle calculation methods, the study of first-principle calculations and simulations of the electronic structure and mechanical properties of CuZr alloys has gradually become mainstream. The electronic structure, total energy, crystal structure, defects, surface properties, mechanical properties [26], and other properties of copper-zirconium alloys can be studied by Density Flood Theory (DFT) calculations, which is a study method that is closer to the real situation and can provide more accurate data. In recent years, the development of machine learning and artificial intelligence has brought new ideas to the simulation study of copper-zirconium alloys. By applying machine learning algorithms to large-scale calculation result data, the properties of copper-zirconium alloys can be predicted and analyzed faster, more accurately, and more intelligently, making computer simulation more efficient [27]. With the continuous development of copper-zirconium alloy simulation research methods, people's understanding of the detailed properties of copper-zirconium alloy materials is more comprehensive, which is more conducive to the optimal design and engineering application of copper-zirconium alloy materials, and has a far-reaching impact on promoting the development of high-end materials and related fields.

2. Calculation Models and Methods

2.1. Calculation Model

Figure.1 illustrates the atomic composition of CuZr alloys with varying Cu and Zr ratios. Figure.1(a) depicts an alloy with 300 Cu and 700 Zr atoms, Figure.1(b) represents an alloy with 400 Cu and 600 Zr atoms, and Figure.1(c) shows an alloy with 500 Cu and 500 Zr atoms. The relative content of Cu and Zr atoms in the CuZr alloy was varied on the basis of the total number of atoms being set at 1000. The initial model had a density of 5 g/cm^3 and the volume of the model is In the following analysis, A: Cu_{300} Zr_{700}, B: Cu_{400} Zr_{600} and C: Cu_{500} Zr_{500}.

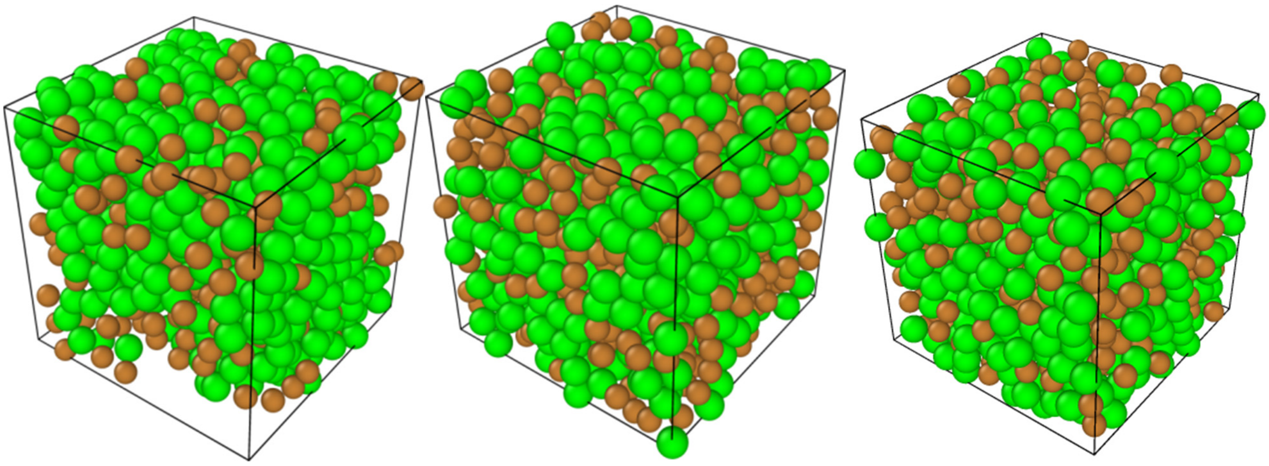

(a) (b) (c)

Figure 1. Models of CuZr alloys with different contents of Cu and Zr atoms (a) represents a CuZr alloy with 300 Cu atoms and 700 Zr atoms, Fig. 1(b) represents a CuZr alloy with 400 Cu atoms and 600 Zr atoms, Fig. 1(c) represents a CuZr alloy with 500 Cu atoms and 500 Zr atoms

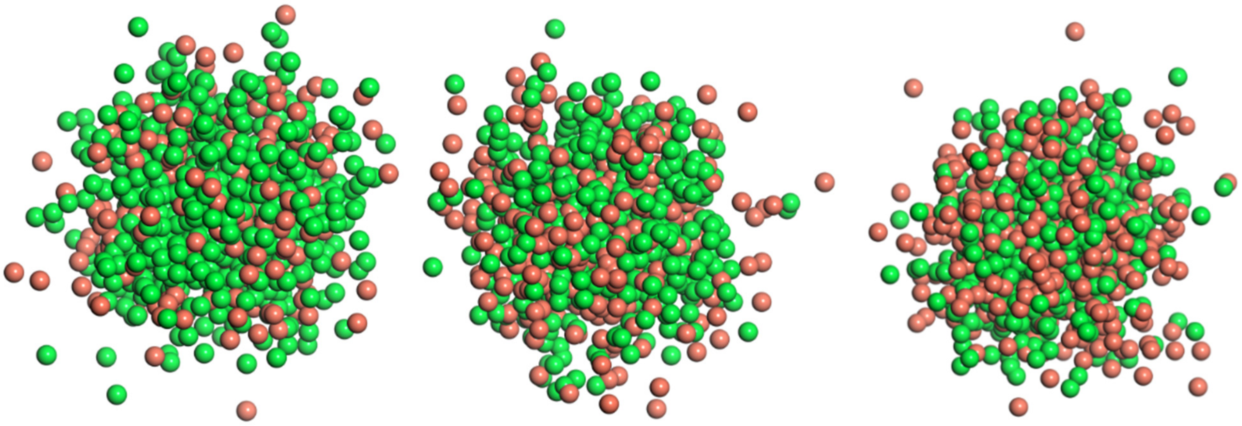
2.2. Calculation Parameters

In order to investigate the influence of Cu content on the structure of CuZr alloy, molecular dynamics simulations were conducted using Material Studio. The simulations employed the following parameters: a time step of 1 fs and a total simulation time of 100 ps. The temperature of the simulation system was set to 300 K, the system of systems was selected as the microcanonical system (N, V , E), and the force field was selected as Universal[28]. The number of simulation steps was set to 100000, and the output frame was set to every 5000 steps. The number of simulation steps was set to 100000, with a frame output every 5000 steps. No pressure was set, and it was treated as a free variable.

3. Results and Discussion

3.1. Structural Optimisation

Following the construction of CuZr alloys with varying relative contents, the geometry optimization of the alloy system was conducted, the parameters, including temperature and time, were established, and finally, the molecular dynamics simulation was performed, resulting in the atomic diffusion images depicted in Figure.2(a) illustrates the atomic diffusion image of the Cu_{300} Zr_{700} component alloy at 300 k. Figure.2 (b) depicts the atomic diffusion picture of the Cu_{400} Zr_{600} component alloy at 300 K, while Fig.(c) illustrates the atomic diffusion picture of the Cu_{500} Zr_{500} component alloy at the same temperature. The analysis suggests that despite the differing relative contents of the constituents in the Cu_{300} Zr_{700}, Cu_{400} Zr_{600} and Cu_{500} Zr_{500} alloys, their atomic diffusion at 300 K exhibits a similar tendency.



(a) (b) (c)

Figure 2. Structures of CuZr alloys obtained by kinetics, long time relaxation at 300 K. (a) $Cu_{300}Zr_{700}$, (b) $Cu_{400}Zr_{600}$, (c) $Cu_{500}Zr_{500}$

3.2. Dynamic Structural Stability Analysis

3.2.1. Relationship of System Temperature with Time

As illustrated in Figure.3, an examination of the collective trend of the curves in Figure.3 (a), Figure.3 (b), and Figure.3 (c) reveals that the temperature fluctuations over time exhibit a periodic nature. This observation suggests that the alloy systems a, b, and c possess a certain degree of stability. Furthermore, the temperature fluctuations are approximately 204 K, which suggests that the Cu content has a minimal impact on the temperature versus time curve at 300 K for the kinetic simulation of the CuZr alloy.

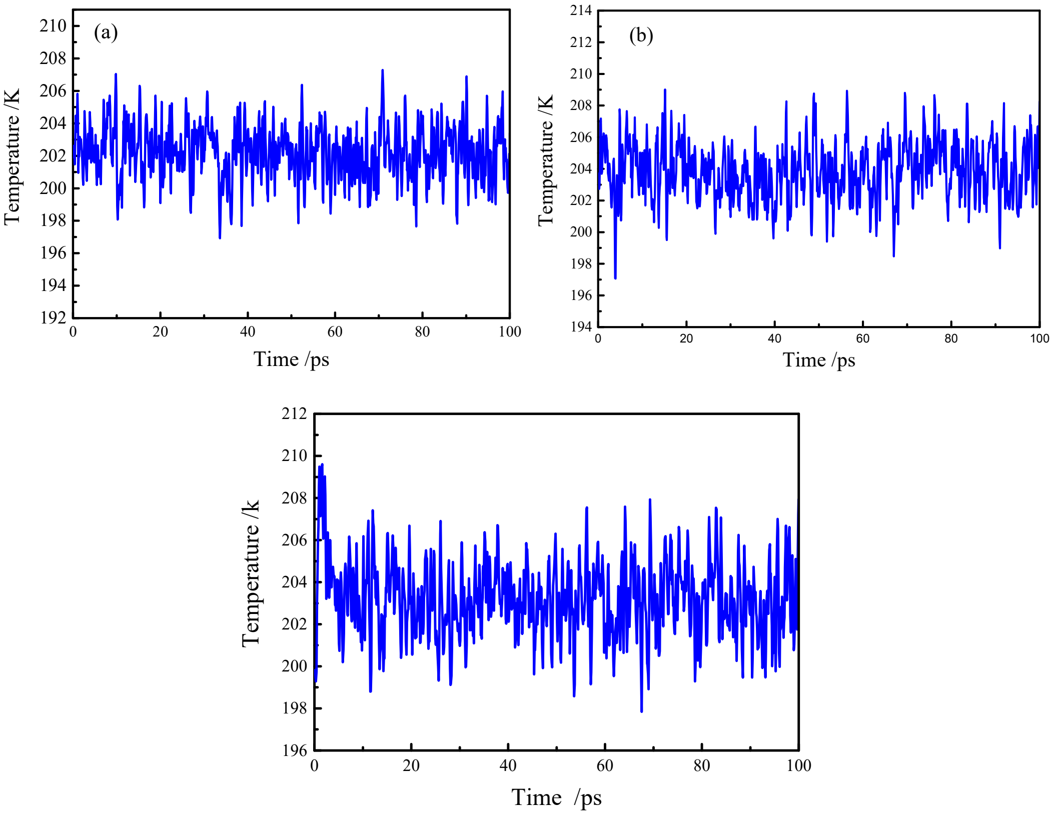


Figure 3. Plots of system temperature versus time at 300 K for different components of CuZr alloys (a) $Cu_{300}Zr_{700}$, (b) $Cu_{400}Zr_{600}$, (c) $Cu_{500}Zr_{500}$

In the context of molecular dynamics calculations, energy analysis can be employed to examine energy fluctuations within simulated systems, thereby facilitating an understanding of the typical energy changes that occur over time. The interactions between atoms can be obtained by calculating the magnitudes, minima, and correlations of potential energies, and by postulating the manner in which atoms move in different environments. The velocity and scope of atomic motion can be determined by calculating the magnitude, correlation, and distribution of kinetic energy. The interactions between atoms or bonds can be obtained by calculating the magnitude, minimum, and correlation of the unbound energies, which allows for speculation on the motion between them. By examining the total energy of the simulation system and the relationships between different energy components, insight can be gained into the stability, dynamic variations, and physical properties of the system. As illustrated in Figure.4, the kinetic energy of the CuZr alloys a, b, and c with varying compositions exhibits periodic oscillations around 600 kcal/mol at 300 K. While the potential energy and the free energy also demonstrate periodic fluctuations, their fluctuation ranges differ. In particular, the kinetic and potential energies of alloy A fluctuate around 70 kcal/mol, those of alloy B around 20 kcal/mol, and those of alloy C around -30 kcal/mol. This demonstrates that the kinetic and potential energies of the alloy decrease progressively as the copper content increases. The total energy is the sum of the potential energy, kinetic energy, and free energy. It can be observed that the total energies of alloys a, b, and c are constant at 684 kcal/mol, 637 kcal/mol, and 584 kcal/mol, respectively. This indicates that an increase in copper content results in a reduction in the total system energy.

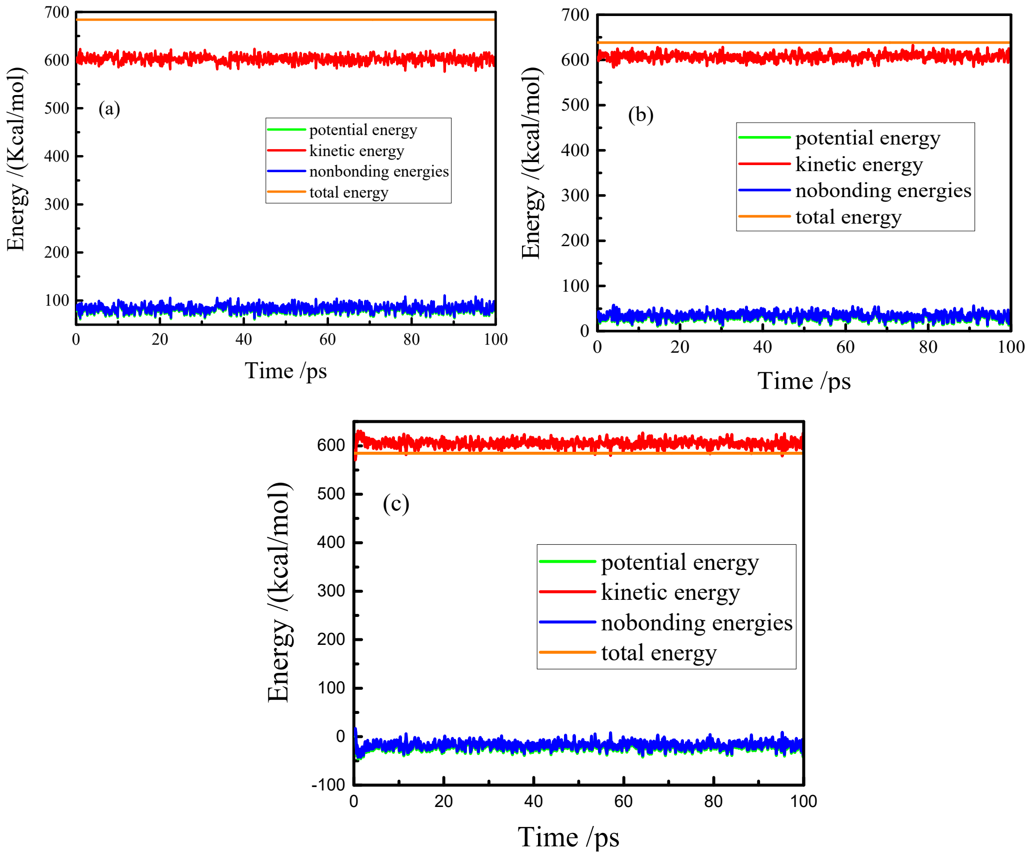


Figure 4. Plots of energy versus time at 300 K for different components of CuZr alloys (a) Cu_{300} Zr_{700}, (b) Cu_{400} Zr_{600}, (c) Cu_{500} Zr_{500}

3.3. Structural Analysis

3.3.1. Radial Distribution Function Analysis

As illustrated in Figure.5, the initial peak of the radial distribution function exhibits a bifurcation, the second peak demonstrates minimal fluctuations, and subsequent peaks are absent, indicating a relatively smooth trend. This suggests that at 300 K, the relative distances between Cu and Zr atoms in the simulation system are not fully fixed, allowing atoms to move freely, indicating that alloys A, B, and C are in an amorphous state. Notwithstanding the disparities in the atomic compositions of Cu and Zr in alloys A, B, and C, their radial distribution functions at 300 K evince analogous overall trends, thereby indicating that the quantity of Cu atoms exerts a negligible influence on the radial distribution function.

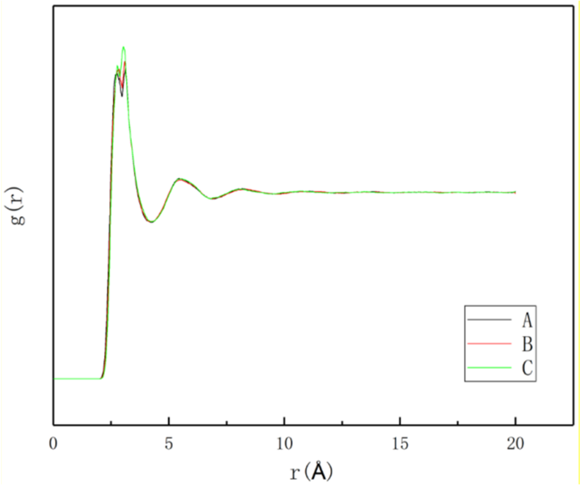


Figure 5. Radial distribution functions of CuZr alloys with different compositions at 300 K

The splitting of the first peak in the radial distribution function during the dynamics simulations of amorphous materials in Material Studio is frequently attributable to simulation conditions, such as temperature and pressure, which induce structural alterations in the amorphous material under specific circumstances. The essence of fission is the appearance of new features in the molecular arrangement, such as irregular voids and structural anomalies. The accuracy of the simulation results and the shape of the radial distribution function are affected by the interaction forces and potential energy expressions between molecules, which must therefore be appropriately selected and set during the simulation. In conclusion, the splitting of the first peak in the radial distribution function during dynamics simulations of amorphous materials in Material Studio can be attributed to structural changes caused by simulation conditions such as temperature and pressure, as well as the selection of computational parameters and force fields Mean square displacement (MSD) analysis.

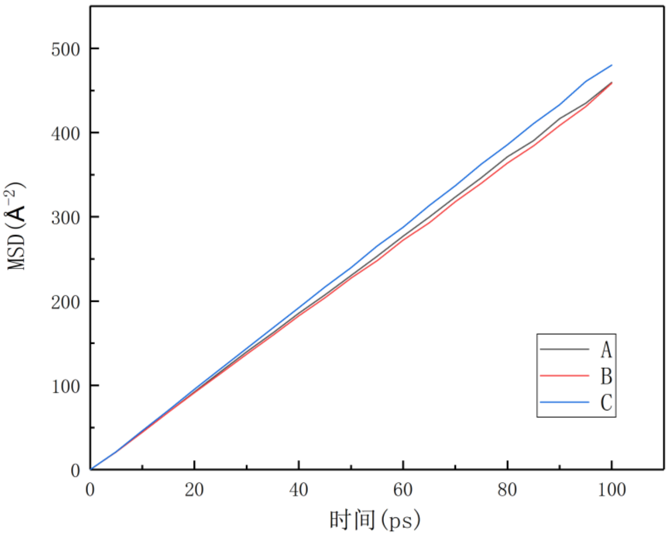


Figure 6. Mean square displacement of CuZr alloys with different compositions at 300 K

Fig.6 depicts the mean square displacement (MSD) of CuZr alloys with different compositions A, B, and C at the same temperature (300 K) varying with time. In accordance with Einstein's law of diffusion, if the mean square displacement is observed to have an upper limit over time, this indicates a solid system. Conversely, if the mean square displacement is seen to increase linearly with time and has no upper limit, this indicates a solid system. From an examination of the values and trends of the mean squared displacement as illustrated in FigURE. 6, it is evident that at 300 K, the MSD exhibits a linear relationship with time, indicating that the atoms within the system display characteristics associated with an amorphous state. At this juncture, the atoms within the system are unrestricted in their capacity for movement and are capable of oscillating over a considerable range. This finding is consistent with the results described by the radial distribution function in Figure. 5. The diffusion coefficient can be calculated from Fig. 6 and the values are given in Table 1. An analysis of Fig. 6 and Table 1 shows that as the Cu content increases, the trends and values of the mean squared displacement for the alloys are similar, with close slopes and diffusion coefficients. This suggests that an increase in Cu content has a negligible impact on the diffusion coefficient.

Table 1. Diffusion coefficients of alloys A, B, and C with different compositions

Sample	A	B	C
Slope	0.0461	0.0455	0.0484
Diffusion coefficient	0.0077	0.0076	0.0081

3.3.2. Interaction Energy Analysis

In order to calculate the interaction energy of CuZr alloy systems with varying relative compositions, three distinct alloy models designated A, B, and C, were constructed. As illustrated in Figure.7, the removal of Zr atoms from the system resulted in the formation of a model comprising solely Cu atoms, as depicted in Figure.7(a). Similarly, the removal of Cu atoms from the system yielded a model comprising solely Zr atoms, as illustrated in Figure.7(b). The software calculations provided the total energies of alloys A, B, and C, as well as the energies of models containing only Cu or only Zr, thus enabling an assessment of the interaction energy of the alloys to be made.

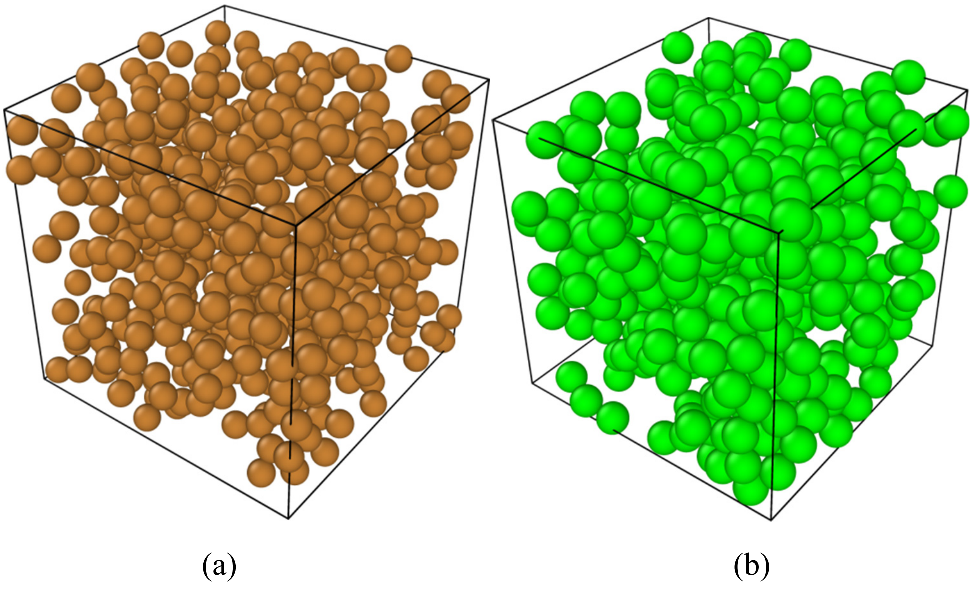

(a) (b)

Figure 7. Atomic models of single components, (a) model containing only Cu, (b) model containing only Zr

Table 2. Energy of alloy system at 300K in dynamic simulation

Sample	Energy of CuZr alloy (kcal/mol)	Energy of Cu (kcal/mol)	Energy of Zr (kcal/mol)	Binding Energy (kcal/mol)
A	-30.47	19.02	-101.30	51.82
B	21.35	37.99	-72.06	55.43
C	78.37	59.53	-39.85	58.69

A review of Table 2 indicates that as the concentration of Cu atoms in a CuZr alloy increases, the total energy of the alloy at 300 K also rises. The energy of models containing only Cu also increases with rising Cu content, and the interaction energy similarly rises with higher Cu content. This suggests that the Cu atom content affects the interaction energy of CuZr alloys, with higher Cu content leading to greater interaction energy.

4. Conclusion

Using molecular dynamics methods, the CuZr alloys with different compositions and temperatures were studied, focusing on their crystal structures, material states, diffusion coefficients, and interaction energies. The preceding studies allow us to draw the following conclusions:

(1) The results demonstrate that the alloy system structure is stable, with different compositions and temperatures producing consistent outcomes. This indicates that the atoms follow specific movement patterns, which is useful for future dynamic analyses.

(2) The mean squared displacement (MSD) trends for CuZr alloys A, B, and C at 300 K exhibit a general similarity, with very close slopes. This suggests that the amount of Cu atoms has a negligible effect on the diffusion coefficient of CuZr alloys.

(3) The interaction energies of CuZr alloys with varying compositions demonstrate that as the Cu content rises, the interaction energy also increases. For alloys with the same composition, the interaction energy increases with temperature, despite the theoretical expectation that it should decrease at higher temperatures. The discrepancies are attributed to temperature-related effects.

Acknowledgments

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Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author.

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