

Molecular dynamics study of the ternary Cu₅₀Ti₂₅Zr₂₅ bulk glass forming alloy

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Abstract. The structure and thermodynamic properties of a ternary Cu₅₀Ti₂₅Zr₂₅ metallic glass forming alloy in solid-liquid to glass phases were studied using molecular dynamics (MD) method based on tight-binding (TB) potentials. An atomic description of the melting, glass formation and crystallization process has been analyzed using different heating and cooling rates. The computed Glass Forming Ability (GFA) parameters are in good agreement with experimental data. The structure analysis of the Cu₅₀Ti₂₅Zr₂₅ based on molecular dynamics simulation will be also presented and compared with available MD results. We have also discussed the crystallization transition with two different interatomic potentials used in this work.

1 Introduction

The understanding of structure and thermal stability of bulk metallic glasses (BMGs) is of great importance from both the fundamental and practical viewpoints. Although the great achievements in preparation and characterization of these materials, the specific details of the liquid-to-glass transition of multicomponent BMGs have not been fully understood yet and are still an open question [1]. Recently, BMG formation in Cu-Zr-Ti alloys has been studied by some researchers [1-5]. The glass forming ability (GFA), crystallization kinetics in the family of the Cu₅₀Zr_{50-x}Ti_x alloys have also been analysed by Men and coworkers experimentally [3]. Among the family of Cu₅₀Zr_{50-x}Ti_x alloys, Cu₅₀Zr₂₅Ti₂₅ alloy has the high GFA, with reduced glass transition temperature T_g/T₁ of 0.566 [2,3].

On the other hand, it has been proposed some theoretical analysis to evaluate GFA of the multi-component bulk amorphous alloy system [5-8]. All these theories are based on the atomistic investigations of BMG alloys. Unfortunately, however, there are less atomistic simulation studies to investigate the structural properties of ternary Cu-Zr-Ti BMGs alloys [1]. According to our knowledge, there are no published simulation results for the structural analysis and GFA parameters of the Cu₅₀Zr₂₅Ti₂₅ alloy using molecular dynamics (MD) calculations. There has been reported results only for Cu₆₀Zr₂₀Ti₂₀ alloy from MD simulations performed with Stillinger-Weber (SW) potentials [1].

In this work, we present first simulated results of the BMG-forming Cu₅₀Ti₂₅Zr₂₅ ternary alloy. MD calculations are first performed with the many body type of tight binding (TB) potentials (called as n-body Gupta potentials) for Cu-Zr-Ti system [9]. In order to investigate the GFA of the Cu₅₀Zr₂₅Ti₂₅ alloy in an atomic level, TB potentials proposed by Cleri and Rosato [9] for the pure Cu, Zr and Ti has been newly developed for the ternary Cu-Zr-Ti system. This potential yields the liquid to glass transition in the ternary Cu₅₀Zr₂₅Ti₂₅ alloy, in reasonable agreement with experimental information. However, the crystallization transition has been evaluated by the MD calculations performed with Morse type interatomic potential which are parameterized for ternary alloys by Dalgic and Celtek [10].

2 Method

As a first step for the molecular dynamics (MD) studies, it is necessary to describe atomic interactions. In this study we have developed two different type potential for ternary alloys. First, a quantum mechanics based tight-binding (TB) potential of Cleri and Rosato [9] has been used in our MD calculations and developed for ternary Cu-Ti-Zr system. In TB model, the energy of a single atom can be divided into two parts as attractive and repulsive ones. The attractive part can be given as,

$$E_B^i = - \left\{ \sum_j \xi_{\alpha\beta}^2 \exp \left[-2q_{\alpha\beta} \left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) \right] \right\}^{1/2} \quad (1)$$

where r_{ij} represents the distance between atoms i and j; r_0 is the interatomic distance between the nearest neighbours distance, ξ is an effective hopping integral and q describes its dependence on the relative inter atomic distance. The α and β variables represent different lattice of unlike neighboring atoms.

The repulsive interaction term is normally assumed to be pairwise, and described by a sum of Born-Mayer ion-ion repulsions:

$$E_R^i = \sum_j A_{\alpha\beta} \exp \left[-p_{\alpha\beta} \left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1 \right) \right] \quad (2)$$

where A is dependent on the experimental values of the lattice parameter. The parameter p is related to the compressibility of the bulk metal. For the hetero-interactions, an arithmetic mean was taken for the parameters related to the distance, $p_{\alpha\beta}$, $q_{\alpha\beta}$ and $r_0^{\alpha\beta}$, while a geometric mean was taken for parameters related to the strength, $A_{\alpha\beta}$ and $\xi_{\alpha\beta}$. The total energy of the system can be described as

$$E_C = \sum_i (E_R^i + E_B^i) \quad (3)$$

In this work, we have also used Morse potential in order to check the effect of the interatomic potential in MD simulations of ternary systems. The potential energy $\phi(r_{ij})$ of two atoms i and j separated by a distance r_{ij} is given in terms of the Morse function by

$$\phi(r_{ij}) = D \left(e^{-2\alpha(r_{ij}-r_0)} - 2e^{-\alpha(r_{ij}-r_0)} \right) \quad (4)$$

where α , D are constants with dimensions of reciprocal distance and energy, respectively; r_0 is the equilibrium distance of the two atoms. The values of Morse potential parameters for Cu₅₀Ti₂₅Zr₂₅ ternary alloy were taken from ref.[10]. In the present work, we focus on TB potential of ternary systems.

In our simulations, we have used the simulation code of DL_POLY [11]. The MD simulations are performed in a cubic box subject to periodical boundary conditions for a system with 1372 particles under zero external pressure. The NPT ensemble with the Berendsen thermostat has been used to control the temperature and pressure. The calculation region was taken in the form of a cubic cell containing 1372 atoms (the sevenfold multiplication along x, y and z of a FCC unit cell consisting of 2 Cu atoms, one of Ti atom and one of Zr atom (Cu₂Ti₁Zr₁). Newton's movement equations are solved by Verlet leapfrog algorithm with a time step 2 fs.

The stable structure at 0 K is obtained through the initial configurations annealed fully at T=300 K and then cooled to T=0 K at a cooling rate of 0.25 K/ps. A series of temperature increases from 0 K to 1700 K with an increment of 50 K for TB potential and of 100K for Morse potential in the simulation of the melting process.

Before starting the cooling process of the system, we equilibrated the liquid system at 1700 K using (NVT) ensemble with 300000 steps. Then, the system is cooled in different cooling rates from 1700 K to 300 K.

3 Results and discussion

The MD simulations using the DL_POLY simulation code [11] have been performed with Gupta potential (TB potential) at the different heating and cooling rates. The input potential parameters for Cu, Ti and Zr are listed in Table 1. We have also present the simulated results of Morse potential only to discuss the crystallization process in this alloy [10].

Fig. 1. shows the temperature dependence of the volume of Cu₅₀Ti₂₅Zr₂₅ ternary alloy at the heating rate of $\gamma=0.5$ K/ps and different cooling rates. In order to obtain the melting temperature T_m and liquidus temperature T_l , we have used $\Delta T=20$ K increment in temperature from 1050 K to 1250 K. The phase transition in Cu₅₀Ti₂₅Zr₂₅ alloy has been defined by two parameters: the change of the total pair distribution functions (PDF) from crystal form to liquid form and discontinuity in the slope given in Fig. 1.

Table 1. TB potential parameters for Cu, Ti and Zr

metal	A(eV)	ξ (eV)	p	q	$r_0(\text{\AA})$
Cu	0.0855	1.2240	10.960	2.278	2.56
Ti	0.1519	1.8112	8.6200	2.390	2.89
Zr	0.1934	2.2792	8.2500	2.249	3.17

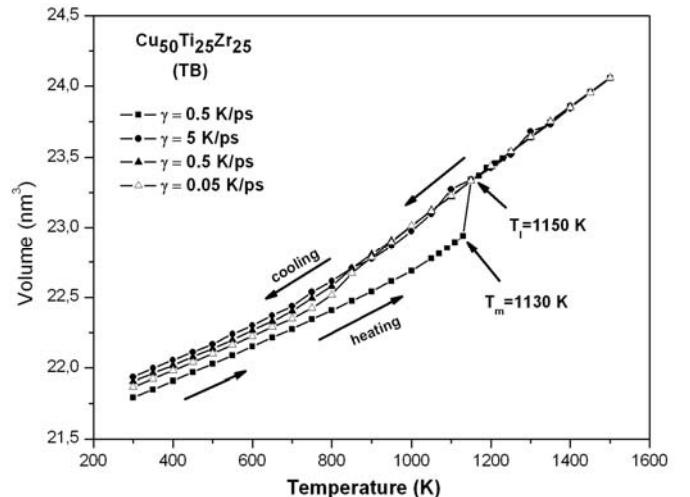


Fig. 1. The temperature dependence of volume of Cu₅₀Ti₂₅Zr₂₅ ternary alloy at heating and cooling process.

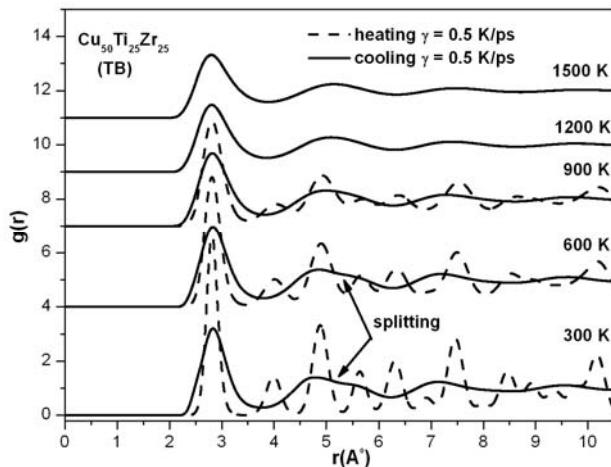
The calculated liquidus temperature $T_l=1150$ K is in good agreement with experimental liquidus temperature of $T_l=1140$ K [2]. We analyze the total PDF to investigate the structural properties of the Cu₅₀Ti₂₅Zr₂₅ ternary alloy as given in Fig 2.

Table 2. GFA parameters of the simulated Cu₅₀Ti₂₅Zr₂₅ bulk glassy alloy.

Interatomic potential	T _m ^{MD} (K)	γ ^{MD} (K/ps)	T _g (K)		T _x (K)		T _l (K)		T _{rg} (T _g /T _l)	
			MD	Exp.	MD	Exp.	MD	Exp.	MD	Exp.
TB	1130±20	5	682	-					0.593	
		0.5	655	-			1150±20		0.570	
		0.05	633	-					0.550	
Morse	1200±20	2	645 ^a	697 ^a	697 ^a	697 ^a	1140 ^a	1140 ^a	0.566 ^a	0.566 ^a
		0.2	657	-			1220±20		0.538	
		0.02	-	750					0.496	

^aref [2-3]

As shown in Fig. 2., two curves of PDF during heating and cooling processes overlap at the same temperature (at the T=1200K and T=1500K) as indicating an equilibrium liquid state. When the system is cooled to 900K, we still observe the structure of liquid, in fact a supercooled region, while system is crystalline state during heating process at same temperature. Cooling to 600K and 300K using three different cooling rates, it is seen a splitting at second peak of g(r) which known as characteristic behavior of metallic glasses.

**Fig. 2.** The simulated total PDF of Cu₅₀Ti₂₅Zr₂₅ in heating and cooling processes at different temperatures.

The simulated partial pair distribution functions (PPDFs) of g_{ij}(r) for Cu-Cu, Cu-Ti, Cu-Zr, Ti-Ti, Ti-Zr and Zr-Zr pairs are given in Figs.3. As shown in our MD calculations during the cooling processes, the second peak of all atom pairs splitting show up the temperatures below 700K. We have also examined the PPDF for all pairs at the cooling rates of 5K/ps and 0.05K/ps used in this study and similar PPDF distributions have been obtained for all pairs.

In this study Wendt-Abraham (WA) parameter ($R^{WA} = g_{min}/g_{max}$) is used to obtain glass transition temperature T_g. Here g_{min} is first minimum value and g_{max} first maximum value of PDF curve. The Wendt-Abraham parameter emphasizes the local character of g(r) permitting a direct comparison between structures and leading to a better estimation of T_g. Fig .4. gives the temperature dependence of WA parameters at the heating rate of 0.5 K/ps and different cooling rates. The model system shows a glass formation at temperatures 682K, 655K and 633K at the cooling rates of 5K/ps, 0.5K/ps and 0.05K/ps, respectively.

Fig.5 shows the WA parameter versus temperature obtained by Morse potential during heating and cooling processes. The Cu₅₀Ti₂₅Zr₂₅ BMG alloy shows a glass formation at temperatures 657K and 605K at the fast cooling rates of 2K/ps and 0.2K/ps while the slower cooling rate of 0.02K/ps leads to crystallization at 750K. Fig 6. shows that g_{min}/g_{max} is fitted to linear function to estimate the glass temperature at the cooling of 5 K/ps. Reduced glass-transition temperature (T_{rg}) can thus obtained by simply dividing glass transition temperature (T_g) by liquidus temperature (T_l) as T_{rg}=T_g/T_l. Table 2. lists glass transition temperature (T_g), liquidus temperature (T_l), melting temperature (T_m), crystallization temperature (T_x) and reduced glass-transition temperature T_{rg} obtained using different two interatomic potentials comparing with the experimental values given in ref. [2,3].

Table 2 shows, the simulated liquidus temperature of TB potential is about 1150K at the cooling rate of 0.5K/ps that is 10K lower than the reported experimental value given in Ref [2,3]. However, MD results based on TB potential were not predicted the crystallization temperature. Table 2 exhibits the computed value of crystallization temperature (T_x) with Morse type potential is close to the reported experimental one. The simulated T_{rg} values are agree well with experiment.

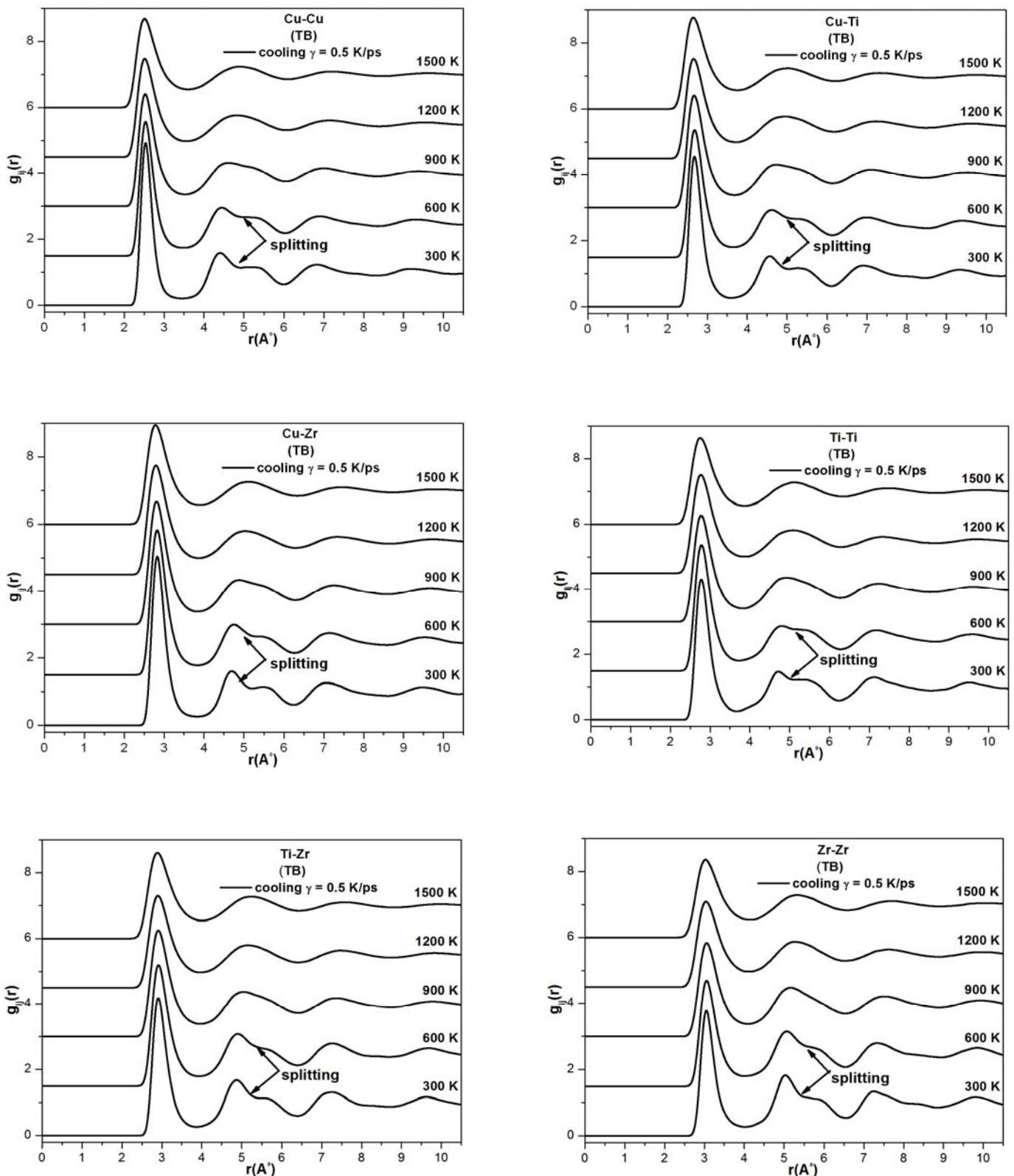


Fig. 3. The PPDF of the Cu-Cu, Cu-Ti, Cu-Zr, Ti-Ti, Ti-Zr and Zr-Zr pairs in simulated $\text{Cu}_{50}\text{Ti}_{25}\text{Zr}_{25}$ alloy at different temperatures.

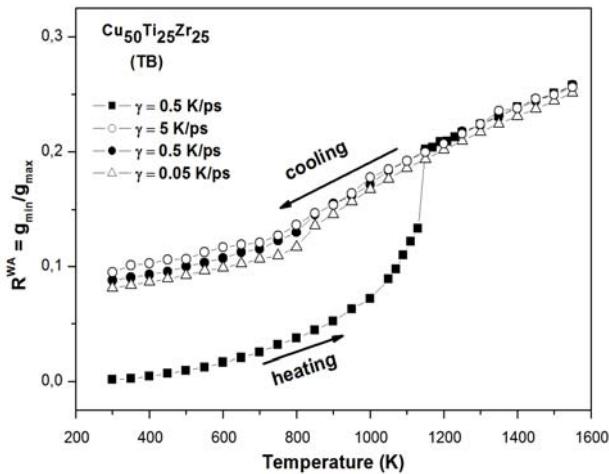


Fig. 4. WA parameters versus temperature for $\text{Cu}_{50}\text{Ti}_{25}\text{Zr}_{25}$ ternary alloy obtained using TB potential.

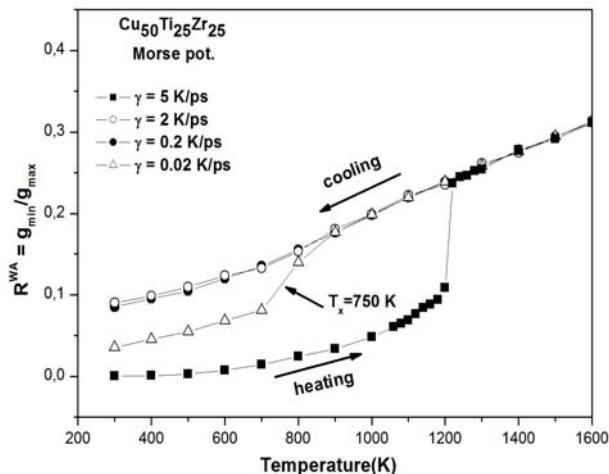


Fig. 5. WA parameters versus temperature for $\text{Cu}_{50}\text{Ti}_{25}\text{Zr}_{25}$ ternary alloy obtained using Morse potential.

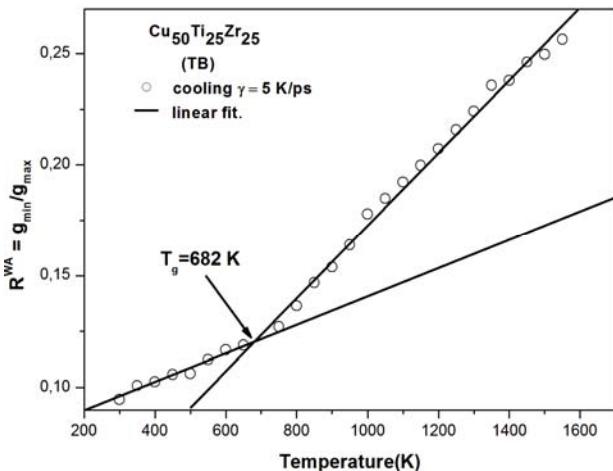


Fig. 6. Temperature dependence of g_{min}/g_{max} values fitted to a linear function to estimate the glass temperature T_g at the cooling rate of $\gamma = 5 \text{ K/ps}$.

4 Conclusion

The present study reports results from MD modeling of the ternary $\text{Cu}_{50}\text{Ti}_{25}\text{Zr}_{25}$ alloy with NPT and NVT molecular dynamic simulation. The two different interatomic potential is used to investigate the GFA ability of this ternary system. For these potentials, the MD simulated and experimental GFA parameters such as T_g , T_l , T_{rg} , T_x values are in a good agreement. It has been noted that the glass transition temperature depends on the cooling rate; the larger cooling rates give the higher the glass transition temperature.

It is also found that the Morse potential yields fcc crystal structure for only at the cooling rate of 0.02 K/ps and amorphous structure for cooling rates of 2 K/ps and 0.2 K/ps , while TB potentials produces amorphous structure for each cooling rates from 5 K/ps to 0.05 K/ps .

Pair distribution functions (PDF) have calculated to analyze the local structure. When the system is cooled with different cooling rates, the splitting of the second peak of $g(r)$ appears in the glass state.

In summary, TB potentials for the Cu-Ti-Zr ternary system is now available to show the glass transition temperature of this alloy but crystallization does not occur. However the glass formation ability (GFA) and crystallization transition can be obtained by the morse potential parameterized newly [10]. The results from MD studies of Morse potential concerning the microscopic structure and dynamics of the ternary bulk metallic glass forming alloy $\text{Cu}_{50}\text{Ti}_{25}\text{Zr}_{25}$ will be reported in elsewhere.

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