Vol 14 No 4, April 2005
1009-1963/2005/14(04)/0802-06
Chinese Physics
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Investigation of multicomponent chemical short-range order in $NiZr_2$

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(Received 28 May 2004; revised manuscript received 22 November 2004)

The local atomic configuration of multicomponent chemical short-range order (MCSRO) in $NiZr_2$ has been investigated by means of molecular dynamics simulation (MD) in a wide temperature range. The potential functions for the system based on the embedded atom method are constructed and the parameters are obtained by fitting the structure and properties of $NiZr_2$ crystal. The static structures such as pair distribution functions and the distribution of coordination number have been calculated. The local atomic configurations of the MCSROs in the melt were demonstrated as distorted coordination polyhedron of the compound structure and/or the structure similar to cubooctahedron analogues. It is indicated by the results of MD simulation that above the melting point the atomic packing of long-range order disappears, but the chemical interaction of coordinated atoms still exists, which leads to the formation of various MCSROs with atomic configurations similar to the stable or metastable unit cell of $NiZr_2$ compound. When the system is just melted, many icosahedral polyhedron configurations appear, which decrease as the over-heating temperature increases.

Keywords: molecular dynamic simulation, structure, chemical short-range order, melt
PACC: 7115Q, 6155H, 6470D

1. Introduction

It has been found that the multicomponent chemical short-range order (MCSRO) in the molten alloy system is a very important concept for understanding the structure of molten and amorphous alloys.[1,2] Formation of the MCSRO in the melt may result in a variation of energy of the liquid and affect the thermodynamics and kinetics of nucleation and growth of crystalline phases. The definition of the MCSRO is similar to the concept employed in the order–disorder transformation phenomenon. At critical ordering temperature the long-range order of a compound disappears but the short-range order of the compound still exists. Similarly, above melting point the packing of long-range order of crystalline should be dissolved, but the chemical interaction of bounding atoms still exist that leads to the forming of MCSRO. As a result, the local atomic configuration of MCSRO could keep the basic characteristics of its compound counterpart, but may have slight distortion.

The main purpose of this work is to study the coexistence of different local atomic configurations in molten $NiZr_2$ by molecular dynamics (MD) simulation. The investigation of atomic configurations of MCSRO will further develop the concept of MCSRO for understanding the mechanism of amorphization.

2. Model and computational procedure

In the present work, the EAM (embedded atom method) potential[3−5] was used for carrying out the MD simulation

$$E = \frac{1}{2}\sum_{i,j}\phi_{ij} + \sum_{i}F_i\left(\rho_i\right), \tag{1}$$

where ϕ_{ij} is a two-body central potential between atom i and j within the separation distance r_{ij}, and $F_i(\rho_i)$ is the embedding energy of atom with the electron density

$$\rho_i = \sum_{j(\neq i)} f_j(r_{ij}). \tag{2}$$

In our MD simulation, the pair interaction is taken as a short-range, purely repulsive potential of the form

$$\phi_{ij}(r) = A_{ij}\exp(-r/B_{ij}), \tag{3}$$

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The density and embedding functions are given by

$$f(r) = c_i \exp\left[-b_i * (r - d_i)\right], \quad (4)$$

$$F(\rho_i) = -\rho_i^{1/2}. \quad (5)$$

The parameters have been obtained by fitting to the experimental cohesive energy, the bulk modulus, and the structure of crystalline $NiZr_2$ with the software GULP1.3.[6] The cutoff distance of the potential is set to be 0.53nm.

Table 1. Parameters of the EAM potential.

	Ni–Ni	Ni–Zr	Zr–Zr
A_{ij}/eV	2136254.9	73932.898	991392.58
B_{ij}/nm	0.01501	0.02057	0.01935
	Ni	Zr	
c_i/eV	1.2357	2.2927	
b_i /nm	0.092876	0.061313	
d_i /nm	0.2490	0.3282	

Table 2. Optimized structure and properties of crystalline $NiZr_2^*$.

	Experimental	Present work (EAM potential)	Massobric *et al*[7] (TB potential)
E_c	6.0	6.02	5.9
B	1.19	1.03	1.16
C_{11}	1.59	1.26	1.47
C_{12}	1.34	0.98	1.00
C_{13}	0.85	0.80	0.95
C_{33}	1.47	1.64	1.67
C_{44}	0.24	0.43	0.54
C_{66}	0.06	0.54	0.59
c	0.5267, 0.5241**	0.5237	0.5124
a	0.6483, 0.6477**	0.6483	0.6611

*The unit of cohesive energy E_c is eV/atom. The bulk modulus and elastic constants are expressed in units of 100GPa, cell dimensions c and a in nm. The experimental data of E_c, B, and elastic constants are taken from the data cited by Massobric *et al* (Ref.[7]).

**Data taken from Ref.[8].

The crystalline structure of tetragonal $NiZr_2$ (space group I4/MCM) is of the $CuAl_2$ C16-structure type. In $NiZr_2$ crystal each Ni atom has 8 Zr atoms and 2 other Ni atoms as the nearest neighbours, and there are 4 Ni atoms and 11 Zr atoms around a Zr atom. The cell parameters are $a = b = 0.6477$nm, c=0.5241nm[8]. The simulated $NiZr_2$ system contains 768 atoms (256 Ni, 512 Zr) in 4×4×4 lattice units. The initial positions of the atoms were set according to the structure of $NiZr_2$ crystal. The const-NPT MD simulation was performed with 5th Gear prediction–correction algorithm, using the MD program XMD2.5.32.[9] The MD time step was set as 1fs. During the simulation, the system was heated from 300K to 2400K under zero external pressure. At each temperature the system evolved over 30000 MD steps with periodic boundary conditions.

3. Simulation results

A series of simulations were performed from 300K to 2400K and several thermodynamic quantities were calculated. The temperature dependence of the potential energy U and the molar volume V of the simulated system are shown in Fig.1. It is found from the trend of the potential energy and volume versus temperature that phase transformation of the simulated system occurred between 1500K and 1530K. The MD calculated melting point of $NiZr_2$ with our model is about 100K higher than the experimental data (for example 1423K reported by Kirkpatrick and Larsen[8]), which may be due to the limited duration of simulations and the factor that extended defects are absent in the model crystal.

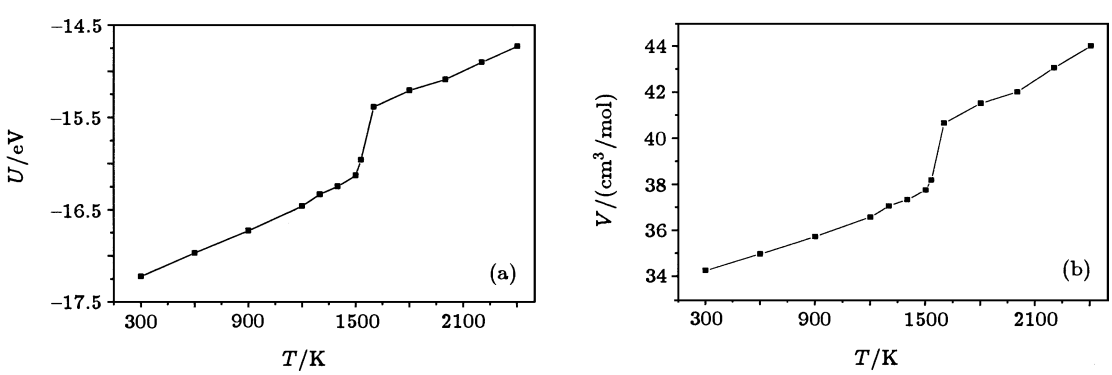


Fig.1. Temperature dependence of calculated potential energy (U) and volume (V) per mole.

The structure of a simulated system is often provided by the pair distribution function (PDF),

$$g_{\alpha\beta(r)} = \frac{V}{N_\alpha N_\beta} \left\langle \sum_{i=1}^{N_\alpha} \frac{n_{i\beta}(r, \Delta r)}{4\pi r^2 \Delta r} \right\rangle, \qquad (6)$$

where $n_{i\beta}(r,\ \Delta r)$ is the number of β-type atoms around a central α-type atom within the distance interval between r and $r+\Delta r$. The pair distribution functions of $NiZr_2$ calculated from our MD simulated structure are plotted in Fig.2. The calculated PDFs of $NiZr_2$ melt can be compared with the experimental results[10] or other MD works for the amorphous $NiZr_2$.[7] The temperature dependence of the shape of PDF curves clearly reflects that the periodic structure of crystal lattice is gradually destroyed with temperature increasing.

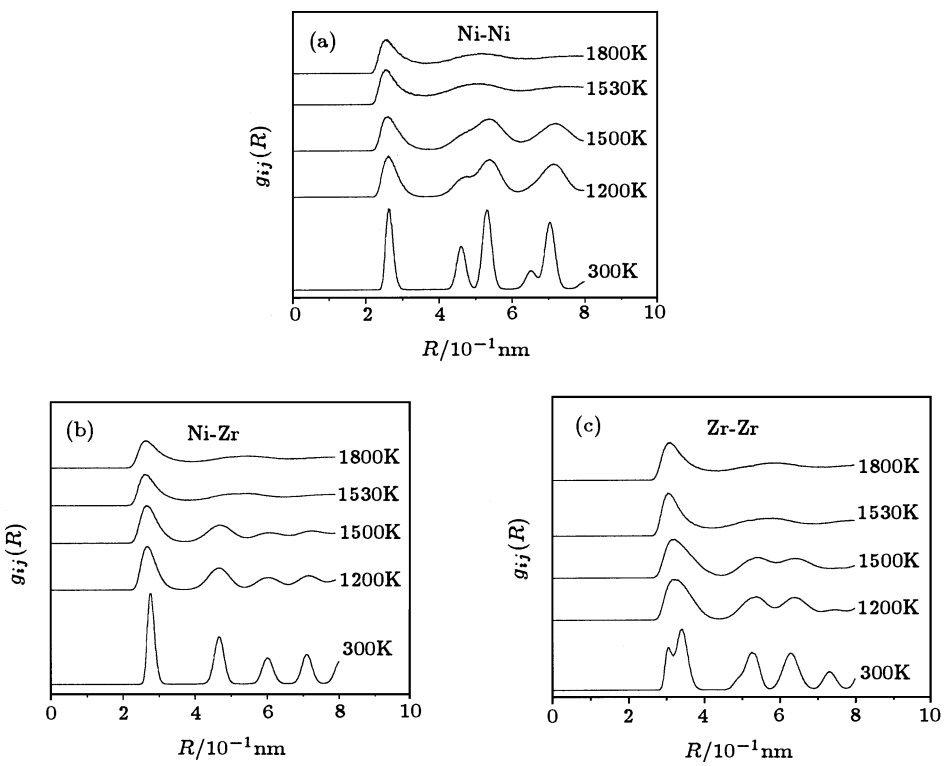


Fig.2. Calculated partial pair distribution functions of $NiZr_2$.

To study the influence of temperature on the order/disorder transformation of $NiZr_2$, we estimated packing degree (PD) and the long-range order degree of the simulated $NiZr_2$ system. The packing degree is represented by the probability of an atom occupying an original lattice site, and the long-range order parameter LRO is defined by LRO=(PD–C)/(1–C), where PD is packing degree mentioned above and C is the molar fraction of the atom in the system. In present work, PD was calculated by

$$\mathrm{PD} = \frac{1}{MN} \sum_{j=1}^{M} \sum_{i=1}^{N} P_i, \qquad (7)$$

assuming that there are M stored configurations and the number of α-type atoms in the simulated system is N. The parameter P_i is unity if the displacement of atom i between its current position and any one original crystal lattice is less than the atom radii, otherwise it is zero. The atom radii are given as R_{Ni}=0.125nm and R_{Zr}=0.16nm. The PD and LRO calculated for Ni atom are plotted in Fig.3 and Fig.4, respectively, from which one can see that in the simulated $NiZr_2$ melt more than 30% of Ni atoms still occupy the original lattice sites though the periodic long-range-order structure is destroyed. On the other hand, at small over-heating (say, temperature lower than 1800K), the long-range order may be maintained to a certain extent. These phenomena indicate the existence of chemical short-range order (CSRO) in the melt, and the form of CSRO may be different due to the increasing of total chemical disorder with temperature.

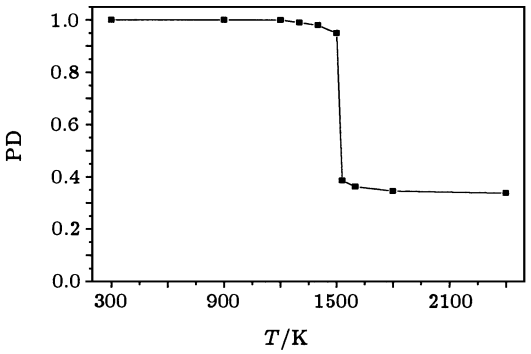


Fig.3. Packing degree (PD) of simulated $NiZr_2$ system. The occupying probability is calculated for Ni atom.

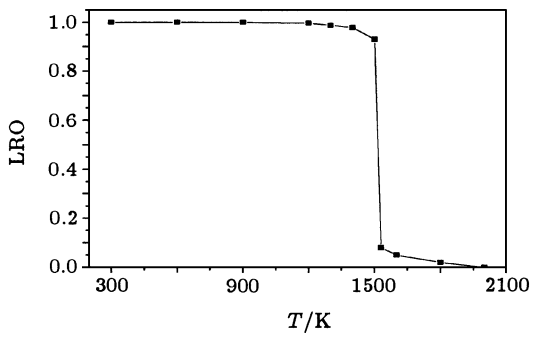


Fig.4. Long-range disorder (LRO) degree of simulated $NiZr_2$ system. The occupying probability is calculated for Ni atom.

The coordination numbers (CN) were obtained by taking the integral of $g(r)$ up to the first minimum:

$$N_{\alpha\beta(r)} = \frac{4\pi N_\beta}{V} \int_0^r r^2 g_{\alpha\beta(r)} \mathrm{d}r. \qquad (8)$$

It was found that the coordination numbers merely have slight change during the temperature increasing from 300K to 1500K, which indicated that the short range ordered structure of tetragonal $NiZr_2$ crystal is quite stable. However, when the temperature increases from 1500K to 1530K, the coordination numbers of N_{Ni-Ni}, N_{Ni-Zr} and N_{Zr-Zr} suddenly change from 2.01, 8.02 and 10.97 to 2.49, 8.47 and 9.50, correspondingly. This dramatic change of CN suggests the occurrence of phase transformation, which is consistent with the result of temperature dependence of system volume and potential energy described above. In order to investigate the form of CSRO in the crystal and the melt of $NiZr_2$, the distribution of total coordination number of Ni and Zr atoms were calculated by counting the number of the neighbours of every Ni/Zr atom in the MD configurations. The cutoff distance for searching the neighbours is defined by the first minimum of the corresponding pair distribution function (PDF). The calculated distributions of total CN of Ni and Zr averaged over 1000 MD configurations are shown in Tables 3 and 4. The total CN of both Ni and Zr rapidly change at simulated melting point (1500–1530K). Before and after melting, the number of Ni atoms with total CN=11 and CN=12 increases and that with total CN=10 (the general situation in the crystalline $NiZr_2$) dramatically decreases. In addition, the total CN of about 30% Ni atoms still keep at 10 at high temperature. As for Zr atoms, there are totally 15 coordinate atoms (4 Ni atoms and 11 other Zr as mentioned above) in the perfect tetragonal $NiZr_2$ crystal. It is shown in Table 4 that there is a remarkable decrease in the number of Zr atoms with CN=15 after melting, however with temperature increasing the number of Zr with smaller CN grows more and more. At the highest temperature, the number of Zr atoms with CN=12–13 is increased by about 50%.

Table 3. Distribution of total coordination number of Ni atoms (averaged over 1000 stored MD configurations).

Total CN	300K	900K	1500K	1530K	1800K	2400K
5	0	0	0	0	0	0.01
6	0	0	0	0	0.01	0.08
7	0	0	0.03	0.03	0.31	0.99
8	0	0	0.38	1.04	2.81	5.34
9	0.06	0.14	6.03	7.88	13.89	17.54
10	99.94	99.73	85.76	26.46	29.12	29.76
11	0	0.12	7.00	35.51	31.20	27.45
12	0	0	0.74	22.52	17.20	14.10
13	0	0	0.06	5.8	4.76	4.09
14	0	0	0.01	0.73	0.66	0.61
15	0	0	0.01	0.05	0.04	0.04

Table 4. Distribution of total coordination number of Zr atoms (averaged over 1000 stored MD configurations).

Total CN	300K	900K	1500K	1530K	1800K	2400K
7	0	0	0	0	0	0
8	0	0	0	0	0	0.03
9	0	0	0	0.01	0.04	0.36
10	0	0	0	0.26	0.49	2.18
11	0	0	0.01	2.56	3.14	8.04
12	0	0	0.10	12.34	12.32	19.52
13	0	0.01	1.18	28.41	25.60	28.12
14	0.00	0.56	10.5	32.20	29.58	24.37
15	100.0	98.94	78.91	18.26	19.55	12.59
16	0	0.49	8.66	5.14	7.43	3.90
17	0	0	0.60	0.74	1.66	0.77
18	0	0	0.03	0.06	0.18	0.10
19	0	0	0	0	0.01	0.01

As can be seen from Tables 3 and 4, the width of the distributions of total coordination number of Ni and Zr atoms increases and the average total CN also changes with increasing temperature, thus multiple structures of CSRO must exist due to the non-uniform coordination number and the dominating forms of CSRO at different temperature must be unlike. Therefore, we analysed the variety of the local structure of the simulated system with the increasing temperature. The perfect $NiZr_2$ tetragonal antiprism structure (with the central atom of Ni and CN=10) is shown in Fig.5(a). The character of the antiprism is that the coordination atoms of a central atom are arranged in four layers with the atom numbers what are 1, 4, 4, 1 in turn. This type of local structure, just having various degrees of slight distortion, is the dominating manner of atoms stowed in the simulated system at temperature lower than 1500K.

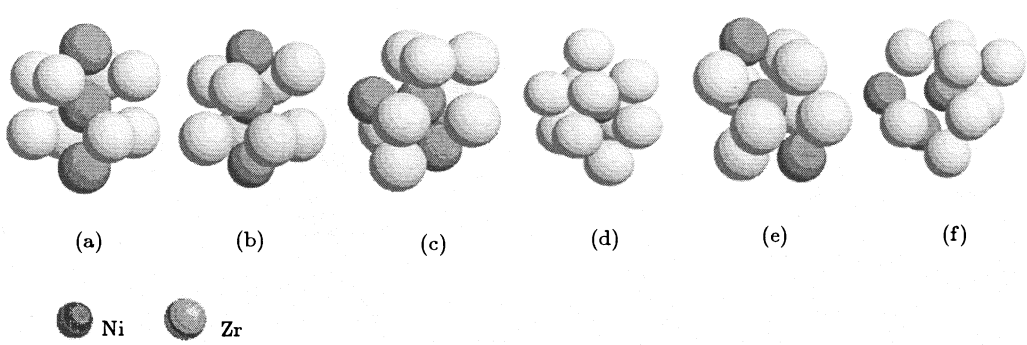


Fig.5. Pictures of tetragonal antiprism (1441, total CN =10) local structure. (a) is the perfect tetragonal antiprism structure in $NiZr_2$ crystal, (b)–(f) are taken from the instantaneous configurations obtained by MD simulations at different temperature. (b), T=1500K, (c) and (d), T=1530K, (e) and (f), T=2400K.

After melting, the abundance of the antiprisms with CN=10 rapidly decreases, and the structural distortion of them as well as the exchange of Ni and Zr atoms are obvious as shown in Figs.5(c) and (d). At the highest temperature of the simulations (2400K), in general the tetragonal antipisms with CN=10 existing in the melt are highly distorted, as in Fig.5(f), but a few tetragonal antiprism structures with relatively slight distortion like Fig.5(e) also can be found. As mentioned above, the number of Ni atoms with 11–12 total nearest neighbours dramatically increases after melting. We analysed those configurations of CN12 and found that some of them have a 3–6–3 stacking structure at 1530K, as shown in Fig.6(b). This type of stacking is just like the coordination figures of cobooctahedron (FCC) or its hexagonal analogue (HCP, see Fig.6(a)). This phenomenon indicates that perhaps the metastable FCC $NiZr_2$ phase occurs in the melt at temperature near the melting point. At higher temperature, the 3–6–3 stacking structures can still be

observed (Fig.6(c)) but they usually have larger distortion. On the other hand, in the simulated melt some coordination figures of CN12 exhibit the icosahedron structure (i-phase, the number of atoms in the layers are 1,5,5,1) shown in Fig.7. As the temperature increases, it is more difficult to find the i-phase structure.

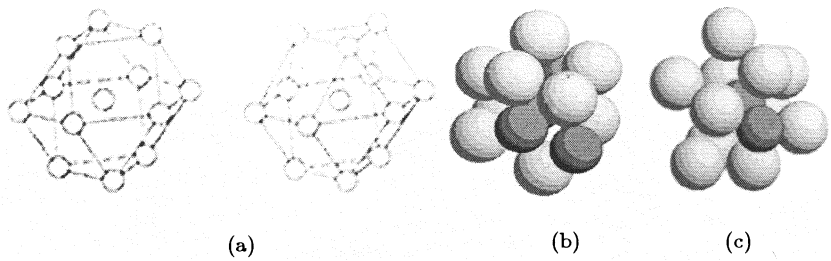


Fig.6. Pictures of CN=12 (3–6–3) stacking structure. (a) are the regular arrangement of cubooctahedron (FCC, the left) and its hexagonal analogue (HCP, the right), the others are the 3–6–3 stacking structure taken from the simulation at (b) T=1530K and (c) T=2400K.

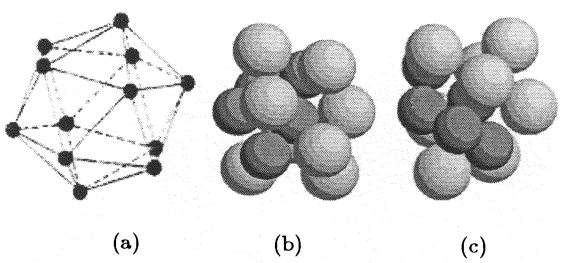


Fig.7. Pictures of i-phase (1551, total CN=12) icosahedron structure. (a) is the regular fivefold icosahedron structure, the others are taken from the simulation at (b) T=1800K and (c) T=2400K.

4. Summary and conclusions

The main purpose of this paper is to investigate the structure of $NiZr_2$ by molecular dynamics simulation. An N-body EAM potential model for the system was constructed by fitting the experimental data of structure and properties of crystalline $NiZr_2$. From the varieties of the total static structure given by the calculated pair distribution functions and the distribution of coordination numbers, and the thermodynamic properties of potential energy and volume of the system with the temperature increasing, it is estimated that the melting point of the simulated system is around 1500–1530K, which is consistent with the experimental result. The structure of the solid state $NiZr_2$ is relatively stable but after melting the long-range order degree is rapidly decreasing. In order to describe the chemical short-range order in $NiZr_2$, the coordination structure in the system has been investigated in detail and some typical pictures of various coordination structures were shown. In conclusion, the characteristics of the chemical short-range order in the $NiZr_2$ melt can be summarized as follows. (1) At small over-heating temperature, MCSRO exhibits distorted $NiZr_2$ tetragonal antiprism structure together with a few FCC and i-phase structures. (2) At increased over-heating temperature, the CSRO with i-phase structure may become less and a few MCSROs exhibit large distorted $NiZr_2$ structure.

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