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Thermodynamic model for glass forming ability of ternary metallic glass systems①

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[Abstract] The thermodynamic model of multicomponent chemical short range order (MCSRO) was established in order to evaluate the glass forming ability (GFA) of ternary alloys. Comprehensive numerical calculations using MSCRO software were conducted to obtain the composition dependence of the MCSRO undercooling in Zr-Ni-Cu, Zr-Si-Cu and Pd-Si-Cu ternary systems. By the MCSRO undercooling principle, the composition range of Zr-Ni-Cu system with optimum GFA is determined to be 62.5~ 75Zr, 5~ 20Cu, 12.5~ 25Ni ($n(\mathrm{Ni})/n(\mathrm{Cu}) = 1 \sim 5$). The TTT curves of Zr-Ni-Cu system were also calculated based on the MCSRO model. The critical cooling rates for Zr-based alloy with deep MSCRO undercooling are estimated to be as low as 100 K/s, which is consistent with the practical cooling rate in the preparation of Zr-based bulk metallic glass (BMG). The calculation also illustrates that the easy glass forming systems such as Pd-based alloys exhibit an extraordinary deep MCSRO undercooling. It is shown that the thermodynamic model of MCSRO provides an effective method for the alloy designing of BMG.

[Key words] thermodynamic model; multicomponent chemical short range order (MCSRO); undercooling; bulk metallic glasses (BMG); glass forming ability (GFA), Zr-Ni-Cu system

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1 INTRODUCTION

Great advancement has been achieved in preparing bulk metallic glass (BMG) by alloy designing since 1990s. Zr-based[1,2], Ti-based[3,4], Fe-based[5] and Pd-based BMGs[6] have been successfully fabricated with the ordinary casting, suck casting and other conventional methods at the cooling rate lower than 100 K/s. It is shown that all the BMGs are composed of more than three components. Some BMGs such as $\mathrm{Co_{67}Cr_3Fe_3Al_5Ga_2P_{15}B_4C}$ even contain eight components. Therefore, how to select the kind and the amount of components is very important in the development of BMG. Theoretical models should then be established to direct the composition designing. So far as present, the alloy designing of BMG is usually conducted according to the following rules: 1) the reduced glass transition temperature proposed by Marcus[7] (T_g/T_m, T_g is the glass transition temperature and T_m is the melting point). For most BMGs, T_g/T_m ratio is usually larger than 0.56; 2) the eutectic rule proposed by Donald et al[8], which is considered that the alloy with the composition near the eutectic point is easy to form amorphous; 3) the empirical rules proposed by Inoue[9] that multicomponent alloy systems consist of more than three elements; significant atomic size differences are above 12% among the constituent elements; and mixing heat among the constituent elements is negative. Although the above rules are proved to be valid for most BMGs, their foresight in the predication of GFA is not good enough. The "trial error" is still the popular method in composition designing of BMGs.

From the viewpoint of crystallization, the formation of BMG is practically a continuous cooling process at the temperature lower than melting point in which the nucleation is impeded and undercooled liquid is kept in the chaotic state. Thermodynamically, this means that great undercooling should be needed to produce homogenuous nucleation. Kinetically, the diffusion rate of atoms reduces and diffusion distance increases so that it is difficult to form a homogenuous nucleation. Therefore, it is reasonable to establish a theoretical model for the composition designing of BMG based on the thermodynamic and kinetic characteristics of alloys.

In this paper, it is considered that the undercooling caused by the co-existence of multicomponent chemical short range orders (MCSROs) is the most important factor for the formation of BMGs. The thermodynamic model of MCSRO is established in order to evaluate the glass forming ability (GFA) of the alloy. Comprehensive numerical calculations using MSCRO software are conducted to obtain the composition dependence of the MCSRO undercooling in Zr-Ni-Cu, Zr-Si-Cu, and Pd-Si-Cu ternary systems. The composition range with optimum GFA is also determined based on the theoretical model and experimen-

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tal results.

2 THEORETICAL FORMULATION

Amorphous alloys are known as short-range ordered materials. It is noticeable that metallic glasses always exhibit strong compound forming tendency and the corresponding inhomogeneity of the concentration resulted from the change of structures[10~12]. Many investigations indicate that the assumption of the random distribution of atoms in the metallic melt disagrees with experimental results. This can only be reasonably interpreted that MCSROs are present in the multicomponent liquid. At any moment the MCSRO may be changed in composition, ordered state and volume, but the MCSRO domains are in a statistically dynamic equilibrium with the random distributed atoms. Therefore the volume fraction and the stoichiometric composition of MCSRO domain can be determined at a given temperature and initial concentration. It should be pointed out that the model of coexisted MCSRO domain are simplified. In fact the lifetime of those MCSRO domains should be longer than the time necessary for atomic diffusion at that temperature.

In the above physical model of liquid structure, the second derivation of the Gibbs energy (G) with respect to the molar fraction (x) satisfies the following equation[13]:

$$\frac{1}{2}\sum_{i=1}^{N-1}\left[\frac{\partial^2 G}{\partial x_i^2}\right](\Delta x_i)^2+\sum_{i,j(i\neq j)}\left[\frac{\partial^2 G}{\partial x_i\partial x_j}\right]\Delta x_i\Delta x_j > 0 \tag{1}$$

where N represents the multicompnent number, i and j represent the component i and j.

Now we consider a metallic melt composed of A_1, A_2, …, A_N component. The base binary system A_i-A_j contains M kinds of MSCO domains, i. e. $A_i^{11}A_j^{12}$, $A_i^{21}A_j^{22}$, …, $A_i^{M1}A_j^{M2}$. M_1 and M_2 represent the composition in $A_i^{M1}A_j^{M2}$ MCSRO domain. The substance amout of the domains is noted as $n(A_i^{11}A_j^{12})$, $n(A_i^{21}A_j^{22})$, …, $n(A_i^{M1}A_j^{M2})$. The substance amount of free atom is noted as $n(A_1^0)$, $n(A_2^0)$, …, $n(A_N^0)$. Then total amount of substance is

$$n=\sum_{i=1}^{N}n(A_i^0)+\sum_{\substack{i=1\\j=i+1}}^{N-1}\sum_{k=1}^{M}n(A_i^{k1}A_j^{k2}) \tag{2}$$

The absolute substance amount, $n(A_1)$, $n(A_2)$, …, $n(A_N)$ are related to the substance amount by the following equation.

$$n(A_i^0)=n(A_i)-\sum_{\substack{j=1\\j\neq i}}^{N}\sum_{k=1}^{M}k_1\cdot n(A_i^{k1}A_j^{k2}) \tag{3}$$

The mixing enthalpy and the entropy in regular melt can be written as follows.

$$\Delta H=\sum_{\substack{i=1\\j=i+1}}^{N-1}\sum_{k=1}^{M}C(A_i^{k1}A_j^{k2})\,n(A_i^{k1}A_j^{k2})+ C(A_i^0,A_j^0)\,n(A_i^0)\,n(A_j^0)/n]+\sum_{p=1}^{N}\sum_{\substack{j=1\\i=j+1}}^{N-1}\sum_{k=1}^{M}[C(A_p^0,A_i^{k1}A_j^{k2})\,n(A_p^0)\,n(A_i^{k1}A_j^{k2})/n] \tag{4}$$

$$\Delta S=-R\sum_{i=1}^{N}\sum_{k=1}^{M}n_i^0\ln x_i^0+\sum_{\substack{i=1\\j=i+1}}^{N-1}\sum_{k=1}^{N}]-R\cdot n(A_i^{k1}A_j^{k2})\ln x(A_i^{k1}A_j^{k2})+n(A_i^{k1}A_j^{k2})\cdot S(A_i^{k1}A_j^{k2})] \tag{5}$$

where $C(A_i^{k1}A_j^{k2})$ is the formation enthalpy of $A_i^{k1}A_j^{k2}$ MCSRO domain, $C(A_i^0,A_j^0)$ represents the interaction coefficient between the A_i and A_j single atom, $C(A_p^0,A_i^{k1}A_j^{k2})$ is the interaction coefficient between A_p single atom and $A_i^{k1}A_j^{k2}$ MCSRO domain, $S(A_i^{k1}A_j^{k2})$ is the additional formation entropy, x_i^0 is the molar fraction of single i atom. $x(A_i^{k1}A_j^{k2})$ is the molar fraction of $A_i^{k1}A_j^{k2}$ MCSRO domain.

The chemical potential μ_i ($i=A_i^0$, …, $A_i^{k1}A_j^{k2}$, …) is expressed as

$$\mu_i=\mu_i^0+RT\ln(n_i/n)+RT\ln\gamma_i \tag{6}$$

where R is the gas constant, T is the temperature, γ is the activity coefficient.

The Gibbs free energy of different species determined by the chemical potentials is

$$\Delta G=\sum_{\substack{i=1\\j=i+1}}^{N-1}\sum_{k=1}^{M}n(A_i^{k1}A_j^{k2})\,\Delta G^0(A_i^{k1}A_j^{k2})]+RT\Big\{\sum_{i=1}^{N}n_i^0\ln(n_i^0\gamma_i^0/n)+\sum_{\substack{i=1\\j=i+1}}^{N-1}\sum_{k=1}^{M}n(A_i^{k1}A_j^{k2})\ln[n(A_i^{k1}A_j^{k2})\,\gamma(A_i^{k1}A_j^{k2})/n]\Big\}$$

$$\Delta G^0(A_i^{k1}A_j^{k2})=\mu^0(A_i^{k1}A_j^{k2})-k_1\mu^0(A_i^0)-k_2\mu^0(A_j^0) \tag{7}$$

The equilibrium value of $n(A_i^{k1}A_j^{k2})$ in Eqns. (6) and (7) is determined by

$$\left[\frac{\partial\Delta G}{\partial n(A_i^{k1}A_j^{k2})}\right]_{T,P,n(A_1),n(A_2),\cdots,n(A_N)}=0 \tag{8}$$

Dynamic equilibrium equation of MCSRO is then obtained from Eqns. (6) and (7)

$$\Big[n(A_i)-\sum_{\substack{i=1\\j\neq i}}^{N}\sum_{k=1}^{M}k_1 n(A_i^{k1}A_j^{k2})\Big]^{k_1}\cdot\Big[n(A_i)-\sum_{\substack{i=1\\j\neq i}}^{N}\sum_{k=1}^{M}k_2 n(A_i^{k1}A_j^{k2})\Big]^{k_2}\Big/\Big[n(A_i^{k1}A_j^{k2})\cdot n^{(k_1+k_2-1)}\Big]=\frac{1}{\exp[-\Delta G^0(A_i^{k1}A_j^{k2})/RT]}=\frac{1}{K(A_i^{k1}A_j^{k2})} \tag{9}$$

where $K(A_i^{k1}A_j^{k2})$ is the dynamic equilibrium constant of $A_i^{k1}A_j^{k2}$ MCSRO domains.

The co-existence of MCSROs in the melt may result in a reduction of Gibbs free energy and then affect the thermodynamics and kinetics of crystallization. When crystalline nuclei form and grow, the coexisted MCSRO near the nucleus is dissolved. Much more energy must be supplied to decompose the neighboring MCSRO domains. In addition, the diffusion for the crystallization may become more difficult because the diffusion distance of the atoms increases. Therefore, in order to form a critical nucleus, the melt containing coexisted MCSRO (noted as MCSRO-melt) need larger undercooling in comparison with single atom (noted as homo-melt). Therefore it is reasonable to evaluate the GFA of an alloy by the difference between the undercooling in MCSRO-melt and in homo-melt. In this paper, the difference is defined as MCSRO undercooling (ΔT_M). The larger the ΔT_M, the higher the GFA of an alloy is.

The Gibbs energy barrier ΔG_n^* to the nucleation of a critical nucleus can be described as

$$\Delta G_n^* = \frac{16}{3}\pi\frac{\sigma^3}{\Delta G_v^2} \tag{10}$$

where σ is molar interfacial energy, ΔG_v is the Gibbs energy driving force.

When homogeneous nucleation occurs at the temperatures T_M and T_H in MCSRO-melt and homo-melt, the Gibbs energy driving forces, ΔG_M and ΔG_H, can be expressed respectively as

$$\begin{aligned}\Delta G_M &= (H_S - H_M) - T_M(S_S - S_M) \\ &= -\frac{L_m \Delta T_M}{T_m} + (H_L - H_M) - \\ &\quad T_M(S_L - S_M)\end{aligned} \tag{11}$$

$$\Delta G_H = -\frac{L_m \Delta T_H}{T_m} \tag{12}$$

where H is enthalpy, S entropy, T_m melting point, L_m fusion latent, ΔT undercooling. L and S represent liquid and solid, respectively.

Assuming interfacial energy σ is not changed, the MCSRO undercooling for certain critical radius of nucleus could be estimated:

$$\begin{aligned}\Delta T_M &= \frac{(H_L - H_M) - T_M(S_L - S_M)}{L_m} T_m \\ &= (G_H - G_M)/\Delta S_m\end{aligned} \tag{13}$$

It is shown that the MCSRO undercooling is related to the difference of Gibbs free energy between the two kinds of melt at T_M and to the entropy of fusion. Larger difference between the Gibbs free energy of MCSRO melt and homo-melt and smaller entropy of fusion at T_m for the solidification of homo-melt are favorable to increase MCSRO undercooling. The Gibbs free energy of homo-melts can be calculated by the well-known formulae[14, 15].

3 EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Zr-Ni-Cu system

On the basis of theoretical model, comprehensive numerical calculations are carried out for Zr-Ni-Cu ternary system by using an MSCRO software. The basic thermodynamic properties of all elements are given. In Zr-Ni-Cu system, the prevailing MSCRO domains possess the following stoichiometric composition: Zr_2Ni and Zr_2Cu. The Gibbs free energy of Zr_2Ni and Zr_2Cu is given in Ref. [16, 17]. Experimental data of the mixing enthalpy of the three binary system were obtained by Witusiewicz et al[18, 19]. The dynamic equilibrium coefficients, the formation enthalpy parameters and the respective interaction parameters are calculated to be

$C(Zr_1, Ni_1) = -191.8\,kJ/mol$,
$C(Zr_2Ni) = -77.5\,kJ/mol$,
$K(Zr_2Ni) = 21.4$,
$C(Zr_1, Cu_1) = -51\,kJ/mol$,
$C(Zr_2Cu) = -36.8\,kJ/mol$,
$K(Zr_2Cu) = 2.44$,
$C(Ni_1, Cu_1) = -13.2\,kJ/mol$

Fig. 1 shows the effect of Zr content on the mixing

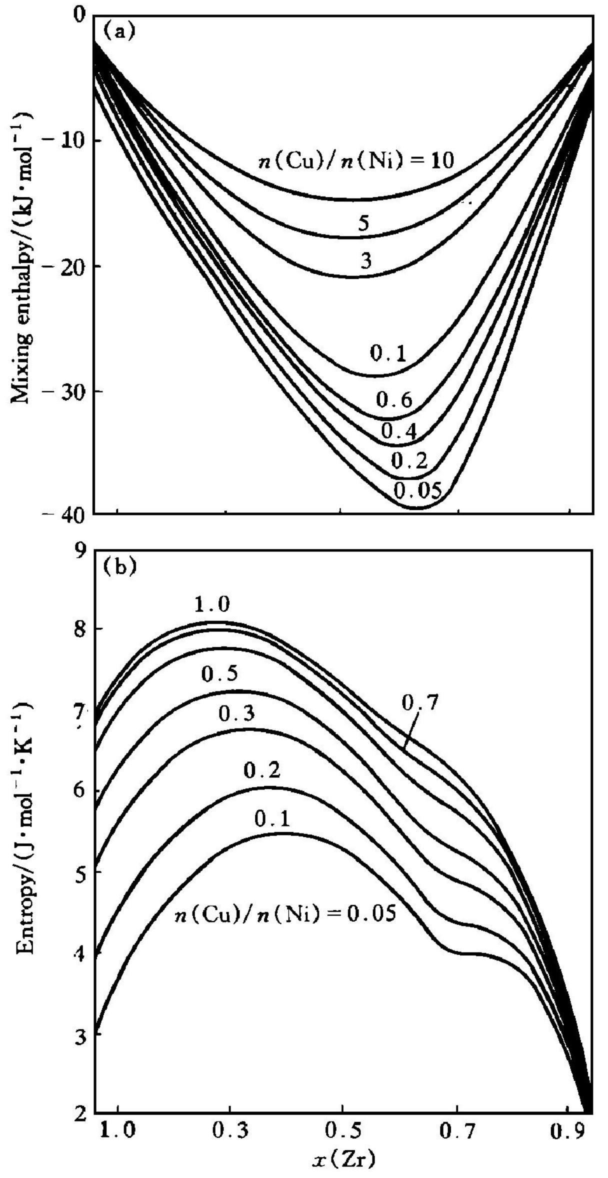

Fig. 1 Effect of Zr content on mixing enthalpy (a) and entropy (b) of Zr-Ni-Cu system at 1600 K

ing enthalpy and entropy in the Zr-Ni-Cu ternary system. It is indicated that both the mixing enthalpy and entropy are related to the ratio of n(Cu) to n(Ni). With decreasing the ratio, the mixing enthalpy becomes more negative and the value of the molar fraction of Zr with the minimum mixing enthalpy moves toward the stoichiometric composition of Zr_2Ni (x(Zr) = 0.67). With increasing the ratio from 0.05 to 1.0, the mixing entropy increases and the molar fraction of Zr with maximum entropy decreases. It is also shown that when the ratio is very low, an additional minimum value occurs in the entropy curve. The minimum entropy corresponds to the Zr mole fraction of 0.67. This means that the mixing entropy of the melt is reduced due to the formation of large amount of MCSRO domains. These results illustrate that both the mixing enthalpy and entropy are related to the formation of the MCSRO domains. Fig. 2 illustrates the dependence of the mole fraction of coexisted Zr_2Ni and Zr_2Cu MCSRO domains on the alloy composition. The mole fractions of MCSRO domains are characterized by parabolic concentration dependence on the mole fraction of Zr. The mole fraction of Zr with the maximum substance amount of Zr_2Ni or Zr_2Cu MCSRO domains is related to the ratio of n(Ni) to n(Cu). With increasing the ratio, the substance amount of Zr_2Ni domain increases and the maximum moves toward higher Zr content, while the case of Zr_2Cu domain is just opposite. However, it seems that the Zr_2Ni MCSRO domain shows higher stability than the coexisted Zr_2Cu domain does. When n(Ni)/n(Cu) = 1, the substance amount of Zr_2Ni is much higher than that of coexisted Zr_2Cu.

The contour lines of the Gibbs free energy of Zr-Ni-Cu homo-melt at 1 600 K are shown in Fig. 3. The Gibbs free energy of the melt at the Zr, Ni and Cu rich corner is much higher than that in other zones. When the melt is composed of 50% Zr, 35% Ni and 15% Cu, the Gibbs free energy of the system reaches the minimum value. Fig. 4 presents the contour lines of MCSRO undercooling in the Zr-Ni-Cu isothermal section at 1 600 K. It is clearly shown that the composi-

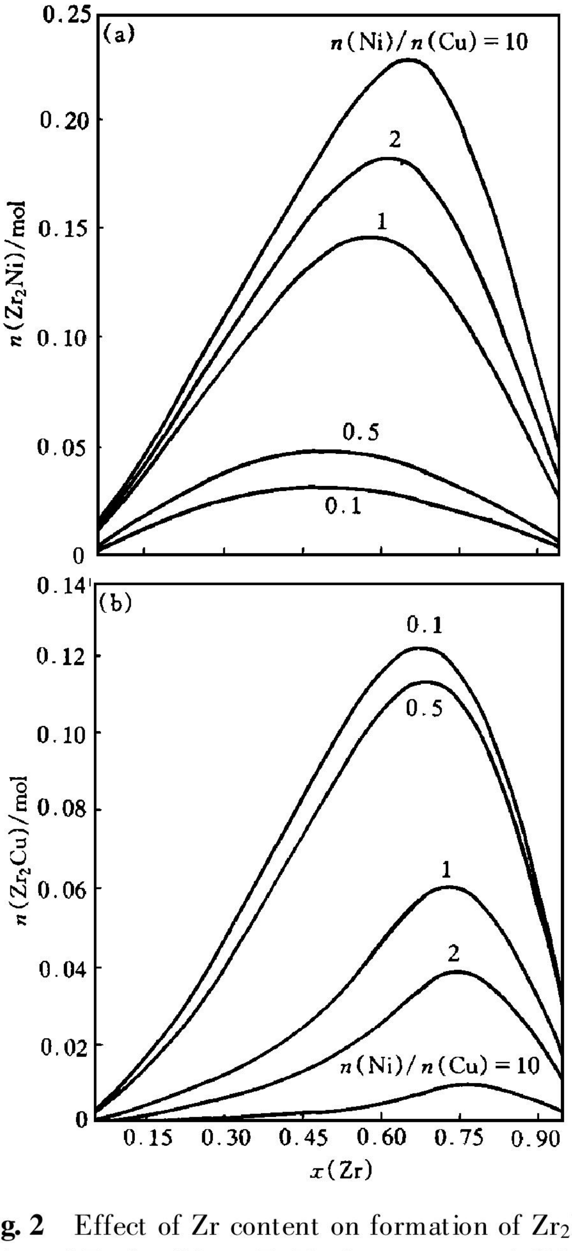

Fig. 2 Effect of Zr content on formation of Zr_2Ni (a) and Zr_2Cu (b) in Zr-Ni-Cu system at 1 600 K

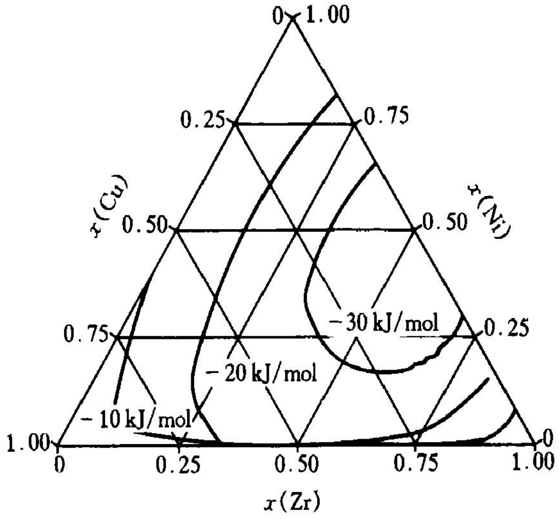

Fig. 3 Contour lines of Gibbs free energy of Zr-Ni-Cu homo-melt at 1 600 K

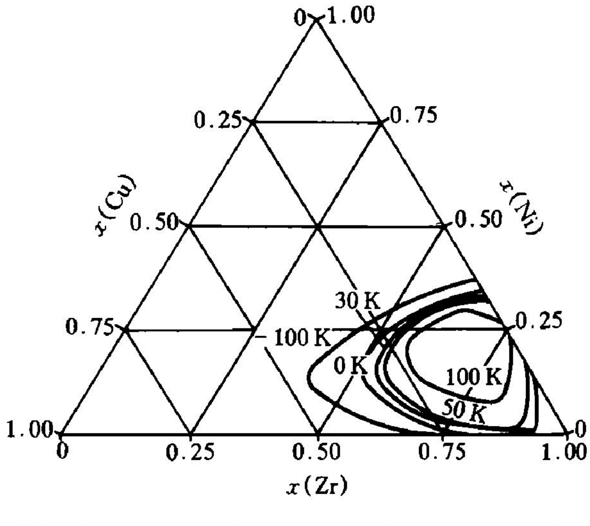

Fig. 4 Contour lines of MCSRO undercooling in Zr-Ni-Cu system

tion range with the maximum MCSRO undercooling is not in agreement with the composition range at which the Gibbs free energy of the homo-melt reaches the minimum. According to the MCSRO undercooling principle, the composition with the best GFA is in the range of 62.5~75, 5~20, 12.5~25 for Zr, Cu and Ni respectively ($n(\mathrm{Ni})/n(\mathrm{Cu})=1\sim 5$).

The above calculation results show that the MCSRO undercooling concept is in consistent with the Inoue's empirical rules[9]. It is easily understood that the negative mixing heat and the rather large difference in atomic size are favorable in principle to form chemical compounds as well as intermetallics and topological close-packed phases. This tendency is reasonable to extrapolate the formation of the chemical short-range order in the liquid structure. Many compound-forming constituents in a melt, of course, should be favorable to form various coexisted MCSRO domains. In Zr-Ni-Cu system, the atomic size differences between Zr and Ni, Zr and Cu, Cu and Ni are 25%, 22% and 3%, respectively, and the mixing heats of both Zr-Ni and Zr-Cu are negative. The calculation results illustrate that the substance amount of Zr_2Ni MCSRO domain is rather larger than that of coexisted Zr_2Cu MCSRO domain because of the larger value of the negative formation enthalpy and the interaction parameter.

It is emphasized that the basic MCSRO undercooling concept requires the co-existence of various MCSRO domains. It is shown that multicomponent alloy system is favorable to form coexisted MCSRO domains. As illustrated in Fig. 4, the MCSRO undercooling of the ternary alloy with the composition of Zr67.5Ni16.25Cu16.25 which contains 0.125 and 0.06 (mole fraction) of Zr_2Ni and Zr_2Cu MCSRO domains respectively, reaches 200 K. If only one kind of MCSRO exists, the melt with the stoichiometric composition of MCSRO can not form amorphous state, but crystallize to form an intermetallic compound. Therefore, if the fourth and fifth alloying element is added to the Zr-Ni-Cu system, the GFA of Zr-Ni-Cu alloy will increase due to the increase in the MCSRO undercooling. For example, there is a strong tendency to form compounds between Al and Zr, Ni, Cu. These elements are favorable to form more MCSRO domains. Recent experimental results of Slipenyuk et al validate this prediction. They made a thick ribbon (0.36 mm) of quaternary alloy of Zr50Ti16.5Cu15Ni18.5 with full amorphous structure. Since the effect of Ti is similar to that of Zr in the reaction with Ni and Cu, the quaternary alloy could be considered to be similar to the ternary alloy of Zr66.5-Cu15-Ni18.5. This composition locates in our predicted optimum composition range of GFA.

In order to further validate the MCSRO principle, we calculated the TTT curves for Zr-Ni-Cu alloys by combining the calculated thermodynamic parameters based on MCSRO model and the experimental data of Zr-based alloys[20, 21]. The TTT curves are shown in Fig. 5. It is illustrated that with increasing the MCSRO undercooling, the TTT curves of the alloy move toward longer time and lower temperature. It means that the alloy with larger MCSRO undercooling exhibits lower average critical cooling rate. The lowest critical cooling rate of Zr70Ni25Cu5 alloy is of the order of 100 K/s. This value is identical to the practical cooling rate for the production of Zr-based BMG alloys[1, 2].

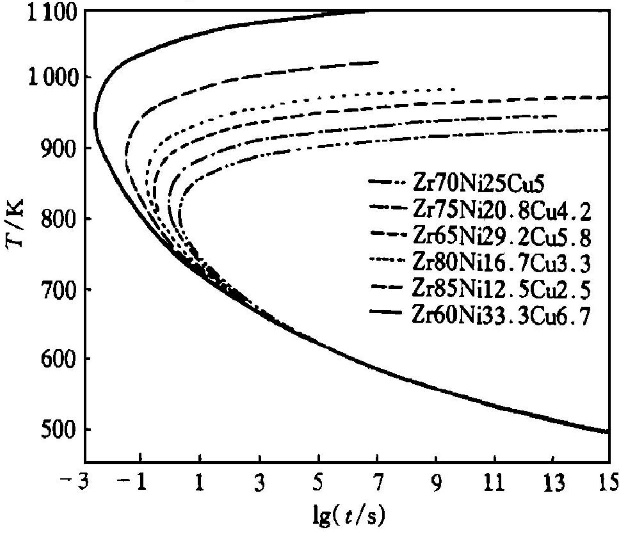

Fig. 5 TTT curves of Zr-Ni-Cu alloys based on MCSRD model

The viewpoint of coexisted MCSRO domains can also be used to interpret why the alloys near the eutectic composition usually exhibit a higher GFA. As shown in Eqn. (4), the MCSRO undercooling is equal to the ratio of the free energy difference between MCSRO-melt and homo-melt to fusion entropy. The alloy system with higher free energy difference between MCSRO-melt and homo-melt and lower fusion entropy will be favorable to the MCSRO undercooling. In multicomponent system, the alloy compositions near eutectic point may be composed of more than two coexisted MCSRO domains, which leads to a more negative Gibbs free energy of liquid or larger free energy difference between MCSRO-melt and homo-melt. However, the fusion entropy at the exactly eutectic composition may be not the smallest. Therefore, it is the composition near eutectic point, but not the exact eutectic composition, could exhibit larger GFA.

3.2 Pd-Si-Cu system

It is experimentally proved that Pd-based alloys are easy to form metallic glass. the MCSRO undercooling of Pd-Si-Cu system are calculated. The predominant MCSRO domains in the melt are selected to be Pd_2Si, Cu_2Pd and Cu_3Si. The Gibbs free energies of these three domains are given in Ref. [13, 22, 23].

Experimental data of the mixing enthalpy of the three binary system are given in Ref. [24, 25]. The dynamic equilibrium coefficients, the formation enthalpy parameters and the respective interaction parameters are calculated to be

$C(\mathrm{Pd_1, Pd_2Si}) = -75\,\mathrm{kJ/mol}$,

$C(\mathrm{Pd_2Si}) = -221\,\mathrm{kJ/mol}$,

$K(\mathrm{Pd_2Si}) = 1\,364$;

$C(\mathrm{Cu_1, Cu_3Si}) = -10\,\mathrm{kJ/mol}$,

$C(\mathrm{Cu_3Si}) = -75.2\,\mathrm{kJ/mol}$,

$K(\mathrm{Cu_3Si}) = 38.2$;

$C(\mathrm{Cu_1, Pd_1}) = -30\,\mathrm{kJ/mol}$,

$C(\mathrm{Cu_2Pd}) = -78.5\,\mathrm{kJ/mol}$,

$K(\mathrm{Cu_3Si}) = 4$

Fig. 6 shows the relationship between the MCSRO undercooling and the concentration of Zr at various ratio of $n(\mathrm{Cu})/n(\mathrm{Si})$. By compared Fig. 6 with Fig. 5, it is shown that the MCSRO undercooling for the Pd-Si-Cu system is extraordinary large (> 500 K), which leads to a larger GFA. The experimental results generally prove that the GFA of Pd-based alloy is better than that of Zr-based alloy. For example, the lowest critical cooling rate of $\mathrm{Pd_{40}Cu_{30}Ni_{10}P_{20}}$ BMG can be as low as 0.10 K/s and the thickness of the BMG sample can be as large as 72 mm. Fig. 7 presents the contour lines of MCSRO undercooling in the Pd-Si-Cu isothermal section. It is clearly shown that the MCSRO undercooling of Pd-Si-Cu in the composition range of 0.45~ 0.65 Pd, 0.25~ 0.35 Si, 0.1~ 0.3 Cu is larger than 150 K. This value is much larger than that of Zr-Ni-Cu system. Therefore, it is shown that the MCSRO undercooling principle is valid to evaluate GFA of an alloy.

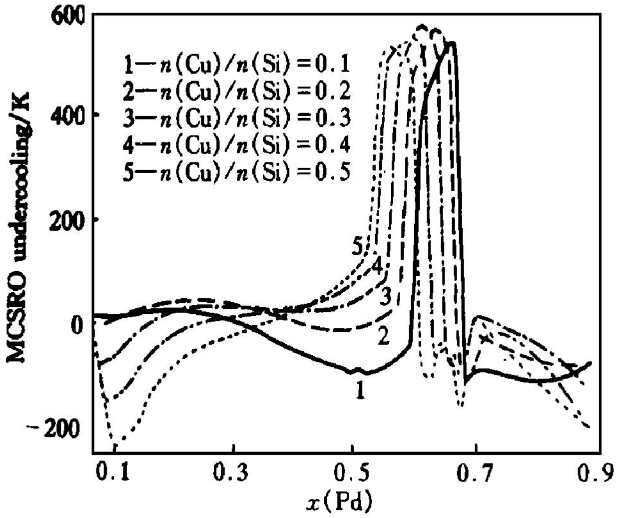

Fig. 6 Undercooling caused by MCSRO in Pd-Si-Cu system at 1 600 K

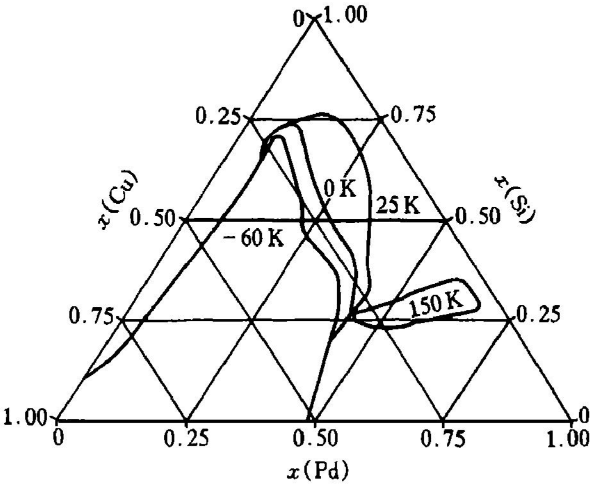

Fig. 7 Contour lines of MCSRO undercooling in Pd-Si-Cu systems

4 CONCLUSIONS

1) A new thermodynamic model to evaluate GFA based on the concept of MCSRO undercooling is proposed. It is considered that coexistence of MCSRO domains affects the thermodynamics and kinetics of homogenuous nucleation. The coexisted MCSRO domains are favorable to form amorphous alloys. The larger the MCSRO undercooling, the better the GFA of an alloy.

2) A simplified model of MCSRO is established to calculate the thermodynamic parameters as well as the MCSRO undercooling. The calculation indicates that the optimum glass forming composition of Zr-Ni-Cu system is in the range of 62.5~ 75Zr, 5~ 20Cu, 12.5~ 25Ni, ($n(\mathrm{Ni})/n(\mathrm{Cu}) = 1\sim 5$). This result is in general consistent with the published experimental results.

3) The MCSRO principle is in accordance with the well-known empirical rules. Negative mixing heats, significant atomic size difference of constituents as well as multi component in an alloy are favorable to form coexisted MCSRO domains and to intensify the MCSRO undercooling. The composition near eutectic point is favorable to form various MCSRO domains in the liquid and produce deep MCSRO undercooling.

4) The MCSRO undercooling principle is also validated by comparison the well-known easy glass-forming system such as Pd-based alloys with Zr-Ni-Cu system. The Pd-Si-Cu system exhibits extraordinary MCSRO undercooling (500 K) in the range of 0.5~ 0.7Zr.

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