Multicomponent Chemical Short Range Order Undercooling and the Formation of Bulk Metallic Glasses

G. L. Chen, X. D. Hui, G. He and Z. Bian

State Key Laboratory for Advanced Metals and Materials, Beijing University of Science and Technology, Beijing 100083, R.R. China

Multicomponent chemical short range order (MCSRO) undercooling principle was proposed as a criterion to evaluate the glass forming ability (GFA) of alloys. The thermodynamic model of MCSRO was established in order to calculate the MCSRO undercooling. Comprehensive numerical calculations using MCSRO 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 criterion, the composition ranges with great GFA in these ternary systems were predicted. It is shown that the prediction by MCSRO undercooling principle is in general consistent with the well-known empirical rules proposed by Inoue. According to the MCSRO undercooling principle, the composition with great GFA in the range of Zr-Ni-Cu system is Zr=62.5–75, Cu=5–20 and Ni=12.5–25, (Ni/Cu=1–5), which is in agreement with the recent experimental results of the quaternary Zr-Ni-Cu-Ti alloy. The calculation also illustrates that Pd-based alloys which easily form a metallic glass exhibit an extraordinary deep MCSRO undercooling. By calculating TTT curves in Zr-Ni-Cu-Ti system, it is shown that the average critical cooling rates are estimated to be as low as ~100 K/s for the alloy with deep MCSRO undercooling. As an example of an effective bulk metallic glass (BMG) design method, a new kind of Zr-Si-Cu BMG is explored based on the MCSRO undercooling principle.

(Received February 13, 2001; Accepted April 16, 2001)

Keywords: multicomponent chemical short range order undercooling, bulk metallic glasses, glass forming ability, Zirconium-nickel-copper system

1. Introduction

During the past few years, an excellent glass forming ability (GFA) has been found in Zr-, Ti-, La-, Pd- and Mg-based multicomponent alloys. This permits the formation of bulk metallic glasses at the cooling rate lower than 100 K/s with ordinary mold casting or other conventional methods. There have been a number of attempts to find a general criterion for the formation of metallic glasses. Marcus and Turnbull\(^1\) introduced a non-dimensionalized parameter, \(\Delta T/T_l^0\) (\(T_l^0\) is the liquidus temperature of ideal solution, \(\Delta T\) is the deviation of the liquidus temperature of practical solution from \(T_l^0\)) to account for the GFA. Donald and Davis\(^2\) proposed a reduced temperature (\(T_{m}^{\text{mix}}-T_l)/T_l\) (\(T_l\) is the liquidus temperature of practical solution, \(T_{m}^{\text{mix}}\) is the temperature related to the melting temperatures and the molar fraction of components) to evaluate the eutectic system composed of metal-metal and metal-metalloid. Recently, Inoue et al.\(^3\) proposed three empirical rules for the formation of BMG: (1) multicomponent alloy systems consisting of more than three elements; (2) significant atomic size differences above 12% among the constituent elements; and (3) negative heats of mixing among the constituent elements. Perhaps, the most successful empirical criterion is the reduced temperature, \(T_g/T_m\) (\(T_g\) is glass transition temperature and \(T_m\) is the melting point). For an alloy with high GFA, \(T_g/T_m\) must be reasonably high, usually >0.5. Nevertheless, this empirical criterion can not give any information on how the thermodynamic and kinetic properties of liquids affect the formation of metallic glasses. In fact, at temperatures below the equilibrium freezing temperature \(T_m\), liquid always has a tendency to transform into a crystalline phase. If the very large undercooling is needed for crystallization or the nucleation is impeded due to some thermodynamic or kinetic reasons, the crystallization could be avoided during continuously cooling. Only in this case the undercooled liquid will be held and the amorphous alloy will be formed. Therefore, it should be important to correlate the GFA with the thermodynamic and kinetic features. In this paper, a new model of GFA based on MCSRO undercooling concept is proposed. By using this model, the GFA of Zr-Ni-Cu ternary systems is evaluated and the optimum composition ranges are predicated. As an example of an effective BMG design method, a new metallic glass system is explored.

2. Theoretical Formulation

2.1 MCSRO undercooling—a new criterion of GFA

Metallic liquids are well known for the absence of long-range structural order. Diffractional experiments, nonetheless, provide ample evidence of short-range structural order. It is noticeable that metallic glasses always exhibit strong compound forming tendency and the corresponding anomalies of the concentration dependence of structures-sensitive quantities. Many investigations indicated that the assumption of the random distribution of atoms in the metallic melt leads to disagreement with experimental observations.\(^4\)-\(^6\) This can only be reasonably interpreted that MCSROs are present in the multicomponent liquid. It is believed that the occurrence of many kinds of MCSRO in the melt of metallic glass alloy is a rule rather than an exception. 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 co-existing MCSROs near the nucleus should be dissolved. Much more energy must be supplied to decompose the neighbor 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) should need larger undercooling in compar-
ing with that containing homogeneous distribution of single atoms (noted homo-melt). On the other hand, the deep undercooling brings about the crystallization at very low temperature at which the viscosity of the undercooled liquid becomes very large. Crystallization may become so difficult that undercooled melt may be held to the glass transition temperature and to form amorphous state. 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, one defined the difference as MCSRO undercooling, $\Delta T_{\text{MCSRO}}$. The larger the $\Delta T_{\text{MCSRO}}$ is, the higher the GFA of an alloy should be.

The Gibbs energy barrier $\Delta G_{n}^{*}$ to the nucleation of a critical nucleus can be described as

$$\Delta G_{n}^{*} = \frac{16}{3\pi} \sigma^{3} \Delta G_{c}^{2}$$

(1)

Where $\sigma$ is molar interfacial energy, $\Delta G_{c}$ is the Gibbs energy driving force.

When homogeneous nucleation occurs at the temperatures $T_{\text{MCSRO}}$ and $T_{\text{homo}}$ in MCSRO-melt and homo-melt, the Gibbs energy driving forces, $\Delta G_{\text{MCSRO}}$ and $\Delta G_{\text{homo}}$, can be expressed respectively as

$$\Delta G_{\text{MCSRO}} = \left( H_{L} - H_{\text{MCSRO}} \right) - T_{\text{MCSRO}} (S_{L} - S_{\text{MCSRO}})$$

$$= \frac{L_{m} \Delta T_{\text{MCSRO}}}{T_{m}} + \left( H_{L} - H_{\text{MCSRO}} \right)$$

$$- T_{\text{MCSRO}} (S_{L} - S_{\text{MCSRO}})$$

(2)

$$\Delta G_{\text{homo}} = - \frac{L_{m} \Delta T_{\text{homo}}}{T_{m}}$$

(3)

Where $H$ is enthalpy, $S$ is entropy, $T_{m}$ is melting point, $L_{m}$ is fusion latent, $\Delta T$ is undercooling. The subscripts MCSRO and homo represent the MCSRO-melt and homo-melt respectively. The subscripts $L$ and $S$ represent liquid and solid.

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

$$\Delta T_{\text{MCSRO}} = \frac{(H_{S} - H_{\text{MCSRO}}) - T_{\text{MCSRO}} (S_{S} - S_{\text{MCSRO}})}{L_{m}} T_{m}$$

$$= (G_{\text{homo}} - G_{\text{MCSRO}}) / \Delta S_{m}$$

(4)

The eq. (4) indicates that the MCSRO undercooling is related both to the difference of Gibbs free energy between the two kinds of melt at the temperature $T_{\text{MCSRO}}$ 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.\(^7\) Then the central problem for the estimation of $\Delta T_{\text{MCSRO}}$ is how to evaluate the $G_{\text{MCSRO}}$.

### 2.2 Thermodynamic model of MCSRO

A simplified physical model of MCSRO is established as follows: the short range ordered elements are described as domains having a well-defined stoichiometric composition, while rest atoms are considered to be randomly distributed. 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 randomly distributed atoms, which are governed by the mass action law. Therefore the volume fraction and the stoichiometric composition of MCSRO domain are determined at a given temperature and concentration by statistically energetic conditions. It should be pointed out that the model of coexisted MCSRO domains in both composition and volume fraction is simplified. However, the lifetime of those MCSRO domains should be longer than the time necessary for atomic diffusion away at that temperature. Based on Gibbs' phase rule all MCSROs form within a single liquid phase. Only when additional conditions are supplied, can the coexisted MCSRO domains lead to a decomposition of the single melt into more than one kind of liquid phase. Therefore, both metallic melt and undercooled melt should firstly satisfy the condition of the single liquid phase. That is, the second derivation of the Gibbs energy $G$ with respect to the molar fraction $c$ satisfies the following equation:

$$\frac{1}{2} \sum_{i=1}^{N} \left( \frac{\partial^2 G}{\partial c_i^2} \right) (\Delta c_i)^2 + \sum_{i,j(i \neq j)} \left( \frac{\partial^3 G}{\partial c_i \partial c_j} \right) \Delta c_i \Delta c_j > 0$$

(5)

where $N$ represents the multicomponent system, and $i, j$ represent the component $i$ and $j$.

Now consider an alloy composed of $A_1, A_2, \ldots, A_N$ components, in which the model parameters for the respective base-binary systems are known and no additional ternary or more than ternary reaction occurs. The base binary system $A_i - A_j$ contains $M$ kinds of MCSRO domains, i.e. $A_{i1}^{11}, A_{i2}^{12}, A_{i3}^{12}, \ldots, A_{i}^{M} M_{j}$. The super-scripts, $M_1, M_2, \ldots$ represent the compositions in MCSRO domain $A_{i}^{M_1} A_{j}^{M_2}$. The molar number of the domains is noted $n_{A_{i}^{11}}, n_{A_{i}^{12}}, \ldots, n_{A_{i}^{M}} M_{j}$. Then total number of moles is

$$n = \sum_{i=1}^{N} n_{A_{i}^{0}} + \sum_{i=1}^{N-1} \sum_{m=1}^{M} n_{A_{i}^{m_1} A_{j}^{m_2}}$$

(6)

The absolute mole numbers, $n_{A_{i}^{11}}, n_{A_{i}^{12}}, \ldots, n_{A_{i}^{M}} M_{j}$, are related to the mole numbers used in eq. (6) by

$$n_{A_{i}^{0}} = n_{A_{i}^{11}} - \sum_{j=1, j \neq i}^{N} \sum_{k=1}^{M} k_1 \cdot n_{A_{i}^{11}} A_{j}^{m_2}$$

(7)

The mixing enthalpy and the entropy in regular melt are written as follows.
\[
\Delta H^{\text{稳}} = \sum_{i=1}^{N-1} \sum_{j=1}^{M} (C_{A_i}^{A_i} \cdot n_{A_i^{A_i}} \cdot n_{A_j^{A_j}} / n) + \sum_{p=1}^{N} \sum_{j=1}^{M} (C_{A_p}^{A_p} \cdot n_{A_i^{A_i}} \cdot n_{A_j^{A_j}} / n) \\
\Delta S = -R \sum_{i=1}^{N} \sum_{j=1}^{M} n_{i}^{0} \ln x_{i}^{0} + \sum_{i=1}^{N-1} \sum_{j=1}^{M} (-R \cdot n_{i}^{0} \ln x_{i}^{0} + n_{A_i^{A_i}} \cdot S_{A_j^{A_j}}) 
\]

where \(C_{A_i}^{A_i} \cdot A_j^{A_j}\) is the formation enthalpy of \(A_i^{A_i} \cdot A_j^{A_j}\) MCSRO domains, \(C_{A_p}^{A_p} \cdot A_j^{A_j}\) is the interaction coefficient between the \(A_i\) and \(A_j\) single atom, \(C_{A_i}^{A_i} \cdot A_j^{A_j}\) is the interaction coefficient between \(A_p\) single atom and \(A_i^{A_i} \cdot A_j^{A_j}\) MCSRO, \(S_{A_i}^{A_i} \cdot A_j^{A_j}\) is the additional formation entropy, \(x_{i}^{0}\) is the molar fraction of single \(i\) atom, and \(x_{A_i^{A_i}}^{A_j^{A_j}}\) is the molar fraction of \(A_i^{A_i} \cdot A_j^{A_j}\) MCSRO.

The chemical potential \(\mu_i\) \((i = A_i^{A_i}, \ldots, A_j^{A_j}, \ldots)\) is expressed as

\[
\mu_i = \mu_i^{\circ} + RT \ln(n_i / n) + RT \ln \gamma_i 
\]

where, \(R\) is the gas constant, \(T\) is the temperature, and \(\gamma\) is the activity coefficient.

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

\[
\Delta G = \sum_{i=1}^{N-1} \sum_{j=1}^{M} (n_{A_i}^{A_i} \cdot A_j^{A_j} \Delta G^\circ_{A_i}^{A_i} \cdot A_j^{A_j}) + RT \left[ \sum_{i=1}^{N} n_{i}^{0} \ln(n_{i}^{0} / n) + \sum_{i=1}^{N-1} \sum_{j=1}^{M} n_{A_i}^{A_i} \cdot A_j^{A_j} \ln(n_{A_i}^{A_i} \cdot A_j^{A_j} / n) \right] 
\]

where \(\Delta G^\circ_{A_i}^{A_i} \cdot A_j^{A_j} = \mu_i^{\circ} - \mu_i^{\circ} - k_1 \mu_j^{\circ} - k_2 \mu_j^{\circ} - \cdot \).

The equilibrium value of \(n_{A_i}^{A_i} \cdot A_j^{A_j}\) in eqs. (10) and (11) is determined by

\[
\frac{\partial \Delta G}{\partial n_{A_i}^{A_i} \cdot A_j^{A_j}} = 0 
\]

Dynamic equilibrium equation of MCSRO is then obtained from eqs. (10) and (11)

\[
\left( n_{A_i} - \sum_{j=1, j \neq i}^{N} \sum_{k=1}^{M} k_j n_{A_i}^{A_i} \cdot A_j^{A_j} \right)^{k_1} \left( n_{A_j} - \sum_{i=1, j \neq i}^{N} \sum_{k=1}^{M} k_j n_{A_i}^{A_i} \cdot A_j^{A_j} \right)^{k_2} \exp(\Delta G^\circ_{A_i}^{A_i} \cdot A_j^{A_j}) = 1 / K_{A_i}^{A_i} \cdot A_j^{A_j} 
\]

where \(K_{A_i}^{A_i} \cdot A_j^{A_j}\) is the dynamic equilibrium constant of \(A_i^{A_i} \cdot A_j^{A_j}\) MCSRO domains.

3. MCSRO Undercooling in Zr–Ni–Cu Ternary System

In order to calculate the MCSRO undercooling for Zr–Ni–Cu ternary system and determine the optimum composition with good GFA, the software named 'MCSRO' program is developed. At the outset, the stoichiometry of the MCSRO domains needs to be defined. It is assumed that the MCSRO domains satisfy stoichiometry which corresponds to the composition of the congruent or incongruent melting compounds existing in the phase diagram of the three based binary Zr–Ni, Zr–Cu and Ni–Cu systems. The molar fractions of selected MCSRO domains have been determined based on the minimum Gibbs free energy criterion, given by eqs. (11), (12) and (13). When the above criterion is used to select the MCSROs for a specific alloy, some simplification was conducted. A large number of experimental results of binary liquid alloys exhibiting compound formation tendency (e.g. Cu–Cu,9 Cu–La,10 Cu–Zr,11 Cu–Si,12 Al–Cu, Al–Ni,13 Al–Zr, Ni–Zr14) show that there is only one or two kinds of predominant MCSRO in a binary alloy. Particularly, the MCSROs are proved to be Cu2Zr and CuZr2 in Cu–Zr alloy11 and Ni2Zr and Ni3Zr in Ni–Zr alloy.14 There is no MCSRO in Cu–Ni alloy. Since the compositions of Zr–Ni–Cu ternary system with good GFA are located at the Zr-rich corner, the effects of Zr2Ni and Zr2Cu MCSRO are emphatically discussed in this paper.

The application of the above relations to calculate the thermodynamic properties involves the knowledge of model parameters such as the dynamic equilibrium constant, the formation enthalpy parameters and the respective interaction parameters. Here one apply a simple scheme of standardisations to determine the model parameters which has been proven successful in the calculation of phase diagrams.15 In Zr–Ni–Cu system, one the basic thermodynamic properties of all elements in the recent reference.16 All the Gibbs free energies of MCSROs are given in references.16–21 The interaction parameters between the free atoms, \(C_{\text{g},\text{b}}\), are determined by experimental data of the mixing enthalpy of the three binary system obtained by Witwieswicz and Sommer et al.22–24

Figure 1 shows the effect of Zr on the mixing enthalpy and entropy in the Zr–Ni–Cu ternary system. It indicates that both the mixing enthalpy and entropy are related to the ratio of \(n_{Cu} / n_{Ni}\). With decreasing the ratio the mixing
Fig. 1 Effect of Zr on the (a) the mixing enthalpy and (b) the entropy of Zr–Ni–Cu system at 1600 K.

Fig. 2 Effect of Zr on the formation of (a) Zr$_2$Ni and (b) Zr$_2$Cu in Zr–Ni–Cu system at 1600 K.

enthalpy becomes more negative and the value of the molar fraction of Zr at which the minimum mixing enthalpy occurs moves toward ~0.67, i.e. the stoichiometric composition of Zr$_2$Ni. With increasing the ratio of $n_{Cu}$ to $n_{Ni}$ from 0.05 to 1.0, the mixing entropy increases and the molar fraction of Zr at maximum entropy decreases. It also shows that when the ratio is very low, an additional minimum occurs in the entropy curve. The minima of entropy corresponds to the molar fraction of Zr at 0.67. This means that the mixing entropy of the melt is reduced due to the formation of a large amount of MCSRO domains. These results illustrate that both the mixing enthalpy and entropy are related to the formation of the MCSRO domains.

Figure 2 illustrates the dependence of the molar fraction of coexisted Zr$_2$Ni and Zr$_2$Cu MCSRO domains on the alloy composition. The molar fractions of MCSRO domains are characterized by parabolic concentration dependence on the molar fraction of Zr. The molar fraction of Zr where the maximum molar numbers of Zr$_2$Ni or Zr$_2$Cu MCSRO domains occur is related to the ratio of $n_{Ni}$ to $n_{Cu}$. With increasing the ratio of $n_{Ni}$ to $n_{Cu}$, the molar number of Zr$_2$Ni domain increases and the maximum moves toward higher Zr content whilst the case of Zr$_2$Cu domain is just opposite. However, it seems that the Zr$_2$Ni MCSRO domain shows higher stability than the coexisted Zr$_2$Cu domain. When the ratio of $n_{Ni}/n_{Cu} = 1$, the molar number of Zr$_2$Ni is much higher than that of the coexisted Zr$_2$Cu.

The contour lines of the Gibbs free energy of Zr–Ni–Cu homo-melt at 1600 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 at other parts. When the melt is composed of 50%Zr, 35%Ni and 15%Cu, the Gibbs free energy of the system reaches the minimum value. Figure 4 presents the contour lines of MCSRO undercooling in the Zr–Ni–Cu isother-
melt, of course, should be favorable to form various coexisted MCSRO domains. The more negative the formation enthalpy of MCSRO, the more stable the MCSRO and the longer the diffusion route. In Zr–Ni–Cu system, the atomic size differences between Zr and Ni, Zr and Cu, and Cu and Ni are 25%, 22% and 3%, respectively, and the mixing heats for both Zr–Ni and Zr–Cu are negative. The calculation results illustrate that the negative heats of mixing is favorable the formation of the coexisted Zr$_2$Ni and Zr$_2$Cu MCSRO domains. In addition, the molar number of Zr$_2$Ni MCSRO domain is rather larger than that of coexisted Zr$_2$Cu MCSRO domain because of the larger value of the negative formation enthalpy ($C_{Zr2Ni}$) and the interaction parameter ($C_{Zr1Ni}$). Figure 5 shows the composition dependence of the MCSRO undercooling on the molar fraction of Zr. By the comparison of Fig. 2 with Fig. 5, it is clearly shown that there is a close correlation between the molar numbers of the coexisted MCSRO domains and the MCSRO undercooling. MCSRO domain with more negative mixing heats, e.g. Zr$_2$Ni, exhibits a much larger effect on the MCSRO undercooling.

In Inoue’s empirical rules, it is emphasized that the BMG should be multicomponent alloy systems consisting of more than three elements. 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 by Fig. 4, the MCSRO undercooling of the ternary alloy with the composition of Zr$_{67.5}$Ni$_{16.25}$Cu$_{16.25}$, which contains 0.125 and 0.06 molar fractions of Zr$_2$Ni and Zr$_2$Cu MCSRO domains respectively, reaches 200 K. If only one kind of MCSRO exists, the melt with the stoichiometric composition of MCSRO can’t 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 MCSRO undercooling. For example, there is strong tendency to form compounds between Al and (Zr, Ni or Cu). These elements are favorable to form more MCSRO domains. Sometimes, the fourth and fifth constituents also affect the dynamics of nucleation so as to result in deep undercooling.

The viewpoint of coexisted MCSRO domains can also be

---

Fig. 3 Contour lines of the Gibbs free energy of Zr–Ni–Cu homo-melt at 1600 K.

Fig. 4 Contour lines of MCSRO undercooling in Zr–Ni–Cu system.
used to understand why near the eutectic composition usually exhibits a great GFA. As shown in eq. (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 eutectics, not the exact eutectic composition, could exhibit larger GFA.

4.2 Validation of MCSRO undercooling principle by experimental results

The above calculation of the Zr–Ni–Cu ternary system has predicted the composition range with larger MCSRO undercooling. This prediction is generally consistent with the ample experiments in Zr-based BMG alloys. The Zr base bulk glass alloy always consists of more than three constituents, such as Zr–Ti–Al–Ni–Cu system. As indicated in above section both the Ti and Al addition to the Zr–Ni–Cu ternary system may intensify the coexistence of various MCSRO domains. Recent experiment results of Slipenyuk et al.\textsuperscript{25} validate this prediction. They made an amorphous thick ribbon (0.36 mm) of quaternary of Zr\textsubscript{70}Ti\textsubscript{10}Cu\textsubscript{10}Ni\textsubscript{15} alloy. 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 Zr\textsubscript{56.5}Cu\textsubscript{15}Ni\textsubscript{18.5}. This composition locates in our predicted optimum composition range of GFA.

It has been experimentally proved that La-based and Pd-based alloys are easily to form metallic glass. For example, the lowest cooling rate can be as low as 0.10 K/s for the Pd\textsubscript{60}Cu\textsubscript{30}Ni\textsubscript{10}P\textsubscript{20} alloy and the thickness of the BMG sample can be as large as ≈72 mm. In order to validate the effectiveness of MCSRO undercooling principle, the MCSRO undercooling of Pd–Si–Cu system are calculated as an example. As proved in Refs. 26) and 27), the predominant MCSRO domains in the melt are selected to be Pd\textsubscript{2}Si, Cu\textsubscript{3}Pd and Cu\textsubscript{5}Si. The molar fraction of every MCSRO domain and the MCSRO undercooling of the alloy are calculated by eqs. (11), (12) and (13). Figure 6 shows the relationship between the MCSRO undercooling and the concentration of Zr at various ratio of n\textsubscript{Cu}/n\textsubscript{Si}. By comparing Fig. 6 with Fig. 5, it is shown that the MCSRO undercooling for the Pd–Si–Cu system is extraordinary (>500 K), which leads to a larger GFA. The experimental results\textsuperscript{28} have generally proved that the GFA of Pd-based alloy is better than that of Zr-based alloy.

We also calculated TTT curves in Zr–Ni–Cu alloys by combining the calculated thermodynamic parameters based on MCSRO model and the experimental data of Zr-based alloys.\textsuperscript{29–31} The TTT curves are shown in Fig. 7. It illustrates that with increasing the MCSRO undercooling, the TTT curve moves toward longer time and lower temperature. It means that the alloy with larger the MCSRO undercooling exhibits a lower average critical cooling rate. The lowest critical cooling rate of Zr\textsubscript{70}Ni\textsubscript{15}Cu\textsubscript{5} alloy is on the order 100 K/s. This value is identical to the practical cooling rate for the production of Zr-based BMG alloys.\textsuperscript{32,33} By adding suitable fourth and fifth alloying elements, such as the Zr–Al–Ni–Cu, Zr–Ti–Cu–Ni–Be and Zr–Ti–Al–Ni–Cu systems, we predict that even lower average critical cooling rate could be obtained.

4.3 Exploration of new glass forming system

So far as present, little investigation has been conducted on the GFA of Zr–Si–Cu system. Because various coexisted MCSROs may form in the Zr–Si–Cu melt, we predict that there exist some compositions that are favorable to form metallic glass. There exist more than 10 kinds of MCSRO domains in Zr–Si–Cu ternary system, such as Si\textsubscript{2}Zr\textsubscript{5}, Si\textsubscript{2}Zr\textsubscript{3}, SiZr, Si\textsubscript{2}Zr, Si\textsubscript{2}Zr\textsubscript{3}, Si\textsubscript{2}Cu, Si\textsubscript{2}Cu\textsubscript{2} etc. According to the previous investigation,\textsuperscript{11,12} the calculation is simplified to consider the coexisted MCSRO domains to be Zr\textsubscript{2}Si, ZrCu\textsubscript{2}, Zr\textsubscript{2}Cu and Cu\textsubscript{5}Si only. In the calculation, the Gibbs free energies of these three compounds are given in Refs. 34), 35) and 36). Experimental data of the mixing enthalpies of the three binary alloys are shown in Refs. 13), 37) and 38).

Figure 8 shows the effect of Zr on the formation of Zr\textsubscript{2}Si and Zr\textsubscript{2}Cu MCSRO domains. The molar number of Zr\textsubscript{2}Si MCSRO domain increases firstly with the increase of the concentration of Zr in the melt. The molar number of Zr\textsubscript{2}Si...
MCSRO domain attains a large value in the composition range of Zr from 0.4 to 0.67. The curve of the molar number of Zr₂Cu MCSRO domain exhibits the two maximum points. The ratio of Cu/Si has a notable effect on the molar fraction of Zr₂Si and Zr₂Cu MCSRO domains. With increasing the ratio of Cu/Si, the molar fraction of Zr₂Si MCSRO domain decreases whilst the molar fraction of Zr₂Cu MCSRO domain increases. The molar fraction of Cu₅Si₃ MCSRO domain is relatively low except for lower Zr content range. The calculated contour line of the MCSRO undercooling in the Zr–Si–Cu system is shown in Fig. 9. The composition range near the Zr rich corner has a large MCSRO undercooling region. The composition range with MCSRO undercooling of 200 K is separated into two composition regions. Nevertheless, coexisted MCSRO domains are the basic condition for large MCSRO undercooling.

5. Summary

(1) A new principle to evaluate GFA based on MCSRO undercooling is proposed. The concept is based on the coexistence of MCSRO in the liquid that has been proved by modern liquid structural experiments. Coexistence of MCSRO domains results in an increase of the resistance to crystallization, leading to deep undercooling. 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 Zr = 62.5–75, Cu = 5–20, Ni = 12.5–25, (Ni/Cu = 1–5). 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 is favorable to form coexisted MCSRO domains and to intensify the MCSRO undercooling. The composition near eutectics is favorable to form various MCSRO domains in the liquid.

(4) The MCSRO undercooling principle is also validated by comparing the well-known easy glass former such as Pb-based alloys with Zr–Ni–Cu system. The Pb–Si–Cu system exhibits extraordinary MCSRO undercooling (∼500 K) in the range of Zr = 0.5–0.7.

(5) The MCSRO undercooling principle can be used as a BMG alloy design method. As an example, the optimum BMG composition of Zr–Si–Cu ternary alloy is predicted to be in the range of Zr = 0.4–0.70, Si = 0.15–0.4, Cu = 0.05–0.3.

REFERENCES