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# **Metallic glass formation in the Cu-Ni-Ti (Zr, Hf) systems studied by thermodynamic calculation**

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## **Abstract:**

For the family of Cu-Ni-Ti (Zr, Hf) systems, which are promising to obtain the bulk metallic glasses, the glass formation regions were calculated based on the extended Miedema's model and Alonso's method. It is found that the calculated glass formation regions of Cu-Ni-Zr and Cu-Ni-Hf systems agree with experimental results well, whereas it is not for the Cu-Ni-Ti system. The composition dependence of glass forming ability in the Cu-Ni-Ti (Zr, Hf) systems were then predicted, and it turns out that the glass forming ability of Cu-Ni-Ti system is largely deviated from the experimental results, then it is assumed that the kinetic factors (low liquidus temperature) instead of thermodynamic factors make the Cu-rich composition an easy glass former in Cu-Ni-Ti system. Meanwhile, the effect of Ti (Zr, Hf) on the glass forming ability was discussed in terms of the mixing enthalpy and atomic size effect.

## **Keywords:**

Bulk metallic glasses; Glass formation regions; Miedema's model; Alonso's method

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## 1. Introduction

Since the first amorphous alloy was obtained by Klement *et al.* via liquid melt quenching (LMQ) in the Au-Si system in 1960,<sup>1</sup> a large number of metallic glasses have been developed in Cu-, Ni-, Zr-, Hf-based system, exhibiting inviting properties such as high mechanical strength and good corrosion resistance.<sup>2</sup> Over the past few decades, bulk metallic glasses (BMGs) have attracted extensive interests due to their unique properties, and BMGs have emerged as a new class of materials with near theoretical strength and large elastic strain. In order to produce bulk metallic glasses (BMGs), one of the fundamental issues is to develop a method/model capable of predicting the quantitative glass formation range (GFR) of a metallic system, e.g. a composition range for a binary metallic system, or a composition region for a ternary metallic system, within which the formation of metallic glass is energetically favored. Concerning this issue, several empirical criteria and models have been proposed in the past decades to predict the GFR of a metal system. For instance, Turnbull has proposed a ratio of the glass transition temperature  $T_g$  to the melting point  $T_m$ , referred to as the reduced glass transition temperature  $T_{rg} = T_g/T_m$  and it was used as a criterion to determine the glass forming ability (GFA) of an alloy.<sup>3</sup> In early 1980s, Egami and Waseda suggested an empirical formula to predict the GFR based on the atomic size effect, which correlates with in the instability of solid solution when solute concentration reaches a critical value.<sup>4</sup> Although these empirical criteria or rules have served guidelines for synthesizing the metallic glasses for decades, they still belong to the empirical models and some essential experimental parameters cannot be

predicted a priori. From the thermodynamic point of view, Miedema's model and Alonso's method have been proposed as an effective semi-empirical approach to predict the metallic glass formation a priori and they have been used to explain some fundamental issues of the metallic glass formation.<sup>5,6</sup>

In the present study, we focus our attention on the metallic glass formation of the ternary Cu-Ni-Ti (Zr, Hf) systems, which have been revealed to be quite promising for obtaining the BMGs. For example, the Cu-Ni-Ti bulk metallic glass composite has good property of shape memory,<sup>7</sup> and the Cu-Ni-Zr system has excellent mechanic property.<sup>8</sup> As the Cu-Ti (Zr, Hf) and Ni-Ti (Zr, Hf) systems are miscible while the Cu-Ni system is an immiscible one. Therefore the content of Ti (Zr, Hf) is the dominating factor for metallic glass formation. Meanwhile, the difference in atomic sizes between the Cu-Ti (Zr, Hf) and Ni-Ti (Zr, Hf) are relatively large, with maximal difference of more than 17%, which facilitates the formation of amorphous alloys. In the present study, thermodynamic calculation based on extended Miedema's model and Alonso's method was employed to predict the GFR and GFA of the intriguing Cu-Ni-Ti (Zr, Hf) systems.

## 2. Thermodynamic calculation

Miedema's model and Alonso's method have been proposed as a thermodynamic approach to predict the glass formation range of a binary system, by comparing the enthalpy of formation of the solid solution and amorphous phase. Generally, the Gibbs free energy of an alloy phase could be calculated by  $\Delta G = \Delta H - T \cdot \Delta S$ , where  $\Delta H$  and  $\Delta S$  are the enthalpy and entropy terms, respectively. As a first

approximation, the entropy term  $\Delta S$  for a concentrated solid solution or an amorphous phase is simply taken as that of an ideal solution. For a ternary alloy system with constituents of A, B and C, the  $\Delta S$  could be calculated as

$$\Delta S = -R[c_A \ln c_A + c_B \ln c_B + c_C \ln c_C] \quad (1)$$

where  $R$  is the gas constant and  $c_A$ ,  $c_B$  and  $c_C$  are the atomic concentrations of metals A, B and C, respectively.

According to the work by Gallego *et al.*,<sup>9</sup> the enthalpy of formation of a ternary solid solution of transition metals A, B, C is given by

$$\Delta H_{ABC}^{ss} = \Delta H_{ABC}^c + \Delta H_{ABC}^e + \Delta H_{ABC}^s \quad (2)$$

where  $\Delta H_{ABC}^c$ ,  $\Delta H_{ABC}^e$  and  $\Delta H_{ABC}^s$  are the chemical, elastic and structural contributions, respectively. The chemical term  $\Delta H_{ABC}^c$  which is related to the electron redistribution can be divided into contributions of three binary subsystems as

$$\Delta H_{ABC}^c = \Delta H_{AB}^c + \Delta H_{AC}^c + \Delta H_{BC}^c \quad (3)$$

where  $\Delta H_{AB}^c$ ,  $\Delta H_{AC}^c$  and  $\Delta H_{BC}^c$  are the chemical terms of the three binary subsystems. For the binary subsystem, the chemical term  $\Delta H_{AB}^c$  is given by

$$\Delta H_{AB}^c = c_A c_B [c_B \Delta \bar{H}_{A \text{ in } B}^{\text{inter}} + c_A \Delta \bar{H}_{B \text{ in } A}^{\text{inter}}] \quad (4)$$

where  $c_A$ ,  $c_B$  and  $c_C$  are the atomic concentrations of metals A and B,  $\Delta \bar{H}_{A \text{ in } B}^{\text{inter}}$  and  $\Delta \bar{H}_{B \text{ in } A}^{\text{inter}}$  are the electron redistribution contribution to the enthalpies of A solved in B and that of B solved in A. Further considering the chemical short-range order (CSRO) of the alloy phases, the right-hand side of Eq. (3) should be multiplied by a factor

$$f_{AB} = 1 + \gamma(c_A^s c_B^s)^2 \quad (5)$$

where  $c_A^s$  and  $c_B^s$  are the cell surface concentrations, which can be calculated by

$$c_A^s = \frac{c_A V_A^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}}, \quad c_A = 1 - c_A^s \quad (6)$$

The  $\gamma$  is an empirical constant which is used to describe the degree of chemical short-range order in different alloys. For the statistically disordered solid solution, there is hardly any degree of chemical short-range order, then the parameter  $\gamma$  should be taken as 0.<sup>10</sup> For ordered alloys (compounds in particular), the short-range order around each type of atoms is entirely fixed and the  $\gamma$  was equal to 8, indicating the highest degree of chemical order.<sup>10,11</sup> For the amorphous phase, it has been revealed by the atomistic simulations as well as several experimental studies that there indeed exist CSRO in Cu-Ni-(Ti, Zr, Hf)-related metallic glasses,<sup>12,13</sup> and the  $\gamma$  was taken as 5 for the amorphous phase and this setting was found to be in reasonable agreement with the actual situation.<sup>10,14</sup>

The elastic term  $\Delta H_{ABC}^e$  is an atomic size mismatch contribution and could also be divided into three terms of binary subsystems,

$$\Delta H_{ABC}^e = \Delta H_{AB}^e + \Delta H_{AC}^e + \Delta H_{BC}^e \quad (7)$$

For the binary subsystem consisted of A and B, the chemical term  $\Delta H_{AB}^e$  is given by

$$\Delta H_{AB}^e = c_A c_B [c_B \Delta \bar{H}_{A \text{ in } B}^{\text{elastic}} + c_A \Delta \bar{H}_{B \text{ in } A}^{\text{elastic}}] \quad (8)$$

where  $c_A$  and  $c_B$  are the atomic concentrations of metals A and B,  $\Delta \bar{H}_{A \text{ in } B}^{\text{elastic}}$  and  $\Delta \bar{H}_{B \text{ in } A}^{\text{elastic}}$  are the elastic contribution to the enthalpies of A solved in B and that of B solved in A.

The structural contribution  $\Delta H_{ABC}^s$  reflects the correlation between the number of valence electrons and the crystal structure of the transition metals. It can be

deduced from the lattice stability  $E_\sigma(Z)$  of each crystal structure  $\sigma$  ( $\sigma = bcc, fcc$  or  $hcp$ ) as a function of the number of valence electrons  $Z$  of the metal,

$$\Delta H_{ABC}^s = E_\sigma(\bar{Z}) - [c_A E_\sigma(Z_A) + c_B E_\sigma(Z_B) + c_C E_\sigma(Z_C)] \quad (9)$$

where  $c_A$ ,  $c_B$  and  $c_C$  are the atomic concentrations of metals A, B and C,  $\bar{Z}$ ,  $Z_A$ ,  $Z_B$  and  $Z_C$  are numbers of mean valence electrons of the alloy phase and valence electrons of the pure metals A, B and C,  $E_\sigma(\bar{Z})$ ,  $E_\sigma(Z_A)$ ,  $E_\sigma(Z_B)$  and  $E_\sigma(Z_C)$  are the lattice stability parameters of the alloy phase and the pure metals A, B and C, respectively.

For the amorphous phase, both the elastic term  $\Delta H_{ABC}^c$  and the structural term  $\Delta H_{ABC}^s$  are absent,<sup>5,6</sup> but the enthalpy difference between the amorphous and crystalline states of pure metals  $\Delta H_{ABC}^{\text{topological}}$  should be considered. The formation enthalpy  $\Delta H_{ABC}^{\text{am}}$  of the amorphous phase can thus be written as

$$\Delta H_{ABC}^{\text{am}} = \Delta H_{ABC}^c + c_A \Delta H_A^{\text{a-s}} + c_B \Delta H_B^{\text{a-s}} + c_C \Delta H_C^{\text{a-s}} \quad (10)$$

where  $c_A$ ,  $c_B$  and  $c_C$  are the atomic concentrations of metals A, B and C,  $\Delta H_A^{\text{a-s}}$ ,  $\Delta H_B^{\text{a-s}}$  and  $\Delta H_C^{\text{a-s}}$  are the enthalpy difference between the amorphous and crystalline states. This quantity is given by

$$\Delta H_i^{\text{a-s}} = \alpha T_{m,i} \quad (11)$$

where  $\alpha = 3.5 \text{ Jmol}^{-1}\text{K}^{-1}$  and  $T_{m,i}$  is the melting temperature of component  $i$ .

By comparing the Gibbs free energies of the solid solution and the amorphous phase, an estimate of the GFA of a ternary transition alloys system can be obtained. Since the entropy terms for concentrated solid solutions and amorphous phases are both taken as ideal solutions, the comparing of the enthalpies of them is enough.

Accordingly, the GFA of a ternary alloy consisting of metals A, B and C can be evaluated as<sup>15</sup>

$$\gamma_{ABC}^* = \text{GFA} \propto \frac{\Delta H_{ABC}^{\text{am}}}{\Delta H_{ABC}^{\text{am}} - \Delta H_{ABC}^{\text{inter}}} \quad (12)$$

The larger the value of the  $\gamma_{ABC}^*$ , the better the GFA of the corresponding composition in the alloy system.

### 3. Results and discussion

The thermodynamic calculation results for Cu-Ni-Ti (Zr, Hf) systems are presented here. As the complicated phase could not nucleate and grow due to the extremely restricted kinetic condition during the process of producing metallic glasses. It follows that the competing phase of amorphous phase is the terminal solid solution phase, whose structure is relatively simple. Accordingly, the issue of predicting the favored glass formation compositions could be converted into an issue of comparing the stability of the amorphous phase versus the solid solution phase. Therefore, by comparing the relative energy status of the amorphous phase versus the solid solution phase, the compositions which are energetically favored for metallic glass formation can thus be located.

Table 1 shows the atomic radius, electronic structure, crystal structure and atomic size difference of these elements. According to Miedema's model, the heats of formation ( $\Delta H_f$ ) of the Cu-Ni, Cu-Ti, Cu-Zr, Cu-Hf, Ni-Ti, Ni-Zr, Ni-Hf, system are +5 kJ/mol, -23 kJ/mol, -14 kJ/mol, -19 kJ/mol, -35 kJ/mol, -49 kJ/mol, -42 kJ/mol, respectively.<sup>6</sup> The parameters used in the thermodynamic calculation of the Cu-Ni-Ti (Zr, Hf) systems are listed in Table 2. For the Cu-Ni system, they are immiscible and the



Gibbs free energy is always positive, however, the proper addition of Ti (Zr, Hf) can highly change the difference in atomic sizes as well as the electron redistribution, which are both highly related with the GFR of the system. According to Miedema's model and Alonso's method, an estimate of the GFR of a ternary transition alloys system can be obtained through comparing the Gibbs free energies of the solid solution and the amorphous phase, if the Gibbs free energy of the amorphous phase is lower than that of solid solution, the amorphous could be obtained for the corresponding composition of the alloy system. Then we project the predicted glass formation region onto the composition triangle which reflects thermodynamic characteristic of each ternary system in Fig. 1. If an alloy composition is located inside the defined green dot region, the amorphous phase is energetically favored, and while it is located outside, the crystalline solid solution is favored. To validate the amorphous region i.e., the glass formation region (GFR) in Fig. 1, the related experimental results were collected and given as the red dots shown.<sup>7,16-34</sup> From Fig. 1, one can see that these experimentally measured glass formation compositions mostly fall within the predicted GFR for the Cu-Ni-Zr (Hf) systems, suggesting that the results predicted by Miedema's model and Alonso's method are acceptable in determining the glass formation region of the Cu-Ni-Zr (Hf) ternary systems. While for the Cu-Ni-Ti system, the thermodynamic calculation is deviated from the experiment results, we speculate that the main factor for metallic glass formation in this system could be kinetic instead of thermodynamic

Furthermore, we pinpoint the compositions with large GFA inside the determined glass formation region. To evaluate the composition dependence of GFA and locate

the compositions with relatively large GFA, the parameter  $\gamma^*$  is further calculated over the entire predicted GFR. Meanwhile, one can see from Fig. 2 that the best glass formers of Cu-Ni-Ti (Zr, Hf) systems calculated based on Miedema's model, Alonso's method and Xia's theory<sup>5,6,15</sup> are at the composition of  $\text{Cu}_1\text{Ni}_{56}\text{Ti}_{43}$ ,  $\text{Cu}_{19}\text{Ni}_{27}\text{Zr}_{54}$  and  $\text{Cu}_{10}\text{Ni}_{56}\text{Hf}_{34}$  as the black pentagrams pointed out. Experimentally, Gargarella et al.<sup>7</sup> have reported that the  $\text{Cu}_{43}\text{Ni}_7\text{Ti}_{50}$  alloy was considered to have the best GFA, while Yang et al.<sup>19</sup> have obtained a series of Cu-Ni-Zr glassy rods, finding the alloy  $\text{Cu}_{20}\text{Ni}_{18}\text{Zr}_{62}$  has the largest reduced glass-transition temperature and Cui et al.<sup>35</sup> have reported that the  $\text{Cu}_{10}\text{Ni}_{45}\text{Hf}_{45}$  has the largest glass formation driving force calculated from atomistic simulation. As indicated above, the experimental results are in good agreement with the present prediction in Cu-Ni-Zr (Hf) systems, despite some minor deviation. The minor deviation may mainly result from that the Miedema's model and Alonso's method are empirical approaches and the model is strictly valid at low temperature.

From the above analyses, one can see that the glass formation regions of the Cu-Ni-Zr and Cu-Ni-Hf systems are similar, while the GFR and GFA/best glass formers of the Cu-Ni-Ti alloy system are different from that of the Cu-Ni-Zr (Hf). Meanwhile, it is found that, the best glass forming composition of the Cu-Ni-Ti system calculated by thermodynamic calculations is largely deviated from the experiment results. Specifically, early studies have shown that the GFA for ternary Cu-Ni-Ti alloy system is good for Cu-rich composition and poor for Ni-rich composition,<sup>36</sup> which is contrary to the thermodynamic calculation result in Fig. 2(a). From the Cu-Ni-Ti phase

diagram,<sup>37</sup> one can see that the liquidus temperature of Cu-rich composition is lower than that of Ni-rich composition, and Gupta et al.<sup>38</sup> have found that the liquidus temperature increases with increasing Ni content of the Cu-Ni-Ti alloy system. Then we speculate that the kinetic factors instead of thermodynamic factors make a much more important role in the glass formation of Cu-Ni-Ti alloy system. Generally, the glass formation process can be influenced by thermodynamic factors as well as kinetic factors, such as cooling rate and overheating during producing etc, and we consider the thermodynamic factors as intrinsic ones. However, for certain alloy systems, the kinetic factors may play a much more important role during glass formation process. Consequently, the predicted GFR and the so-called GFA could exhibit some deviation from the practically observed characteristics. For the Cu-Ni-Ti alloy system, the main kinetic factors that exert effect on the glass formation are glass transition temperature ( $T_g$ ) and cooling rate etc. It is in general accepted that the glass transition temperature ( $T_g$ ) is not a strong function of composition and the liquid should be undercooled to below  $T_g$  for the glass formation. As a result, if for a given alloy with higher liquidus temperature, the cooling time would be longer and it is in favor of the nucleation instead of glass formation, while for the alloy with lower liquidus temperature, the cooling time would be shorter at the same cooling rate and it restrain the nucleation, then the metallic glass would be obtained. Accordingly, the kinetic consideration of low liquidus temperature make the Cu-rich composition an easy glass former, while the higher liquidus temperature of the Ni-rich composition gives it a poor glass forming ability with larger possibility to obtain the crystalline phases such as CuTi, NiTi, etc.

Thereby, for the Cu-Ni-Ti ternary alloy system in which the kinetic factor play a principle role in the glass formation, the thermodynamic calculation based on Miedema's model and Alonso's method may be not quite accurate.

#### **4. Conclusion**

Based on the Miedema's model and Alonso's method, the GFR and GFA of the Cu-Ni-Ti (Zr, Hf) ternary alloy systems have been predicted. It is found that thermodynamic calculation of GFR and GFA are in good agreement with the experiment results for the Cu-Ni-Zr (Hf) systems, while for the Cu-Ni-Ti alloy system, the calculated results are largely deviated from experimental results in terms of the Cu and Ni contents, and it is assumed that the kinetic factors instead of thermodynamic factors make a much more important role in the glass formation of Cu-Ni-Ti alloy system. Specifically, the kinetic consideration of low liquidus temperature reduces the cooling time with less nucleation, making the Cu-rich composition an easy glass former, while the higher liquidus temperature of the Ni-rich composition gives it a longer cooling time and stimulates nucleation with larger possibility to obtain the crystalline phases such as CuTi, NiTi, etc., and the Ni-rich composition would have a poor glass forming ability.

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## References

- 1 W. Klement, R. H. Willens and P. Duwez, *Nature*, 1960, **187**, 869-870.
- 2 J. S. C. Jang, K. C. Wu, S. R. Jian, P. J. Hsieh, J. C. Huang and C. T. Liu, *J Alloy Compd*, 2011, **5091**, S109-S114.
- 3 D. Turnbull, *Transactions of the Metallurgical Society of Aime*, 1961, **221**, 422-439.
- 4 T. Egami and Y. Waseda, *J Non-Cryst Solids*, 1984, **64**, 113-134.
- 5 J. A. Alonso, L. J. Gallego and J. A. Somoza, *Nuovo Cimento*, 1990, **12**, 587-595.
- 6 F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema and A. K. Niessen, *Cohesion in Metals: Transition Metal Alloys*, Elsevier Science Publishers B. V, Amsterdam, 1988.
- 7 P. Gargarella, S. Pauly, K. K. Song, J. Hu, N. S. Barekar, M. S. Khoshkhoo, A. Teresiak, H. Wendrock, U. Kuehn, C. Ruffing, E. Kerscher and J. Eckert, *Acta Mater*, 2013, **61**, 151-162.
- 8 W. H. Wang, C. Dong and C. H. Shek, *Mat Sci Eng R*, 2004, **44**, 45-89.
- 9 L. J. Gallego, J. A. Somoza and J. A. Alonso, *J Phys-Condens Mat*, 1990, **2**, 6245-6250.
- 10 R. H. de Tandler, M. R. Soriano, M. E. Pepe, J. A. Kovacs, E. E. Vicente and J. A. Alonso, *Intermetallics*, 2006, **14**, 297-307.
- 11 A. R. Miedema, *Journal of the Less-Common Metals*, 1973, **32**, 117-136.
- 12 I. Kaban, P. Jovari, V. Kokotin, O. Shuleshova, B. Beuneu, K. Saksl, N. Mattern, J. Eckert and A. L. Greer, *Acta Mater*, 2013, **61**, 2509-2520.

- 13 I. Bakonyi, *J Non-Cryst Solids*, 1995, **180**, 131-150.
- 14 T. L. Wang and B. X. Liu, *J Alloy Compd*, 2009, **481**, 156-160.
- 15 L. Xia, S. S. Fang, Q. Wang, Y. D. Dong and C. T. Liu, *Appl Phys Lett*, 2006, **88**.
- 16 P. Gargarella, S. Pauly, M. Stoica, G. Vaughan, C. R. M. Afonso, U. Kuehn and J. Eckert, *APL Materials*, 2015, **3**.
- 17 X. F. Wu, Z. Y. Suo, Y. Si, L. K. Meng and K. Q. Qiu, *J Alloy Compd*, 2008, **452**, 268-272.
- 18 R. Ristic, M. Stubicar and E. Babic, *PHILOSOPHICAL MAGAZINE*, 2007, **87**, 5629-5637.
- 19 H. Yang, J. Q. Wang and Y. Li, *J Non-Cryst Solids*, 2006, **352**, 832-836.
- 20 G. Duan, D. H. Xu and W. L. Johnson, *Metall Mater Trans a*, 2005, **36A**, 455-458.
- 21 D. H. Xu, B. Lohwongwatana, G. Duan, W. L. Johnson and C. Garland, *Acta Mater*, 2004, **52**, 2621-2624.
- 22 A. Inoue and W. Zhang, *Mater Trans*, 2004, **45**, 584-587.
- 23 H. R. Wang, Y. L. Gao, X. D. Hui, G. H. Min, Y. Chen and Y. F. Ye, *J Alloy Compd*, 2003, **349**, 129-133.
- 24 C. J. Hu and P. Y. Lee, *Mater Chem Phys*, 2002, **74**, 13-18.
- 25 C. F. Li, L. M. Wang and A. Inoue, *Mater Lett*, 2001, **51**, 203-207.
- 26 J. Garaguly, A. Lovas, K. Tompa and J. Takacs, *J Alloy Compd*, 1997, **253**, 114-117.
- 27 L. Stojanova and K. Russev, *Mat Sci Eng A-Struct*, 1997, **226**, 483-486.

- 28 M. Ming and Z. Altounian, *J Non-Cryst Solids*, 1996, **205-207**, 633-636.
- 29 G. Peto, I. Bakonyi, K. Tompa and L. Gucci, *Phys Rev B*, 1995, **52**, 7151-7158.
- 30 O. Haruyama, I. Kanazawa, N. Asahi, M. Ito and T. Iwashita, *J Non-Cryst Solids*, 1995, **192-193**, 451-455.
- 31 T. Zhang, A. Inoue and T. Masumoto, *Mat Sci Eng A-Struct*, 1994, **181**, 1423-1426.
- 32 M. Vanrossum, M. A. Nicolet and W. L. Johnson, *Phys Rev B*, 1984, **29**, 5498-5503.
- 33 Z. Altounian and J. O. Stromolsen, *Phys Rev B*, 1983, **27**, 4149-4156.
- 34 K. Buschow, *J Appl Phys*, 1981, **52**, 3319-3323.
- 35 Y. Y. Cui, X. Bai, S. Y. Luo, Q. Wang, J. H. Li and B. X. Liu, *J Alloy Compd*, 2013, **552**, 55-59.
- 36 B. S. Murty, M. M. Rao and S. Ranganathan, *Mat Sci Eng A-Struct*, 1995, **196**, 237-241.
- 37 Q. Y. Zhang and H. S. Zhuang, *San Yuan He Jin Xiang Tu Shou Ce*, China Machine PRESS, 2011.
- 38 P. G. Gupta, *Phase Diagrams of Ternary Ni Alloys*, Indian Institute of Metals, Calcutta, 1990.

## Tables

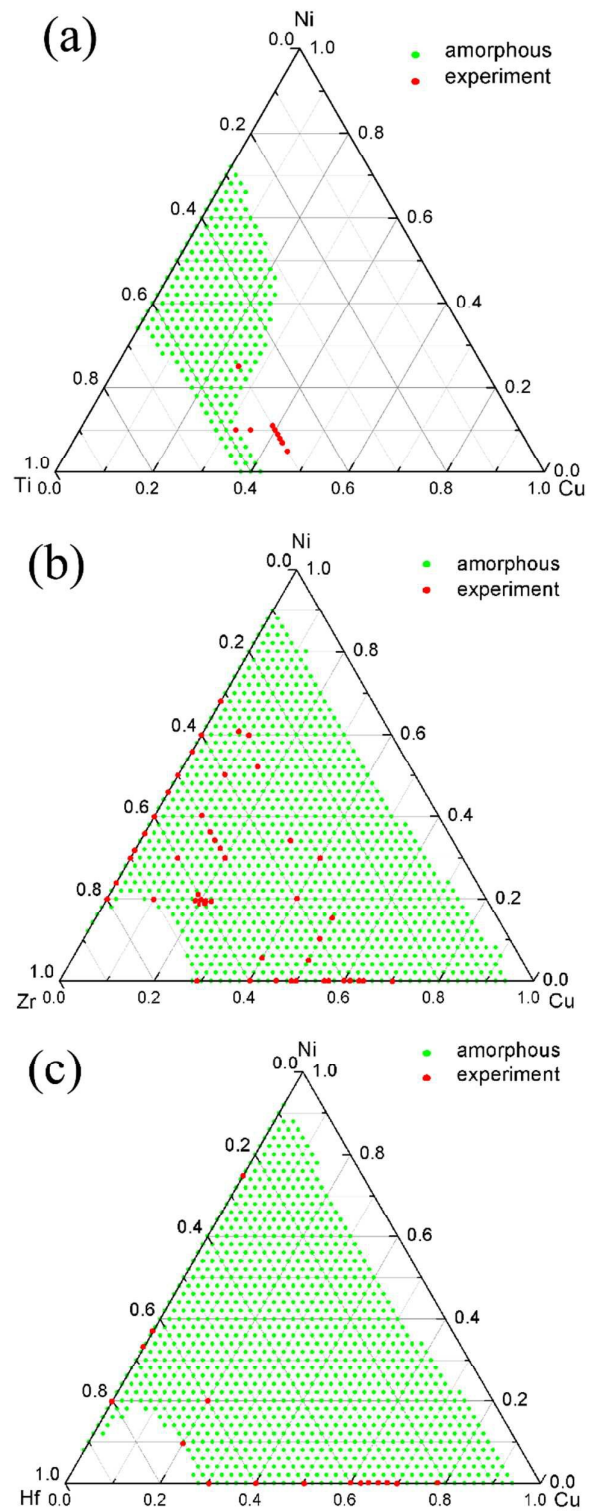
**Table 1.** Atomic radius, atomic size difference, electronic structure and crystal structure of the elements in the Cu-Ni-Ti (Zr, Hf) systems.

Elements	Atomic radius(Å)	Electronic structure	Crystal structure	$ r_i - r_{Cu} /r_{Cu}$	$ r_i - r_{Ni} /r_{Ni}$
Cu	1.28	3d <sup>10</sup> 4s <sup>1</sup>	fcc	0	2.4%
Ni	1.25	3d <sup>8</sup> 4s <sup>2</sup>	fcc	2.4%	0
Ti	1.47	3d <sup>2</sup> 4s <sup>2</sup>	hcp	14.8%	17.6%
Zr	1.60	4d <sup>2</sup> 5s <sup>2</sup>	hcp	25.6%	28.0%
Hf	1.62	4f <sup>14</sup> 5d <sup>2</sup> 6s <sup>2</sup>	hcp	26.6%	29.6%

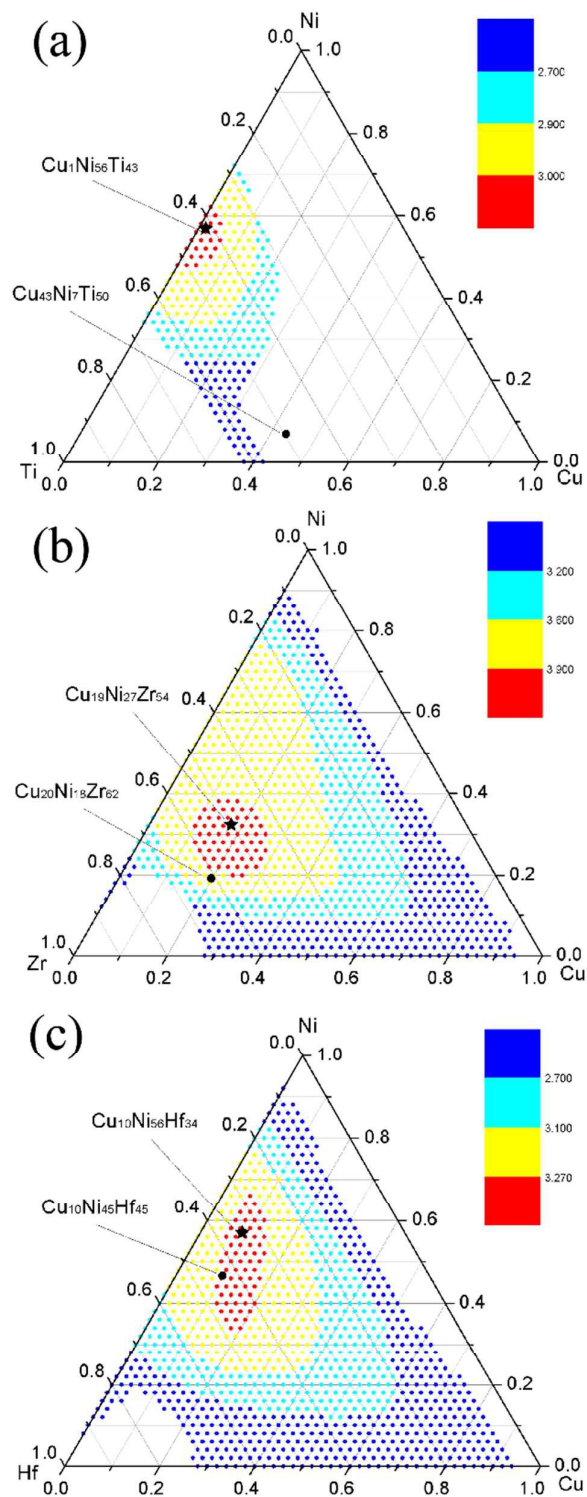


**Table 2** The parameters used in the thermodynamic calculation of the Cu-Ni-Ti (Zr, Hf) system (ref. 6).  $\Delta\bar{H}_{A \text{ in } B}^{\text{inter}}$ ,  $\Delta\bar{H}_{B \text{ in } A}^{\text{inter}}$ ,  $\Delta\bar{H}_{A \text{ in } B}^{\text{elastic}}$ ,  $\Delta\bar{H}_{B \text{ in } A}^{\text{elastic}}$  and  $E_{\sigma}(Z_A)$  are expressed in KJ mol<sup>-1</sup>,  $T_{m,i}$  is expressed in K.

	$E_{\sigma}(Z_A)$	$T_{m,i}$	$\Delta\bar{H}_{A \text{ in } B}^{\text{inter}}$	$\Delta\bar{H}_{B \text{ in } A}^{\text{inter}}$	$\Delta\bar{H}_{A \text{ in } B}^{\text{elastic}}$	$\Delta\bar{H}_{B \text{ in } A}^{\text{elastic}}$
Cu	1.5	1357.6				
Ni	-2.0	1726.0				
Ti	-2.5	1943.0				
Zr	-2.5	2125.0				
Hf	-2.5	2500.0				
Cu-Ni			+14	+14	+0.09	+2.58
Cu-Ti			-33	-40	+20.41	+32.81
Cu-Zr			-78	-110	+61.33	+94.57
Cu-Hf			-58	-81	+74.99	+97.04
Ni-Ti			-126	-154	+38.38	+40.31
Ni-Zr			-165	-237	+93.09	+95.49
Ni-Hf			-145	-204	+116.68	+107.26



**Fig. 1.** Glass formation compositions of the (a) Cu-Ni-Ti, (b) Cu-Ni-Zr and (c) Cu-Ni-Hf alloy systems predicted by thermodynamic calculation.



**Fig. 2.** Calculated  $\gamma_{ABC}^*$  in the GFRs of (a) Cu-Ni-Ti, (b) Cu-Ni-Zr and (c) Cu-Ni-Hf alloy system. The red regions are the compositions which have the largest  $\gamma_{ABC}^*$ , *i.e.*, the best GFA as well as vicinity compositions.

**Metallic glass formation in the Cu-Ni-Ti (Zr, Hf) systems studied by  
thermodynamic calculation**

Y. Y. Wang, Q. Wang, J. H. Li and B. X. Liu

For the family of Cu-Ni-Ti (Zr, Hf) systems, which are promising to obtain the bulk metallic glasses, the glass formation regions were calculated based on the extended Miedema's model and Alonso's method. It is found that the calculated glass formation regions and glass forming ability of Cu-Ni-Zr and Cu-Ni-Hf systems agree with experimental results well but not for the Cu-Ni-Ti system. It turns out that the glass forming ability of Cu-Ni-Ti system is largely deviated from the experimental results, then it is assumed that the kinetic factors (low liquidus temperature) instead of thermodynamic factors make the Cu-rich composition an easy glass former in Cu-Ni-Ti system.

