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# An important factor powerfully influencing the Al–Ni-based alloys' glass-forming ability

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## Abstract

In order to get better glass-forming abilities (GFAs), Ni atoms are partially replaced by Cu and Co atoms in  $\text{Al}_{84}\text{Ni}_{12}\text{Zr}_4$  alloys. Thermal analysis shows that the reduced crystallization temperature  $T_{\text{rx}}$  has no direct correlation with the GFA of the alloys. However, it is notable that prepeaks have been found in the total structure factors of the amorphous  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  and  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  alloys. In addition, the results prove that the intensity of the prepeaks influences the GFA powerfully. The amorphous alloys with larger intensity of the prepeak show better GFA. The influence of prepeaks on the GFA can be explained by the atomic configuration difference among the liquid, crystal and glass states.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

During recent years, several kinds of bulk metallic glasses have been developed, including Pd based, Zr based, Mg based, Cu based and so on [1–6]. All the above mentioned alloys have been proved to form full glass phase by casting into rods with up to 10 mm in diameter corresponding to a comparatively low critical cooling rate. However, although dozens of Al-based alloys which contain more than 80% aluminium were discovered to transform into amorphous phase at high cooling rate, bulk glasses based on aluminium have still not been developed and the largest dimension already reported can be only up to 0.2 mm using the mould casting method [7]. Besides, several empirical rules have been developed for estimating the GFA of the alloys. But Al-based glass-forming alloys do not always abide by these rules. For these reasons, it is valuable to investigate which factors play a key role on the GFA in the Al-based glass-forming alloys.

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With the development of the amorphous materials, increasing attention is focused on the atomic structure. Despite their lack of long-range translational and orientational order, covalent amorphous solids can exhibit structural order over both short and medium length scales [8]. The structure factor  $S(Q)$  which is usually used in the research of liquid has gradually been employed as one research tool for glass, and the prepeaks prior to the first peak appear on  $S(Q)$  curves of some special alloy systems. Until now the reason for the presence of the prepeak on the  $S(Q)$  is disputable. Chemical short order and medium-range order usually correspond to the prepeak. The liquid Al–Ni [9, 10], Al–Fe [11, 12] and glass-forming Al–Fe–Ce alloys [13], whose structure clearly deviates from a random hard sphere packing and exhibits a obvious prepeak on the  $S(Q)$  curves, have induced wide attention for their anomalies in local atom packing.

Inoue and his co-workers [7, 9] have developed the amorphous Al–Ni-based alloys by a single-roller melt spinning technique. The experimental results show that the Al–Ni–Zr alloys can form fully amorphous phase and have relatively high GFA. In our work, Cu and Co atoms are used replacing the Ni atoms in order to investigate the key factor influencing the GFA. Prepeaks which reflect the local atom orderly packing appear on the total structure factor curves calculated from the x-ray diffraction intensity of the amorphous Al–Ni–Zr ribbons. By relating the height of the prepeaks to the corresponding GFA, we have found the qualitative correlation between the prepeaks and the GFA.

## 2. Experimental procedure

Ingots of Al–Ni–Zr–Cu and Al–Ni–Zr–Co were prepared from high-purity elements in an arc furnace under argon atmosphere. Amorphous ribbons were obtained by the single-roller melt-spinning technique under a partial argon atmosphere. The diameter of the copper roller was 35 cm. The cooling rate for amorphous formation is controlled by the rotating rate of the copper wheel. The revolution rate is from 2400 to 600 revolutions per minute, giving a circumferential speed from 44 to 11 m s<sup>-1</sup>. The ribbons were 20–30 μm in thickness and 4–6 μm in width.

Both the experimental and simulated results have proved the prepeaks on the liquid's total structure factor are influenced by the temperature [10, 13]. With increasing temperature, the intensity of the prepeaks decreased. In order to cancel the influence of the temperature on the prepeaks of the liquid alloys, we reheated all the ingots up to approximately 50 K above the liquidus temperature and then quenched them into the amorphous state.

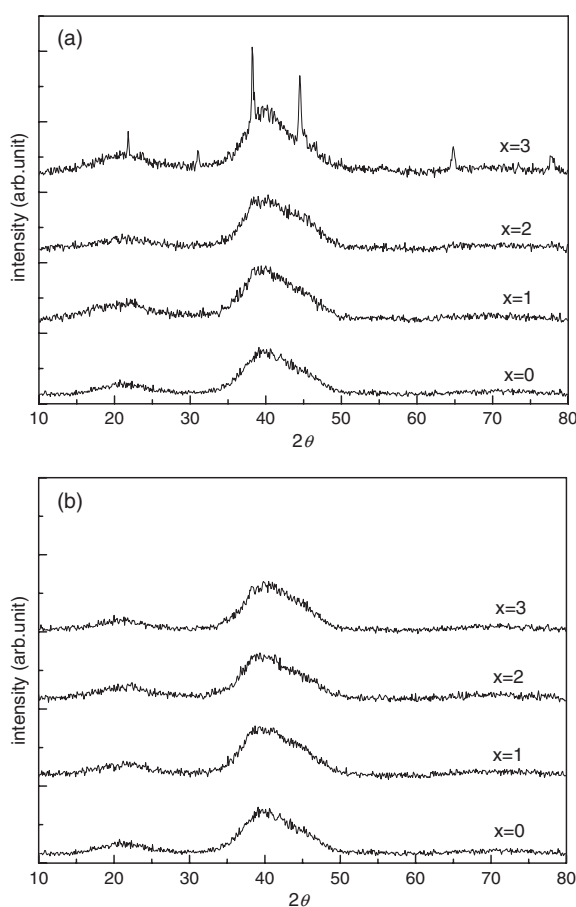
As-quenched ribbons were assessed by XRD (x-ray diffraction analysis) (D/max-rB) using Cu K $\alpha$  radiation and TEM analysis (Hitachi-800). The thermal analysis was performed by using a differential scanning calorimetry (Netzsch DSC404).

The method for obtaining the total structure factor  $S(Q)$  can be found in many works [11, 13, 14]. There are two main equations for calculating  $S(Q)$ :

$$S(Q) = I_{\text{eu}}^{\text{coh}}(Q) / \langle f^2(Q) \rangle \quad (1)$$

$$\langle f^2(Q) \rangle = \sum_i c_i f_i^2(Q) \quad (2)$$

where  $Q = 4\pi \sin \theta / \lambda$  is the magnitude of the scattering vector, and  $\lambda$  is the wavelength.  $I_{\text{eu}}^{\text{coh}}$  is the coherent scattering intensity per atom in electron units;  $c_i = N_i / N$ ,  $N_i$  is the number of type- $i$  atoms and  $f_i(Q)$  is the type- $i$  atomic scattering factor.

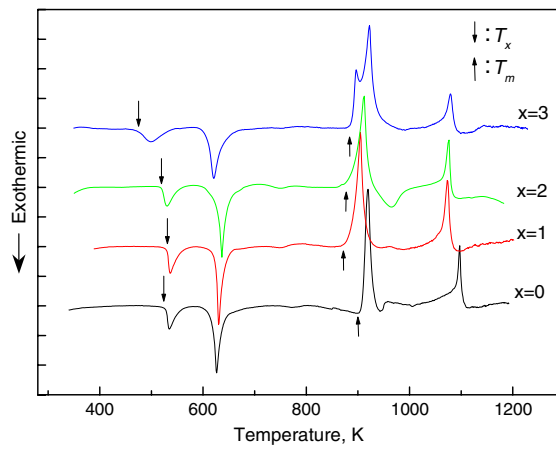


**Figure 1.** XRD diffraction patterns of the quenched (a)  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  and (b)  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  ribbons.

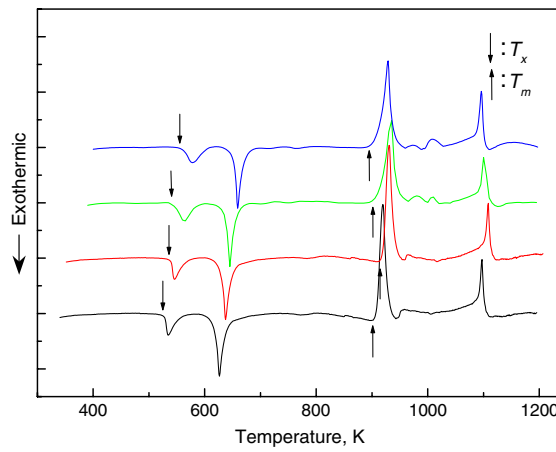
### 3. Results

The quenched ribbons of  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  and  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  ( $x = 1, 2, 3$ ) form fully amorphous phase except  $\text{Al}_{84}\text{Ni}_9\text{Zr}_4\text{Cu}_3$ , which is proved by the XRD results (figure 1). Figures 2 and 3 show the DSC curves of the  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  and  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  amorphous ribbons heated at  $20 \text{ K min}^{-1}$ . The thermal parameters are listed in table 1. There are no obvious  $T_g$  points on DSC curves of  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  and  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$ , which is similar to most Al-based amorphous samples.

For DSC curves of  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  alloy ribbons, the upset temperatures of crystallization  $T_x$  decrease from 528 to 483 K with increasing Cu content. In addition, the  $T_x$  of  $\text{Al}_{84}\text{Ni}_9\text{Zr}_4\text{Cu}_3$  is extremely low compared with the other three, which may be caused by the mixed phase. The upset temperatures of melting  $T_m$  have changed in a more complex way: when the 1 at% Ni atoms are replaced by Cu atoms, the  $T_m$  drops from 898 to 870 K; when adding Cu from 1 to 3 at% continuously, the  $T_m$  increases gradually. The changing tendencies of thermal parameters of  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  amorphous ribbons are comparably regular (figure 3). Both  $T_x$  and  $T_m$  increase with increasing Co content.



**Figure 2.** The DSC curves of the amorphous  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  ribbons at the heating rate of  $20 \text{ K min}^{-1}$ .



**Figure 3.** The DSC curves of the amorphous  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  ribbons at the heating rate of  $20 \text{ K min}^{-1}$ .

**Table 1.** The related parameter of the amorphous  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  and  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  alloys.

Alloys	$v_0$ ( $\text{m s}^{-1}$ )	$T_x$ (K)	$T_m$ (K)	$T_{rx}$
$\text{Al}_{84}\text{Ni}_{12}\text{Zr}_4$	22	528	898	0.588
$\text{Al}_{84}\text{Ni}_{11}\text{Zr}_4\text{Cu}$	11	533	870	0.609
$\text{Al}_{84}\text{Ni}_{10}\text{Zr}_4\text{Cu}_2$	22	517	876	0.591
$\text{Al}_{84}\text{Ni}_9\text{Zr}_4\text{Cu}_3$	>44	483	882	0.574
$\text{Al}_{84}\text{Ni}_{11}\text{Zr}_4\text{Co}$	15	540	910	0.593
$\text{Al}_{84}\text{Ni}_{10}\text{Zr}_4\text{Co}_2$	38	546	901	0.606
$\text{Al}_{84}\text{Ni}_9\text{Zr}_4\text{Co}_3$	44	560	898	0.624

Inoue and co-workers [15] have proposed the concept of the reduced crystallization behaviour  $T_{rx}$  as one criterion of the GFA. In this theory, it is proved that in some amorphous

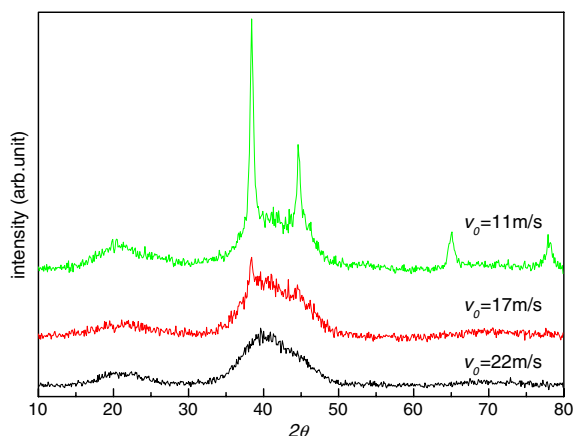


Figure 4. XRD patterns of the  $\text{Al}_{84}\text{Ni}_{12}\text{Zr}_4$  ribbons quenched at different circumferential speeds.

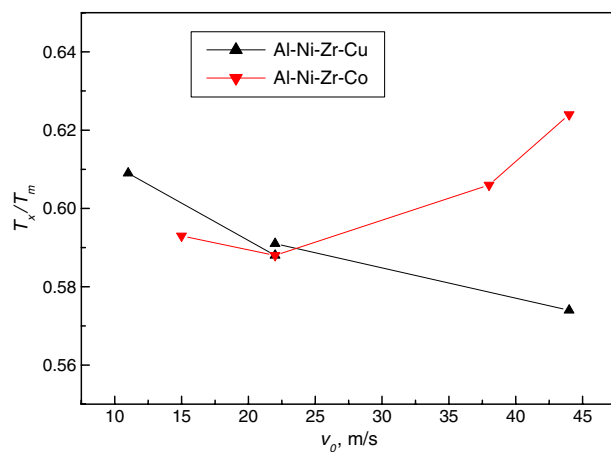


Figure 5. Correlation between the reduced crystallization temperature  $T_{rx}$  and the critical cooling rate  $v_0$ .

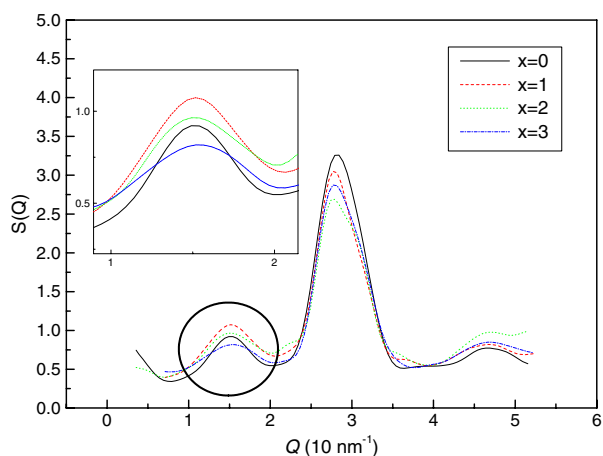
alloy systems larger  $T_{rx}$  usually corresponds to better GFA. This parameter can be calculated by the equation

$$T_{rx} = T_x/T_m. \quad (3)$$

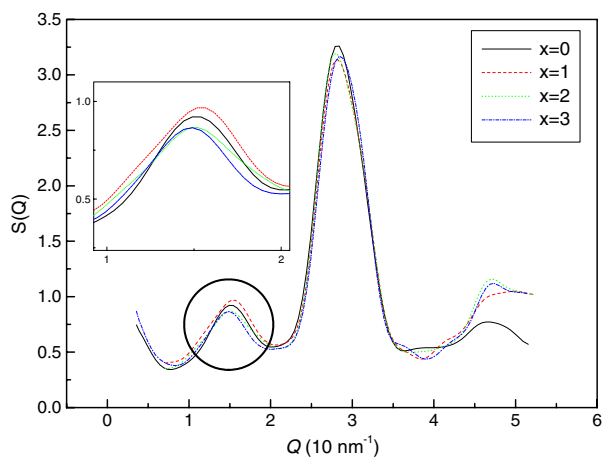
We also calculated the  $T_{rx}$  of the  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  and  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  amorphous alloys, and the results are listed in table 1.

In order to examine the critical cooling rates of the alloys, we have quenched them at different circumferential speeds. Take  $\text{Al}_{84}\text{Ni}_{12}\text{Zr}_4$  for example (figure 4);  $22 \text{ m s}^{-1}$  was selected as the critical cooling rate and the values have been listed in table 1. Figure 5 shows the curves which reflect  $T_{rx}$  plotted as the function of the critical cooling rate. From the curves it can be clearly summarized that there is no direct correlation between  $T_{rx}$  and the critical cooling rate  $v_0$  for both  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  and  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  amorphous alloys.

The total structure factors of  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  and  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  alloy ribbons which are calculated from the XRD results are shown in figures 6 and 7. The prepeaks at about  $Q_1 = 1.5$  are perfectly present in all the researched alloys. Table 2 lists the values



**Figure 6.** The total structure factors of amorphous  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  alloy quenched at a temperature approximately 50 K higher than the liquidus line.

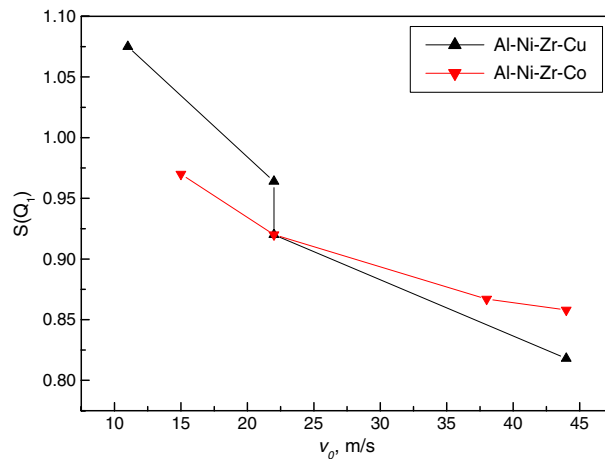


**Figure 7.** The total structure factors of amorphous  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  alloy quenched from a temperature approximately 50 K higher than the liquidus line.

of  $Q_1$  and  $S(Q_1)$ , where  $Q_1$  represents the prepeak position. The positions of the prepeaks  $Q_1$  almost keep stable for  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  alloys, while they increase with increasing  $S(Q_1)$  for  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  alloys. Figure 8 shows the total structure factors proposed as the function of the critical cooling rate. The result attracts our interest that the larger  $S(Q_1)$  corresponds to lower critical rate  $v_0$ . This means the large prepeak forming tendency can be profitable for excellent glass-forming ability (GFA).

#### 4. Discussion

The GFA of Al-based alloys is often abnormal compared with other glass-forming alloys. For example, Inoue has found the  $\Delta T_x$  ( $\Delta T_x = T_x - T_g$ ) of the Al–Ni–Ce alloys with poor GFA is larger than the good glass-forming alloys' [17] and the glass-forming component range of the Al–RE (RE represents the rare earth elements) alloys deviates from the eutectic point [18].



**Figure 8.** Correlation between the intensity of the prepeak  $S(Q_1)$  and the critical cooling rate.

**Table 2.** The values of  $Q_1$  and  $S(Q_1)$  of  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  and  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  alloys.

$\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$			$\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$		
$x$	$Q_1$	$S(Q_1)$	$x$	$Q_1$	$S(Q_1)$
0	1.521	0.919	0	1.521	0.919
1	1.522	1.079	1	1.545	0.966
2	1.514	0.960	2	1.514	0.862
3	1.528	0.809	3	1.489	0.860

For most of the alloy systems which have good glass-forming ability, it has been proved that the parameter  $T_{rg}$  ( $T_{rg} = T_g/T_m$ , where  $T_g$  represents the glass transition temperature) or  $T_{rx}$  can be regarded as the criterion of the GFA. Moreover, usually the larger the parameter  $T_{rx}$  is, the better GFA the alloy has. However, some research results [16] show that not all the glass-forming alloys abide by this rule. Figure 5 shows that the GFA of the alloys studied above has no direct correlation with the parameter  $T_{rx}$  either. The results indicate  $T_{rx}$  cannot act as the criterion for the GFA of the alloys studied above, and there are other factors playing important roles in the forming process of the amorphous phase.

It is well known that the glass solid or amorphous phase should have a chaotic structure and does not possess the long-range order characteristic. However, figure 8 shows the prepeaks which indicate the ordered structure are beneficial to the GFA. How do the prepeaks influence the GFA of this alloy system?

For the glass and liquid, the presence of the prepeak is explained by Li [14]: that it is a consequence of complex chemical order and the interaction potential gives rise to the network structure that manifests the presence of the medium-range order. Since the discovery of the quasicrystalline phase in Al–Mn alloys [19], icosahedral order in liquid alloys has been generally accepted. Using molecular dynamics simulation, Li [10] has studied the origin of the prepeak's presence in the  $\text{Ni}_3\text{Al}$  alloys during the quenching process and pointed out that two kinds of defective icosahedra (containing 1311 and 1321 bond pairs) resulted in the presence of the prepeaks in the rapidly cooling liquid structure. Wang also uses molecular dynamics simulation searching the cluster structure in the liquid and glass states of the  $\text{Ni}_3\text{Al}$  [20] and Al–Fe [21, 22] alloys. The results demonstrate that in the quenching process 1551 bond pairs



which is one typical icosahedral order are dominant in number. What is more, the structure corresponding to the prepeak is the combination of the icosahedra and defective icosahedra bond pairs and is medium range in size. So the intensity of the prepeaks  $S(Q_1)$  indicates the number of the medium-range order clusters contained in the liquid or glass.

When the liquid phase solidifies to the solid phase, if the icosahedral characteristic bond pairs (such as 1311, 1321, 1551, 1541 and so on) can transfer into crystal characteristic bond pairs (such as 1421, 1661, 1441 and 1422) freely, the solid structure is more likely to form a crystal. Otherwise, the alloys would like to form a glass phase easily. In other words, this kind of alloys has good GFA.

Cu and Co atom addition to Al–Ni–Zr alloys influences the medium-range order clusters and is reflected in the  $S(Q_1)$  of the glasses' total structure factors. The fact that more medium-range order clusters are contained in the glass state indicates the icosahedral characteristic clusters are more likely to keep steady than change into the crystal characteristic cells.

It is noticeable that the results above are consistent with the model proposed by Tanaka [23], in which the correlation among icosahedral short-range ordering, fragility, glass formability and quasicrystal formation in metallic glass formers was predicted. Formation of local icosahedral clusters reduces the Gibbs free-energy difference and also increases the interface tension between the supercooled liquid and the crystal. As a result, the supercooled liquids with larger density of the icosahedral cluster, which is reflected as the intensity of the prepeaks here, are always stronger and have better glass-forming ability.

What is more, Das and co-workers [24] found that the alloy liquids with larger prepeak on the total structure factor have smaller value of the diffusion coefficients though using both simulation and the neutron scattering method. It is well known that difficulty of atomic rearrangement is beneficial to the GFA, and the diffusion is one key route for the atomic rearrangement. Supposing the prepeaks' intensity has heredity from liquid to glass, this research fruit can also be employed to explain our results.

## 5. Conclusion

The  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Cu}_x$  and  $\text{Al}_{84}\text{Ni}_{(12-x)}\text{Zr}_4\text{Co}_x$  ( $x = 1, 2, 3$ ) amorphous ribbons have been prepared though melt quenching. The results of the thermal analysis show that the reduced crystallization temperature is not suitable to occupy the criterion for the GFA. From the total structure factors we can see the prepeaks clearly, and the intensity of the prepeak has a powerful influence on the GFA of the studied amorphous alloys. The atomic configuration difference among the liquid, crystal and glass states which is cited from the simulation results can explain the prepeaks' effect.

## Acknowledgments

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## References

- [1] Drehman A J, Greer A L and Turnbull D 1982 *Appl. Phys. Lett.* **41** 716
- [2] Inoue A 2000 *Acta Mater.* **48** 279
- [3] Masuhr A, Waniuk T A, Busch R and Johnson W L 1999 *Phys. Rev. Lett.* **82** 2290
- [4] Ma H, Xu J and Ma E 2003 *Appl. Phys. Lett.* **83** 2793
- [5] Peker A and Johnson W L 1993 *Appl. Phys. Lett.* **63** 2342

- [6] Xu D H, Duan G and Johnson W L 2004 *Phys. Rev. Lett.* **92** 245504
- [7] Inoue A 1998 *Prog. Mater. Sci.* **43** 365
- [8] Elliott S R 1991 *Nature* **354** 445
- [9] Horio Y, Inoue A and Masumoto T 1994 *Mater. Sci. Eng. A* **179/180** 596
- [10] Li H and Pederiva F 2003 *Phys. Rev. B* **68** 054210
- [11] Qin J Y, Bian X F, Sliusarenko S I and Wang W M 1998 *J. Phys.: Condens. Matter* **10** 1211
- [12] Il'inskii A, Sliusarenko S, Slukhovskii O, Kaban I and Hoyer W 2002 *Mater. Sci. Eng. A* **325** 98
- [13] Zhang L, Wu Y S, Bian X F, Li H, Wang W M, Li J G and Lun N 1999 *J. Phys.: Condens. Matter* **11** 7959
- [14] Li H 2004 *J. Phys. Chem. B* **108** 5438
- [15] Inoue A, Zhang T, Zhang W and Takeuchi A 1996 *Mater. Trans. JIM* **37** 99
- [16] Zhao Z F, Zhang Z, Wen P, Pan M X, Zhao D Q, Wang W H and Wang W L 2003 *Appl. Phys. Lett.* **82** 7969
- [17] Inoue A 1998 *Prog. Mater. Sci.* **43** 407
- [18] Inoue A, Zhang T, Kita K and Masumoto T 1989 *Mater. Trans. JIM* **30** 870
- [19] Shechtman D, Blech I, Gratias D and Cahn J W 1984 *Phys. Rev. Lett.* **53** 1951
- [20] Wang L, Bian X F and Yang H 2002 *Phys. Lett. A* **302** 318
- [21] Wang L, Cong H R, Zhang J X, Bian X F, Li H and Qin J Y 2002 *Phys. Lett. A* **301** 477
- [22] Wang L, Cong H R and Bian X F 2002 *Mater. Sci. Eng. A* **341** 197
- [23] Tanaka H 2003 *J. Phys.: Condens. Matter* **15** L491
- [24] Das S K, Horbach J, Koza M M, Mavila Chatoth S and Meyer A 2005 *Appl. Phys. Lett.* **86** 011918