Vol 11 No 6, June 2002
1009-1963/2002/11(06)/0592-04

Chinese Physics

© 2002 Chin. Phys. Soc.
and IOP Publishing Ltd

Effects of nickel on the crystallization of $Zr_{70}Cu_{20}Ni_{10}$ amorphous alloy*

Wang Huan-Rong(王焕荣)[a], Ye Yi-Fu(叶以富)[a,b], Zhang Jun-Yan(张均艳)[a],
Teng Xin-Ying(滕新营)[a], Min Guang-Hui(闵光辉)[a],
Shi Zhi-Qiang(石志强)[a], and Tian Xue-Lei(田学雷)[a]

[a] *Key Laboratory of Liquid Structure and Heredity of Materials, Ministry of Education, Shandong University, Jinan* 250061, *China*
[b] *College of Resource and Environmental Engineering, East China University of Science and Technology, Shanghai* 200237, *China*

(Received 6 December 2001; revised manuscript received 28 February 2002)

Differential scanning calorimetry (DSC) and x-ray diffraction (XRD) are employed to investigate the effects of nickel on the crystallization of the amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy. We have found that the crystallization process of the amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy is strongly influenced by the addition of nickel. Addition of 10 at% Ni to the $Zr_{70}Cu_{30}$ amorphous alloy makes the crystallization process proceed from a single-stage mode to a double-stage mode. The activation energy for crystallization of the amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy is calculated to be about 388kJ·mol^{-1} on the basis of the Kissinger equation. The effects of nickel on the crystallization of the amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy are discussed in terms of the genetics of metals.

Keywords: crystallization, Zr–Cu-based amorphous alloys, x-ray diffraction, differential scanning calorimetry

PACC: 6140

1. Introduction

Recently, discoveries of bulk amorphous alloys, such as La–Al–Ni,[1] Zr–Ti–Ni–Cu–Be,[2,3] Zr–Al–Ni,[4] Zr–Cu–Ni–Al[5] and Zr–Ti–Ni–Cu–Al[6] etc, have attracted much attention due to their exceptional good glass forming ability (GFA). It is of interest to note that all these alloy systems contain the element Ni, which plays an important role in preparing these bulk amorphous alloys and possesses some particular properties. For example, Maret *et al*[7,8] attributed the pre-peak in the structure factor of $Ni_{33}Y_{67}$ metallic glass and liquid $Al_{80}Ni_{20}$ alloy to the interaction between Ni atoms. Wang and coworkers[9] investigated the crystallization behaviour of Ni and the amorphous Si multi-film. We have found a pronounced pre-peak in the structure factor of the liquid $Cu_{70}Ni_{30}$ alloy and we believe that it is strongly related to the Ni–Ni interactions.[10] Furthermore, the formation of a ternary amorphous Zr–Cu–Ni alloy does not satisfy the widely accepted criteria of glass formation proposed by Inoue,[11] i.e. a significant difference in atomic size ratios above 12% among the three main constituent elements (only 3% between Cu and Ni atoms) and negative heats of mixing among the three main constituent elements (positive value of 4kJ·mol^{-1} between Cu and Ni atoms).[12] Extensive studies have been made on binary amorphous Zr–Cu alloys by many researchers.[13,14] However, the effects of Ni on the crystallization of the amorphous Zr–Cu-based alloy are not involved as yet. Therefore, it remains an urgent problem to make an in-depth study on the effects of Ni on the glass forming ability (GFA) of Zr–Cu-based alloys, which will provide some useful information in the alloy design for achieving new bulk amorphous alloys. Unfortunately, so far, few experimental studies have been carried out on such a subject except for some thermodynamic calculations.[15,16] The main purpose of this paper is to investigate the effects of Ni on the GFA of Zr–Cu-based alloys.

2. Experimental procedures

The pre-alloy with a nominal composition of $Zr_{70}Cu_{20}Ni_{10}$ was prepared by melting the pure zirconium (99.95%), high-purity copper (99.999%) and nickel (99.999%) with an arc furnace in a water-cooled copper boat under argon atmosphere of 99.999% purity. The alloy ingot was remelted several times to en-

*Project supported by the National Natural Science Foundation of China (Grant No 59871025).

sure homogeneity. Melt-spun ribbons with a thickness of about 40μm of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloys at different cooling rates were produced by means of vacuum melt-spinning. The diameter of the copper roller was about 200mm and all the experiments were performed in a high-purity argon atmosphere of 1.3×10^5Pa before the chamber was cleaned in a vacuum of 3×10^{-3}Pa. X-ray diffraction experiments were carried out with a D/max-rB diffractometer. The thermal properties of the melt-spun ribbons were checked by using a Netzsch DSC404 calorimeter.

3. Results and discussion

Figure 1 shows the x-ray diffraction (XRD) patterns of the melt-spun ribbons of the $Zr_{70}Cu_{20}Ni_{10}$ amorphous alloy at different cooling rates. It can be seen that each pattern shows a broad peak at the position of about 2θ=36.5°, indicating that all the ribbons are fully amorphous. Through careful observation we can see that the width of the first peak broadens gradually with increasing surface velocity from 20 to 40m·s^{-1}, suggesting that a more random dense-packing structure exists in the amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy obtained at a high cooling rate.

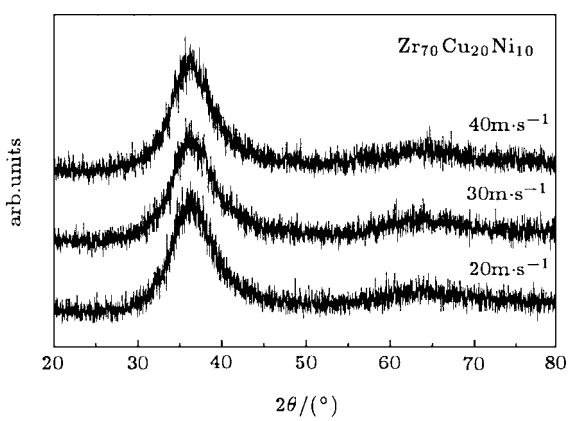


Fig.1. XRD patterns of melt-spun $Zr_{70}Cu_{20}Ni_{10}$ ribbons at different cooling rates.

Typical DSC traces of melt-spun $Zr_{70}Cu_{20}Ni_{10}$ alloy at different heating rates are shown in Fig.2 and the corresponding thermodynamic parameters are listed in Table 1. It can be clearly seen that all the DSC curves exhibit two exothermic peaks, indicating that the crystallization process of the amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy proceeds via a double-stage mode. Compared with the $Zr_{70}Cu_{30}$ amorphous alloy without Ni, which crystallizes through one exothermic peak (shown in Fig.3), the addition of Ni to the Zr–Cu-based alloys alters the crystallization path. Furthermore, addition of Ni to the $Zr_{70}Cu_{30}$ alloy increases the crystallization temperature from 382 to 418°C at a heating rate of 20K·min^{-1}, implying that the Ni element effectively improves the thermal stability of Zr–Cu-based alloys.

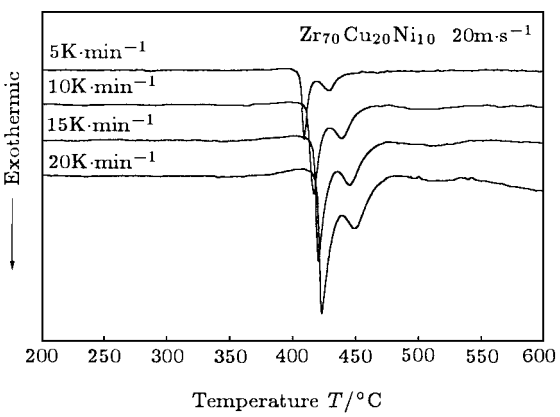


Fig.2. DSC scans of melt-spun $Zr_{70}Cu_{20}Ni_{10}$ ribbons at different heating rates.

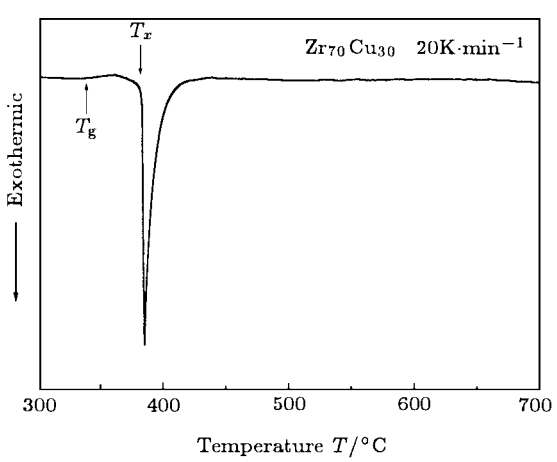


Fig.3. DSC scan of melt-spun $Zr_{70}Cu_{30}$ alloy.

Table 1. Thermodynamic parameters of the amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy.

Heating rate/K·min^{-1}	Glass transition temperature T_g/°C	1st peak temperature T/°C	2nd peak temperature T/°C
5	406.2	409.5	429.5
10	411.8	417.1	439.3
15	415.6	420.5	445.6
20	418.0	423.2	449.2

The activation energy for crystallization E_α can be obtained based on the Kissinger equation[17]

$$\mathrm{d}\left[\ln\left(\frac{\Phi}{T_X^2}\right)\right]\Big/\mathrm{d}\left(\frac{1}{T_X}\right) = -\frac{E_\alpha}{R}, \qquad (1)$$

where Φ is the heating rate, T_X is the onset temperature for crystallization, and R is the gas constant. A plot of $\ln(\Phi/T_X^2)$ versus $1/T_X$ yields a straight line with a slope $-E_\alpha/R$. The relationship between $\ln(\Phi/T_X^2)$ and $1/T_X$ is shown in Fig.4. According to the slope of the fitted line we can calculate the activation energy for crystallization of the $Zr_{70}Cu_{20}Ni_{10}$ amorphous alloy to be around 388kJ·mol^{-1}, which is much higher than that of the $Zr_{70}Cu_{30}$ amorphous alloy (269kJ·mol^{-1}).[18]

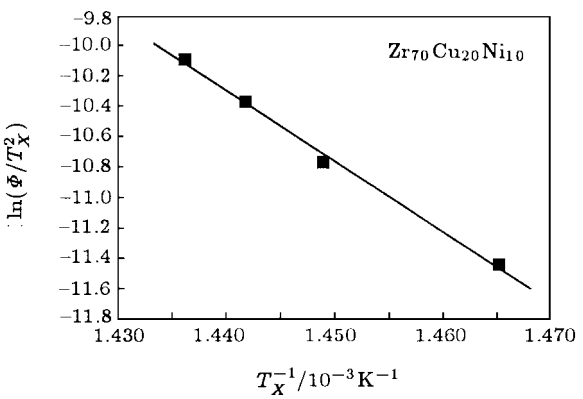


Fig.4. Relationship between $\ln(\Phi/T_X^2)$ and $1/T_X$.

The crystallization of metallic glasses, as well as that of undercooled melts, proceeds by nucleation and growth mechanisms. Both nucleation and growth are controlled by the atomic mobility. The atomic transport in undercooled melts is usually described as viscous flow. The temperature dependence of the viscosity η is described quite often by the Vogel–Fulcher–Tamman equation[19,20]

$$\eta = A\exp\left(\frac{B}{T - T_0}\right), \qquad (2)$$

where T_0 is an ideal glass transition temperature below T_g, and A and B are constants. The temperature dependence of the diffusivity D is given by an Arrhenius-type equation[19]

$$D = D_0\exp\left(-\frac{Q}{RT}\right), \qquad (3)$$

where Q is the activation energy for the transfer of atoms across the surface of the nucleus, which is about equal to the activation energy for diffusion.

A higher activation energy for crystallization of the $Zr_{70}Cu_{20}Ni_{10}$ amorphous alloy than that of $Zr_{70}Cu_{30}$ alloy can be clarified from the point of view of genetics. It is known that there is a close relationship between the liquid structure and its amorphous structure. Amorphous alloys produced by the liquid quenching technique always inherit some structural information of liquids, which can exert an influence on their properties. Since no direct experimental results about the liquid structure of a ternary Zr–Cu–Ni alloy are available, we can explain this phenomenon from the point of view of genetics of metal materials.

Based on the theory of genetics of metals, the size of atomic clusters in a melt decreases gradually with increasing temperature. This process will not cease until external conditions exert an influence on it. Under such conditions some small atomic clusters may be preserved in the melt and pass their structural information down to the solid during rapid quenching. Thermodynamic calculations of liquid Zr–Cu and Zr–Ni alloy systems have been studied by many researchers, e.g. Turchanin *et al.*,[21] Gaukel *et al.*,[22] Aihara *et al.*,[23] and Witusiewicz *et al.*[15,24] A common feature of Zr–Cu and Zr–Ni alloy systems is that Cu and Ni, having smaller atomic radii, are more easily diffusive than Zr atoms with larger atomic radii. The liquid structure of the Cu–Ni alloy, however, is not clear as yet. We have investigated the liquid structure of the $Cu_{70}Ni_{30}$ alloy, which has a large undercooling tendency, and we found a distinct pre-peak around a scattering vector magnitude of 13.5nm^{-1}.[8] We think that the origin of the pre-peak in the structure factor of the liquid $Cu_{70}Ni_{30}$ alloy is due to the interactions among Ni–Ni atomic pairs. This behaviour indicates that a stable medium-range order exists in the $Cu_{70}Ni_{30}$ melt, i.e. the so-called micro-heterogeneity of liquid alloys.

During rapid quenching of the ternary Zr–Cu–Ni alloy from a liquid state, some stable atomic clusters may probably pass down to the amorphous alloy. Because the crystallization products of the amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy are mainly Zr_2Cu and Zr_2Ni, it is necessary for Cu and Ni atoms to make a long-range redistribution to form these two crystalline phases during heating. On the other hand, due to the restriction of atomic clusters, Cu and Ni atoms cannot easily make a long-range rearrangement, and thus the thermal stability of Zr–Cu-based alloys is greatly improved. In other words, the higher GFA of the $Zr_{70}Cu_{20}Ni_{10}$ alloy than that of the $Zr_{70}Cu_{30}$ alloy

results from the difficulty of precipitation of Zr_2Cu and Zr_2Ni, which is caused by the existence of atomic clusters containing Cu and Ni atoms.

As regards the two exothermic peaks in the DSC curves of the amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy, as shown in Fig.2, it can be determined on the basis of different diffusivities of Cu and Ni atoms. It is known that the diffusivity of the Cu atom is larger than that of the Ni atom.[14] Thus the Zr_2Cu crystalline phase first precipitates from the amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy. After that, the Zr_2Ni phase will precipitate gradually. Therefore, we consider that the first exothermic corresponds to the precipitation of Zr_2Cu and the second corresponds to the precipitation of the Zr_2Ni phase.

4. Conclusions

In conclusion, the addition of Ni to the Zr–Cu-based alloys effectively increases the thermal stability and alters the crystallization process. The origin of higher GFA and activation energy for the crystallization of the $Zr_{70}Cu_{20}Ni_{10}$ alloy than those of the $Zr_{70}Cu_{30}$ alloy can be attributed to the effects of Ni. The existence of atomic clusters containing Cu and Ni atoms plays an important role in increasing the GFA of the $Zr_{70}Cu_{30}$ alloy. The first exothermic peak in the DSC traces of the amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy corresponds to the precipitation of Zr_2Cu and the second corresponds to the precipitation of the Zr_2Ni crystalline phase.

References

[1] Inoue A, Zhang T and Masumoto T 1989 *Mater. Trans. JIM* **30** 965

[2] Peker A and Johnson W L 1993 *Appl. Phys. Lett.* **63** 2342

[3] Zhang J, Luo J L, Bai H Y, Wang W H, Chen Z J and Meng J B 2001 *Acta Phys. Sin.* **50** 1747 (in Chinese)

[4] Inoue A, Zhang T and Masumoto T 1990 *Mater. Trans. JIM* **31** 177

[5] Zhang T, Inoue A and Masumoto T 1991 *Mater. Trans. JIM* **32** 1005

[6] Xing L Q, Eckert J, Löser W and Schultz L 1999 *Appl. Phys. Lett.* **74** 664

[7] Maret M, Chieux P, Hicter P, Atzmon M and Johnson W L 1987 *J. Phys. F: Metal Phys.* **17** 315

[8] Maret M, Chieux P, Pomme T and Pasturel A 1990 *Phys. Rev.* B **42** 1598

[9] Wang W H, Bai H Y and Wang W K 1998 *Acta Phys. Sin.* **47** 1149 (in Chinese)

[10] Wang H R, Tian X L, Teng X Y, Shi Z Q, Ye Y F, Min G H and Qin J Y 2002 *Chin. Phys. Lett.* **19** 233

[11] Inoue A 2000 *Acta Mater.* **48** 279

[12] Takeuchi A and Inoue A 2000 *Mater. Trans. JIM* **41** 1372

[13] Wang H R, Teng X Y, Shi Z Q, Ye Y F and Min G H 2001 *Acta Phys. Sin.* **50** 2192 (in Chinese)

[14] Gillessen F and Herlach D M 1988 *Mater. Sci. Eng.* **97** 147

[15] Witusiewicz V T and Sommer F 2000 *Metall. Mater. Trans.* **31B** 277

[16] Hui X D, Chen G L, He G, Bian Z and Wang X M 2001 *Trans. Nonferr. Met. Soc. China* **11** 684

[17] Altounian Z, Tu G H and Strom-Olsen J O 1982 *J. Appl. Phys.* **53** 4755

[18] Saida J, Matsushita M and Li C 2000 *J. Mater. Sci. Lett.* **35** 3539

[19] Köster U and Meinhardt J 1994 *Mater. Sci. Eng.* A **178** 271

[20] Köster U, Meinhardt J, Roos S and Liebertz H 1996 *Appl. Phys. Lett.* **69** 179

[21] Turchanin A A, Tomilin I A, Turchanin M A, Belokonenko I V and Agraval P G 1999 *J. Non-Cryst. Solids* **250-252** 582

[22] Gaukel C, Kluge M and Schober H R 1999 *J. Non-Cryst. Solids* **250-252** 664

[23] Aihara T, Kawazoe J Y and Masumoto T 1995 *Mater. Trans. JIM* **36** 835

[24] Witusiewicz V, Arpshofen I and Sommer F Z 1997 *Z. Met.kd.* **88** 866