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Crystallization behavior of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy annealed at 380 ℃①

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[Abstract] Crystallization behavior of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy isothermally annealed at 380 ℃ was first investigated by employing the differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). It has been found that an exothermic peak appears in the DSC trace when the annealing time is about 17～18 min, indicating a certain phase transformation occurs in the matrix of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy. Meanwhile, isothermal annealing experiments for amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy ranging from 360 ℃ to 400 ℃ with a temperature interval of 10 ℃ were also carried out, from which no exothermic reaction can be observed except for the case of 380 ℃. This behavior indicates that the phase transformation during isothermal annealing of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy is strongly temperature- and time-dependent. Further investigations are required to reveal the nature of such phenomenon.

[Key words] crystallization behavior; amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy; isothermal annealing; differential scanning calorimetry (DSC); transmission electron microscopy (TEM); local Avrami exponent

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1 INTRODUCTION

Recently, discoveries of a series of bulk amorphous alloys, such as La-Al-Ni[1], Zr-Ti-Ni-Cu-Be[2], Zr-Al-Ni[3], Zr-Cu-Ni-Al[4] and Zr-Ti-Ni-Cu-Al[5], have received much attention due to their exceptional good glass forming ability (GFA). It is of interest to note that all these above-mentioned 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[6, 7] attributed the prepeak in the structure factor of $Ni_{33}Y_{67}$ metallic glass and liquid $Al_{80}Ni_{20}$ alloy to the interaction between Ni atoms. Moreover, the formation of ternary amorphous Zr-Cu-Ni alloy does not satisfy the widely accepted criteria of glass formation proposed by Inoue[8], i.e., 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 them (positive value of 4 kJ/mol between Cu and Ni atoms)[9]. Therefore, it remains an urgent problem to study the glass formation of ternary Zr-Cu-Ni alloys in depth. Unfortunately, no experimental studies were carried out on such event except for some thermodynamic calculations so far[10, 11]. The main purpose of this paper is to investigate the crystallization behavior of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy isothermally annealed at 380 ℃ by employing DSC and TEM.

2 EXPERIMENTAL

Prealloy with the nominal composition of $Zr_{70}Cu_{20}Ni_{10}$ was prepared by melting pure zirconium (99.95%), high-purity copper (99.999%) and nickel (99.999%) in an arc furnace with a water-cooled copper boat under an argon atmosphere of 99.999% purity. The alloy ingot was remelted several times to ensure homogeneity. Melt-spun ribbon with a thickness of about 30～40 μm of $Zr_{70}Cu_{20}Ni_{10}$ alloy was produced by vacuum melt-spinning. The diameter of the copper roller was about 200 mm and the experiment was performed under high-purity argon atmosphere before the chamber was cleaned in a vacuum of 3×10^{-3} Pa. The surface velocity of the copper roller was around 20 m/s. Amorphicity of the melt-spun ribbon was studied by a D/max-rB diffractometer. Thermal properties of the melt-spun ribbon were checked by using a Netzsch DSC404 calorimeter. TEM experiments were performed in an H-800 microscope, operated at 150 kV.

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3 RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern of the as-quended $Zr_{70}Cu_{20}Ni_{10}$ alloy. It is seen that only one broad peak at the position of $2\theta = 36.5°$ can be observed, indicating that the melt-spun $Zr_{70}Cu_{20}Ni_{10}$ ribbon is fully amorphous. Fig. 2 shows the DSC traces of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy at different heating rates. It can be observed that all the traces exhibit two exothermic peaks, suggesting that the crystallization process of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy proceeds via a double-stage mode. To determine the origins of these two exothermic reactions, TEM experiments are performed for amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy at 425 ℃ and 450 ℃, respectively. Fig. 3 shows the bright field TEM images of partially crystallized amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy at 425 ℃ and 450 ℃, respectively. The main crystalline phases are indexed to be tetragonal Zr_2Cu at 425 ℃ and Zr_2Ni at 450 ℃, respectively. It is interesting to note that the Zr_2Ni particles are nano-scaled, which are determined to be approximately 20 nm. Based on these results, it seems reasonable to conclude that the first exothermic reaction mainly corresponds to the precipitation of Zr_2Cu phase, while the second one corresponds to the formation of nano-scale Zr_2Ni phase.

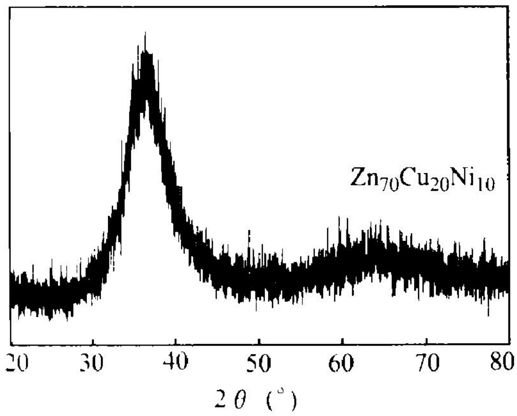

Fig. 1 X-ray diffraction pattern of melt-spun $Zr_{70}Cu_{20}Ni_{10}$ alloy

The activation energy for crystallization E_a of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy can be obtained based on the Kissinger equation[12]:

$$d\left[\ln\left(\frac{\Phi}{T_x^2}\right)\right] \Big/ d\left(\frac{1}{T_x}\right) = -\frac{E_a}{R} \qquad (1)$$

where Φ is the heating rate and T_x the onset temperature for crystallization, R is the gas constant. A plot of $\ln(\Phi/T_x^2)$ versus $1/T_x$ yields a straight line with a slope $-E_a/R$. According to the slope of the fitted line we can calculate the activation energy for crystallization of $Zr_{70}Cu_{20}Ni_{10}$ amorphous alloy to be around 388 kJ/mol.

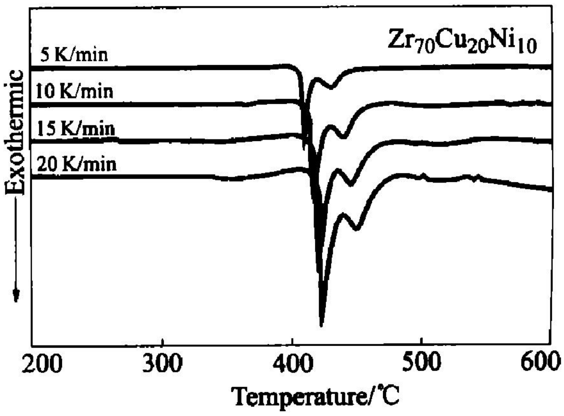

Fig. 2 DSC traces of melt-spun $Zr_{70}Cu_{20}Ni_{10}$ alloy at different heating rates

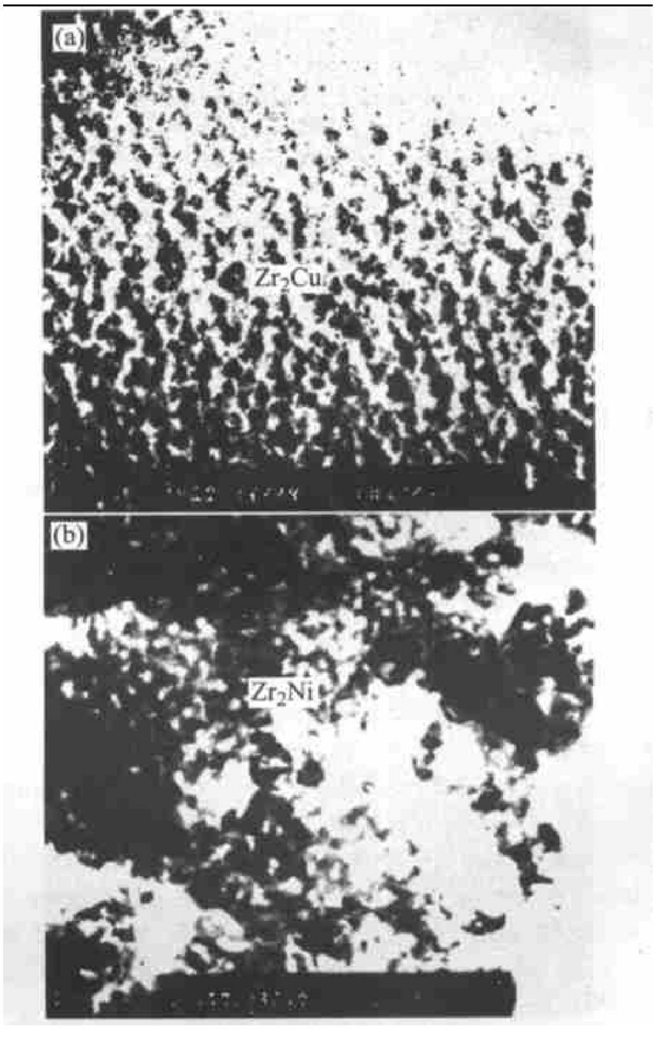

Fig. 3 Bright-field TEM images of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy at
(a) —425 ℃; (b) —450 ℃

DSC scans of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy isothermally annealed at 380 ℃ are shown in Fig. 4. It can be seen that an exothermic peak occurs in the DSC scans when the annealing time is about 17~ 18 min. In order to determine whether this exothermic peak is caused by oxidation, the experiment for the same specimen was repeated and such exothermic reaction was still found. Meanwhile, isothermal annealing experiments for

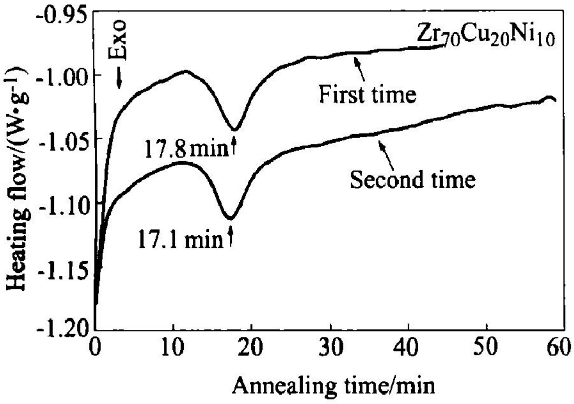

Fig. 4 DSC curves of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy isothermally annealed at 380 ℃

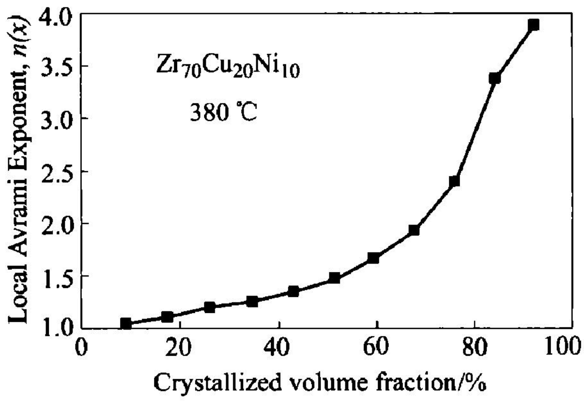

Fig. 5 Plot of crystallized volume fraction x against local Avrami exponent $n(x)$

amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy ranging from 360 ℃ to 400 ℃ with a temperature interval of 10 ℃ were also carried out and no exothermic peak can be observed. Based on the facts, it seems to conclude that the exothermic peak in DSC curve of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy annealed at 380 ℃ is not caused by oxidation but a phase transformation. According to the above-mentioned facts, it is known that this phase transformation is strongly temperature- and time-dependent.

In order to shed more light on the crystallization behavior of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy isothermally annealed at 380 ℃, the local Avrami exponent, which is very successful in describing the crystallization process of many amorphous alloys, e. g., Pd-Si, Fe-Si-B and Fe-Cr-Si-B alloys[13], is utilized. The definition of local Avrami exponent can be expressed as follows: $n(x) = \partial \ln[-\ln(1-x)]/\partial \ln[t-\tau]$, where x is the crystallized volume fraction, τ the incubation time, t the annealing time, and $n(x)$ the local Avrami exponent. The $n(x)$ values can be obtained from the plot of $\ln[-\ln(1-x)]$ against $\ln(t-\tau)$ at a specific temperature.

The relationship between the local Avrami exponent $n(x)$ and the crystallized volume fraction x of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy annealed at 380 ℃ is shown in Fig. 5. It can be seen that when the crystallized volume fraction $x < 50\%$, the local Avrami exponent $n(x) < 1.5$, implying that the crystallization process is mainly controlled by one-dimensional nucleation and growth with a constant nucleation rate. When the crystallized volume fraction $50\% < x < 80\%$, the local Avrami exponent $n(x) < 3.0$, indicating that the crystallization process is dominated by surface crystallization. When the crystallization volume fraction x is beyond 90%, three-dimensional nucleation and growth become the master of the crystallization. No transient nucleation phenomenon occurs because the local Avrami exponent $n(x)$ is smaller than 4.0.

The appearance of an exothermic peak in the DSC traces of amorphous alloys under isothermal annealing conditions can be attributed to several reasons. Zhang et al[14] thought the exothermic peak in the DSC scan of amorphous $Al_{90}Fe_5Ce_5$ alloy results from the precipitation of an icosahedral phase. Inoue et al[15] attributed it to the formation of nano-scaled Zr-Pd clusters in studying the crystallization process of Zr-Cu-Al-Pd amorphous alloy, which act as a nucleation site of $Zr_2(Cu, Pd)$ phase. The authors of this paper think that the occurrence of the exothermic peak in the DSC curve of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy annealed at 380 ℃ might be caused by the formation of a new crystalline phase, which can only be formed under particular temperature and time conditions. In other words, this new crystalline phase is quite temperature- and time-dependent. Further investigations are required to determine the origin of such phenomenon.

4 CONCLUSIONS

1) Melt-spun ribbon of amorphous $Zr_{70}Cu_{20}$-Ni_{10} alloywas produced and the activation energy for crystallization was calculated to be about 388 kJ/mol based on the Kissinger equation. The continuous heating DSC curves exhibit two exothermic peaks, the first exothermic reaction mainly corresponds to the precipitation of Zr_2Cu phase, while the second one corresponds to the formation of nano-scale Zr_2Ni phase.

2) An exothermic peak appears in the DSC curves of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy annealed at 380 ℃ for 17~18 min. It is confirmed that the exothermic peak is not caused by oxidation but a phase transformation, which is very sensitive to the temperature and time. Nevertheless, further investigations are required to understand the nature of the exothermic peak in the DSC scan of amorphous $Zr_{70}Cu_{20}Ni_{10}$ alloy annealed at 380 ℃.

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