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Crystallization behavior of $Zr_{52}Cu_{18}Ni_{15}Al_{10}Ti_5$ bulk glass with quenched-in crystals①

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Abstract: $Zr_{52}Cu_{18}Ni_{15}Al_{10}Ti_5$ bulk glass samples with a diameter of 8 mm prepared by copper mold with water-cooling have a mixing structure of amorphous phase and quenched-in crystals. By isothermal annealing at different temperatures, the crystallization process of the glass alloy is shown to be a multi-staged crystallization reaction as follows: Am + quenched-in crystals → Am′ + cellular phase + (Zr, Ti)-Al → Am′ + cellular phase + (Zr, Ti)-Al + $(Zr, Ti)_2(Cu, Ni)$. Morphology of the quenched-in crystals changes from dot or dendritic phase in the as-cast bulk glass to cellular phase at different annealing states. The residual region surrounded by the cellular phase has a mixing structure of nano-scale phase and amorphous phase.

Key words: bulk glass; quenched-in crystals; crystallization; nano-scale phases **Document code:** A

1 INTRODUCTION

The crystallization behavior in multi-component amorphous alloys is complicated, depending greatly on alloy composition and microstructure, heating process and as-cast amorphous state, and so on. Sometimes metastable phases appear before thermally stable equilibrium phase. The crystallization process of Zr-based bulk glass, focusing mainly on quaternary Zr-Al-Cu-Ni and ternary Zr-Al-Cu alloys, has been investigated extensively[1,2], and the existence of intermetallic compound Zr_2Cu or $Zr_2(Cu, Al)$ has been confirmed. Nevertheless, the study of crystallization of penternary Zr-Al-Cu-Ni-Ti alloy has seldom been reported. In the previous work, Xing et al[3] reported that the quenched-in crystals precipitated from the as-cast Zr-Al-Cu-Ni-Ti bulk glass alloy have a super-saturated structure in which lots of Al element and Ti element were trapped; some other workers[4] reported that the quenched-in crystals are an Al-rich phase. He et al[5~7] reported that the micro-mechanical properties of bulk glass with quenched-in crystals increase with increasing annealing temperature, how the precipitation mechanism of some intermetallic compound changes at different annealing states, and what can affect the glass formation ability of $Zr_{52}Cu_{18}Ni_{15}Al_{10}Ti_5$ alloys. However, little is known about the process of crystallization of Zr-Al-Cu-Ni-Ti bulk glass with quenched-in crystals. Glass samples containing quenched-in crystals can be obtained by two methods. One is to decrease the cooling rate, the other is to increase the oxygen content in the alloy. In the present study, the quenched-in crystals were obtained by properly increasing the thickness of the samples and the oxygen content in the alloy. The aim of the present study is to examine in detail the crystallization process of Zr-Al-Cu-Ni-Ti bulk glass with quenched-in crystals.

2 EXPERIMENTAL

Master alloys were made by induction melting mixture of 99.99% pure Zr, Al, Cu, Ni and Ti. The samples were prepared by casting melt into a water-cooled copper mold. Oxygen content of the alloys were added by reducing the vacuum degree of the atmosphere. In order to survey the crystallization process of $Zr_{52}Cu_{18}Ni_{15}Al_{10}Ti_5$ (mole fraction, %) bulk glass, the samples were annealed isothermally at 673 and 753 K for 600 s, respectively. X-ray diffraction (XRD) was used to identify the precipitated phases. Thermal stability associated with glass transition and super-cooled region was examined by differential scanning calorimetry (DSC). The microstructure and the nano-structure were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM samples were etched for 60 s using a 10% HF water solution. The compositions of the quenched-in crystals and the amorphous matrix were analyzed simultaneously by energy dispersive X-ray spectroscopy (EDX).

3 RESULTS

Fig.1 shows the DSC curve of d8 mm $Zr_{52}Cu_{18}Ni_{15}Al_{10}Ti_5$ bulk glass alloy. It is clear that the glass transition temperature and the peak temperature of crystallization are about 628 K and 751.13 K, respec-

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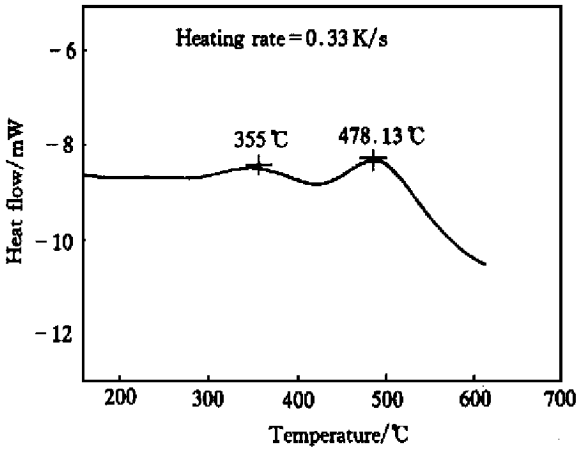

Fig.1 DSC curve of d8 mm $Zr_{52}Cu_{18}Ni_{15}Al_{10}Ti_5$ bulk glass alloy with quenched-in crystals

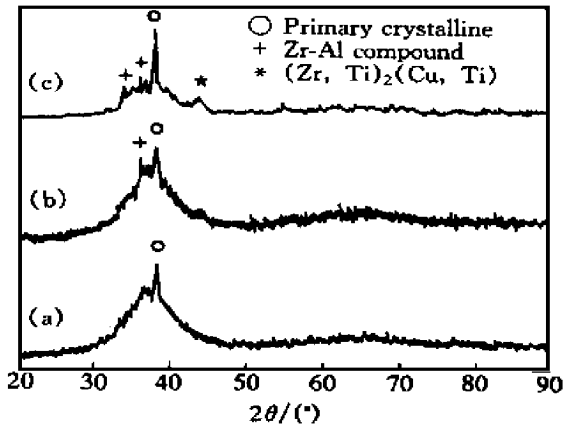

Fig.2 X-ray curves for (a) as-cast (b) 673 K, 600 s treated and (c) 753 K, 600 s treated bulk glasses

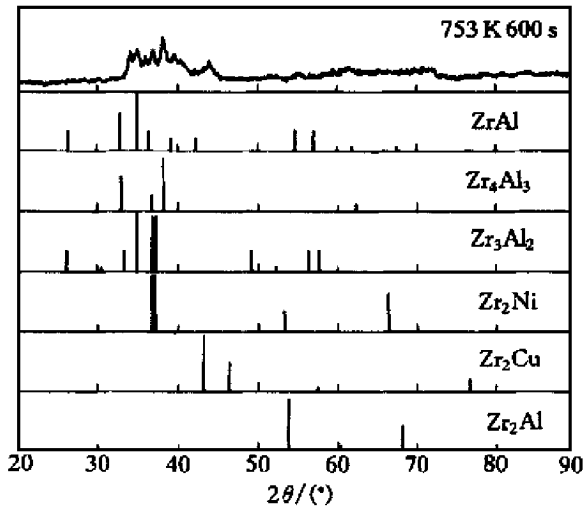

Fig.3 X-ray diffraction peaks simulated by computer

tively. In order to understand the precipitation behavior of the crystals from the super-cooled region and the crystallization region, the difference of crystallization behavior at different annealing states was examined, namely, 673 K, 600 s for the super-cooled region, and 753 K, 600 s for the crystallization region. Fig.2 shows the X-ray diffraction patterns of the samples after different annealing treatments. It can be noticed that the progress of crystallization occurs by the precipitation of several different phases. To identify those precipitated phases, the X-ray diffraction peaks of several possible intermetallic compounds are simulated according to alloy component by computer, as seen in Fig.3. It is found that the precipitation of Zr-Al intermetallic compounds do not depend on annealing temperature, however, $Zr_2(Cu, Ni)$ phase only precipitates at high temperatures. This implies that the precipitation of Zr-Al compounds is much easier than that of $Zr_2(Cu, Ni)$ phase. Fig.4 shows the microstructure of the samples at different annealing states. The quenched-in crystals precipitated from bulk glass present black dot or dendritic morphology, and change to continuous cellular shape after annealing. The possible reason is that the crystals grow and connect with each other. The small regions surrounded by the cellular phase were examined by TEM, as shown in Fig.5. It is clear that those small regions consist of nano-scale phases and an amorphous phase. The size of the nano-scale phases is about 35 ~ 50 nm. It is particularly noticed that the nano-scale phase precipitates firstly at the boundaries of the cellular phases and shows an anomalous shape for 673 K, 600 s treatment, and a spherical shape for 753 K, 600 s treatment. Fig.6 shows the isothermal DSC curve and Johnson-Mehl-Avrami (J-M-A) plot of $Zr_{52}Cu_{18}Ni_{15}Al_{10}Ti_5$ bulk glass alloys. Table 1 shows the results of composition analyses of the quenched-in crystals and the amorphous matrix by EDX.

4 DISCUSSION

4.1 Crystallization kinetics

The crystallization kinetics of the $Zr_{52}Cu_{18}Ni_{15}Al_{10}Ti_5$ bulk glass with quenched-in crystals was examined as a function of annealing time on isothermal annealing at 673 K by Johnson-Mehl-Avrami (J-M-A) equation[8,9]. Fig.6 shows the J-M-A plot where $\ln(-\ln(1-x))$ values are plotted as a function of $\ln t$. The Avrami exponent (n value) is evaluated from the slope of the linear J-M-A plot. It can be seen that n value is not constant. This suggests that the crystallization process has two stages at least: in the first stage, n value is about 2.4; in the second stage, n value is near 3.1. According to the transformation theory, if the quenched-in nuclei are dispersed homogeneously in metal glass alloys, the crystallization behavior of the alloys should have several cases[10]: n is about between 3.0 and 4.0 for three-dimension growth of phases ($N=0$, $I\neq 0$ for $n=4.0$; $N\neq 0$, $I=0$ for $n=3.0$); n is between 2.0 and 3.

0 for two-dimension growth of phases ($N = 0$, $I \neq 0$ for $n = 3.0$; $N \neq 0$, $I = 0$ for $n = 2.0$); n is less than 2.0 for one-dimension growth of phases, where N is the density of the quenched-in nuclei and I is the rate of nucleation.

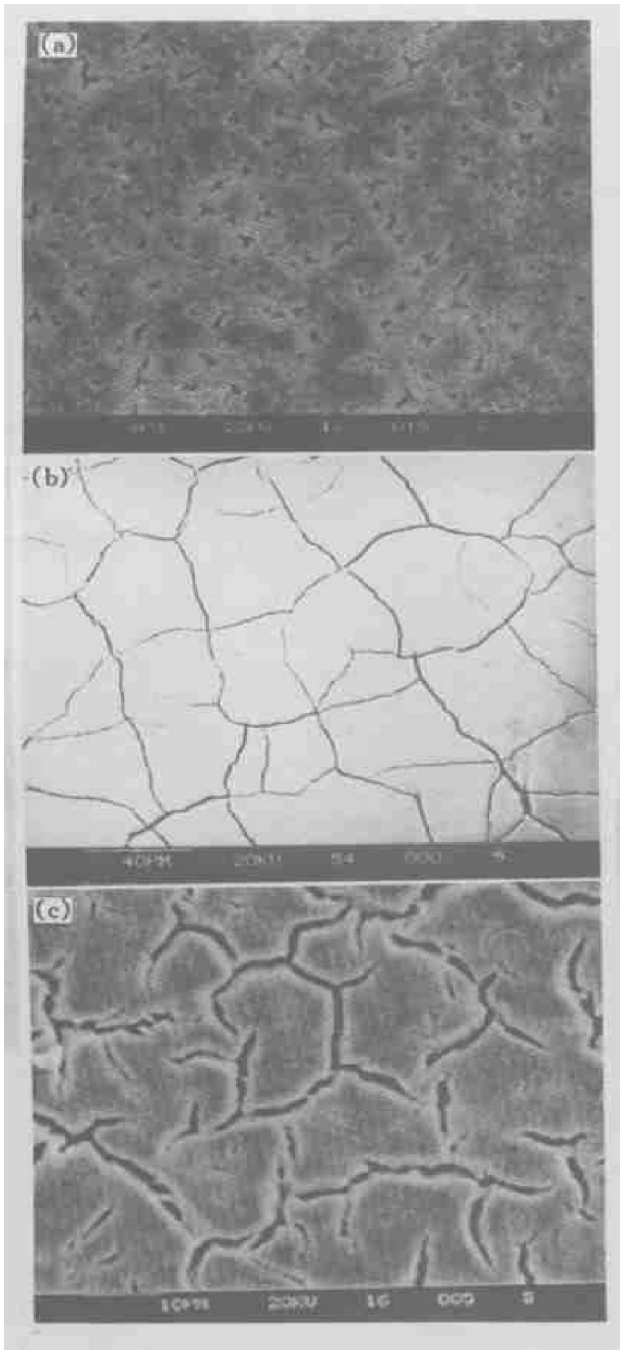

Fig.4 Microstructure of samples at different annealing states
(a) —As-cast; (b) —673 K, 600 s; (c) —753 K, 600 s

According to the above description and the microstructure at several annealing states, it is thought that the first stage of the crystallization process of $Zr_{52}Cu_{18}Ni_{15}Al_{10}Ti_5$ bulk glass is controlled by the growth process of the primary phase, and that the second stage is the nucleation and the growth of Zr-Al intermetallic compound.

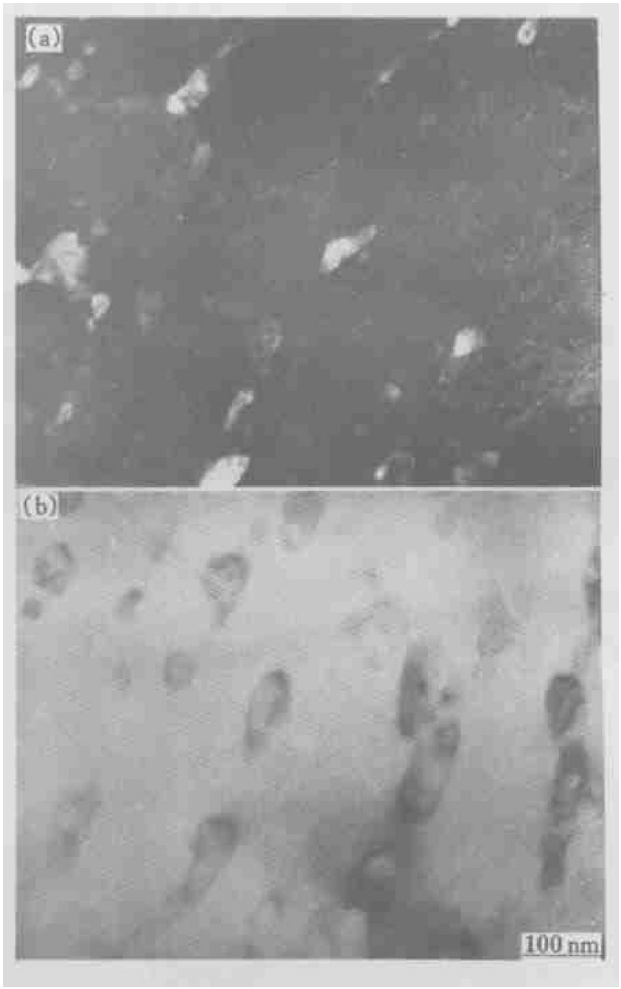

Fig.5 TEM morphologies of precipitation phase
(a) —Dark-field image for 673 K, 600 s treated bulk glass;
(b) —Bright-field image for 753 K, 600 s treated bulk glass

4.2 Temperature dependence of crystallization structure

It has previously been reported[1] that the single-stage crystallization reaction of Zr-Al-Cu-Ni bulk amorphous alloy occurs by simultaneous precipitation of $Zr_2(Al, Ni)$ and $Zr_2(Cu, Ni)$ compounds. However, the existence of the as-quenched crystals and addition of Ti element cause the change in the crystallization reaction from the single-stage crystallization reaction to the multi-stage crystallization reaction: Am + as-quenched crystals → Am′ + cellular phase + (Zr, Ti)-Al → Am′ + cellular phase + (Zr, Ti)-Al + $(Zr, Ti)_2(Cu, Ni)$. By analyzing Table 1, it is found that the average atom percentage content of Al element in the quenched-in crystals is nearly two times as much as that of the amorphous matrix. This implies that the quenched-in crystals are an Al-rich phase, which is consistent with previous reports[3,4]. So, the transition layer between the cellular phase and the amorphous matrix should be Al-rich. It is not necessary for a long range diffusion of Al to form Zr-

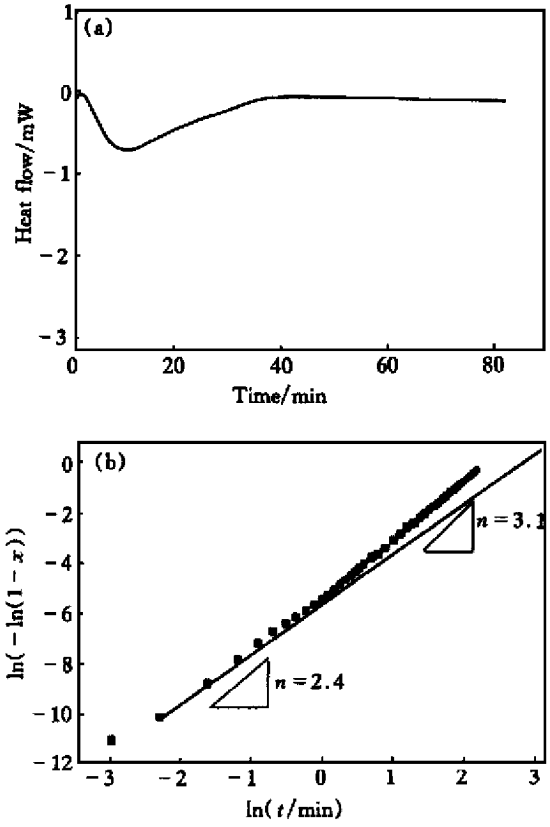

Fig.6 Isothermal DSC curve (a) and J-M-A plot (b) of $Zr_{52}Cu_{18}Ni_{15}Al_{10}Ti_5$ bulk glass with as-quenched crystals at 673 K annealing state

Table 1 Composition analyses of quenched-in crystals and amorphous matrix (mole fraction, %)

Phase	Zr	Al	Cu	Ni	Ti
Amorphous matrix	41.902	14.042	19.939	18.755	5.362
Quenched-in crystals	40.547	25.976	21.096	8.201	4.181

Al intermetallic compound at the interface; furthermore, because of higher energy at the boundaries, the activation energy of nucleation and growth become much lower. On the other hand, the mixing enthalpy is nearly zero for Zr-Ti pair and Ti can be soluble to Zr infinitely. Furthermore, Ti has strong negative heat of mixing against Cu and Ni, and is insoluble to Cu and Ni. This implies that the addition of Ti increases the total content of Zr+Ti. Because of the above-described two factors, Zr-Al phases will be prior to nucleating at the boundaries and precipitate firstly at the interface. Fig.5(a) shows the morphology of the precipitation phases at 673 K for 600 s.

Because of the growth of quenched-in crystals, the residual regions surrounded by the cellular phase shift to a single amorphous phase. The single amorphous phase is rather stable. The nucleation of $(Zr, Ti)_2(Cu, Ni)$ phase only depends on the clusters[11] frozen during forming bulk glass. This suggests that nucleation of $(Zr, Ti)_2(Cu, Ni)$ phase is homogeneous and higher activation energy of nucleation is necessary. This is the reason why $(Zr, Ti)_2(Cu, Ni)$ phase can precipitate at higher temperatures. Fig.5(b) shows the morphology of the nanoscale phases at 753 K for 600 s.

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