KINETIC STUDY ON FORMATION OF BULK GLASS STATE $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ ALLOY[①]

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ABSTRACT Bulk glass state $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy sample with a diameter of 6 mm was prepared by melt injection. Its thermal properties were determined by DTA and DSC analyses. The critical cooling rate for glass formation in $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy was evaluated to be 13.4 K/s, 19.0 K/s and 32.6 K/s from the empirical model and the kinetic model of glass formability respectively by using the DTA and DSC data. The real cooling rate in center of wedge-shaped samples was estimated by testing the glass state area on the longitudinal cross sectional structure of the wedge-shaped samples. The key factors which affect crystallization and growth were discussed.

Key words Zr-based glass state alloy bulk glass state alloy melt injection critical cooling rate

1 INTRODUCTION

Most metallic alloys usually have a lower glass transition temperature T_g, their glass state are formed in the condition of faster cooling rates more than 10^5 K/s, thus, they are limited in use because of their very small size at least in one dimension. Since the bulk glass state alloys with three dimensional size more than 1 mm have been developed by Inoue and his co-workers in 1990's[1,2], the stronger glass forming ability (GFA) have been found in Zr-, Ti-, La-, Pd- and Mg-based multicomponent alloys. The characteristics for high GFA are proposed and summarized by Inoue in three respects[3]: (1) the alloy consisting of more than three elements, (2) significantly different atomic size ratios above about 12%, and (3) optimum negative heats of mixing among the constituent elements. On the other hand, all these glass forming alloys exhibit high reduced glass transition temperature T_g/T_m, high reduced crystallization temperature T_x/T_m and wide supercooled liquid region $\Delta T_x = T_x - T_g$ (T_m is the melting temperature, T_g is the glass transition temperature and T_x is the crystallization temperature). During the cooling, the nucleation and crystal growth from the liquid are very difficult, which lead to glass state formation at a relative lower cooling rate less than 10^2 K/s. At such low critical cooling rate the bulk glass alloys could be obtained by mold casting or other conventional methods. In this paper, melts injection method is developed for preparation of bulk glass alloys. The bulk glass Zr-Ni-Al-Cu-Ti multicomponent alloy is investigated by using thermal analysis, its thermal properties is examined and used to evaluate the alloy critical cooling rate R_c. The difference of R_c calculated by different models is discussed.

2 EXPERIMENTAL

The $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ (mole fraction, %) alloy was prepared by melting pure metals with purity above 99.8% by electromagnetic induction in a water-cooled copper crucible in argon atmosphere and then casting into a metallic mold to form pre-alloy ingots with a diameter of 12 mm and a length of 80 mm. Then the ingots were remelted in the SiO_2 crucible under argon atmosphere and injected into the typi-

① Received Jul. 28, 1998; accepted Oct. 9, 1998

cal water-cooled copper mold to form bulk glass alloys with desired shape and size. All the bulk glass alloys were examined by X-ray diffractometry and optical microscopy to check the glass state. The as-prepared specimens were polished and etched using 4 mL HF + 40 mL HNO_3 + 25 g CrO_3 + 70 mL H_2O at ambient temperature for 30 s for optical microscopy. The specimens with a complete glass state were examined by differential thermal analysis (DTA) and differential scanning calorimeter (DSC) by continuous heating and cooling at 0.167 K/s and 0.333 K/s respectively to determine the transition temperature T_m, T_g and T_x.

3 EXPERIMENTAL RESULTS

Fig.1 shows the DTA curves of bulk glass state $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy obtained at two different continuous heating and cooling rates. From the DTA traces, the offset temperature for fusion, T_L, upon heating and onset temperature of solidification, T_{xc}, upon cooling can been determined. Fig.2 shows the bulk glass $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy with diameter of 6 mm to 8 mm and length of 30 mm to 35 mm, from which a good luster appearance can been seen. Fig.3 is the X-ray diffraction pattern taken from the cross section of the cylindrical samples, which shows that the sample with a diameter of 6 mm is complete glass state, but the sample with diameter of 8 mm contains obvious crystalline phase which is determined to be Zr_2Ni, Zr_3Al_2, and ZrNi. Thus, the largest diameter of bulk glass samples for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy is between 6 mm and 8 mm under this experimental condition. In Fig. 4 the wedge-shaped samples with tip angle of 10° reach the highest cooling rate on the tip, and with increase of the sample thickness the cooling rate decreases, so that, glass state has formed on tip area, with increase of sample thickness crystal phase appears (the bright area on tip is glass state and more dark contrast area is crystal state shown in Fig.4). $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ sample (indicated as alloy A in Fig.4) shows higher GFA than $Zr_{65}Ni_{10}Al_{7.5}Cu_{17.5}$ sample (indicated as alloy B in Fig.4). Fig.5 shows bulk glass $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy DSC curve at continuous heating rate of 0.333 K/s from which the glass transition temperature T_g and crystallization temperature T_x were determined as 630.61 K and 709.90 K respectively, and the supercooled liquid region ΔT_x is 79.29 K.

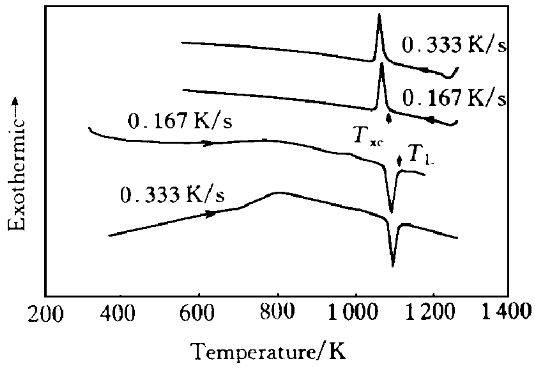

Fig.1 DTA curves of $Zr_{52.5}Ni_{14.6}$-$Al_{10}Cu_{17.9}Ti_5$ alloy

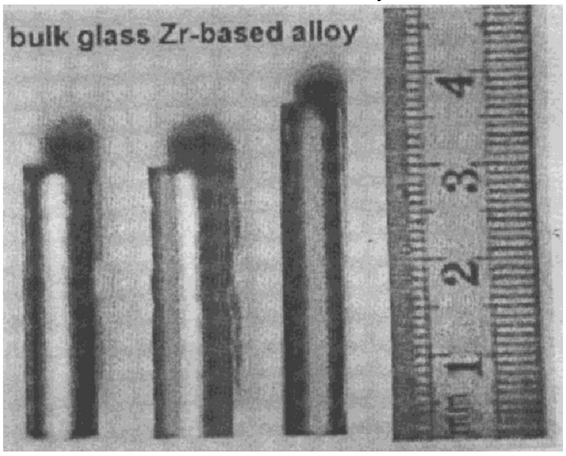

Fig.2 Outer surface appearance of cylindrical glass $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy prepared by melt injection

4 DISCUSSION

4.1 Calculation of critical cooling rate R_c

Two empirical model can be used to evaluate the critical cooling rate R_c for formation of glass state. Firstly, based on the crystallization kinetic model developed by Uhlmann[4], for a given value fraction x to crystallize, the time t (in seconds) is given by

$$t = \frac{9.32\eta}{kT}\left\{\frac{a_0^9 x}{f^3 N_v^0}\frac{\exp\left(\frac{1.024}{T_r^3 \Delta T_r^2}\right)}{\left[1 - \exp\left(\frac{-\Delta H_f^m \Delta T_r}{RT}\right)\right]^3}\right\} \quad (1)$$

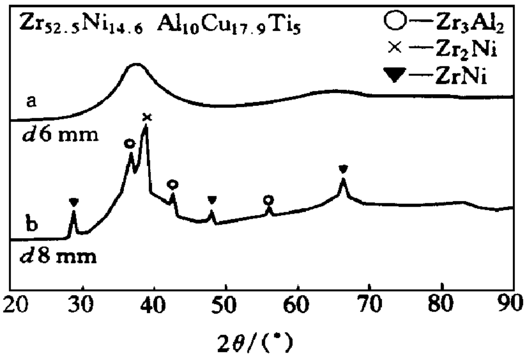

Fig.3 X-ray diffraction pattern taken from cross sectional surface of $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy with diameters of 6 mm and 8 mm

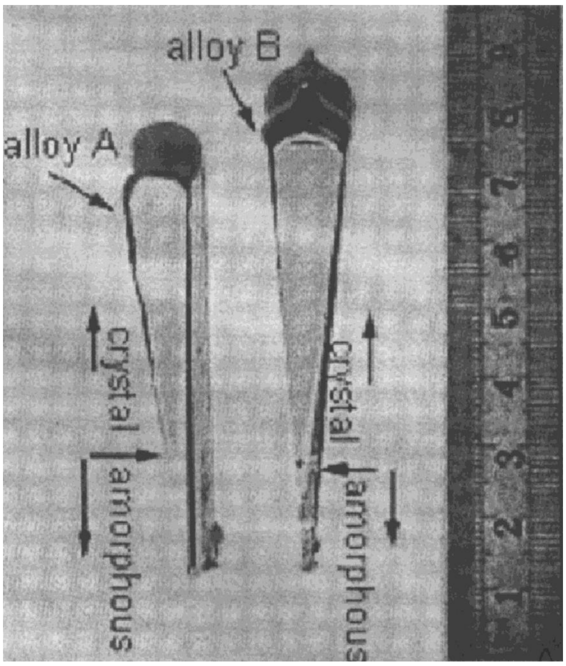

Fig.4 Longitudinal cross sectional structure of wedge-shaped samples of $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$(A) and $Zr_{65}Ni_{10}Al_{7.5}Cu_{17.5}$(B) alloys

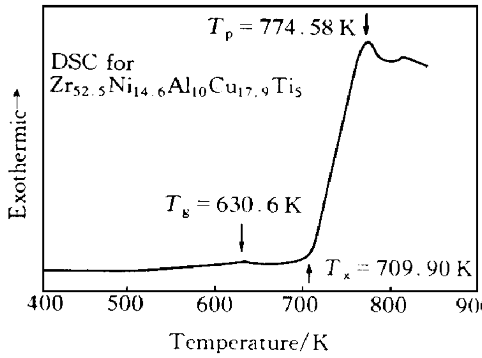

Fig.5 DSC curves of bulk amorphous $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy

where η is the liquid viscosity in poise for the alloy, k is Boltzmann constant, R is the ideal gas constant, a_0 is the average atomic diameter, N_v^0 is the numbers of atoms in an unit volume, f is the fraction of sites on the interface where atoms are preferentially added or removed, ΔH_f^m is the molar heat of fusion, T_r is reduced temperature, and ΔT_r is reduced supercooled temperature ($T_r = T/T_m$, $\Delta T_r = 1 - T_r$). Eqn.(1) relates temperature T to time t and gives the time-temperature-transformation (TTT) curve. Thus the critical cooling rate R_c for formation of glass state can be determined by the linear cooling curve required to avoid the nose of TTT curve and is given by

$$R_c \approx (T_m - T_n)/t_n \quad (2)$$

where t_n and T_n are the time and the temperature at the nose of the TTT curve respectively. The other factors in Eqn.(1) can be calculated or evaluated as follows: when $x = 10^{-6}$, it can be thought as complete glass state, thus let $x = 10^{-6}$ · a_0 obtained from an atomic percent weighted average for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy is 0.296 nm. For ideal liquid mixing, $N_v^0 = 1.414/a_0 = 54.53$ atom/nm^3. f is taken as 1. ΔH_f^m was determined by integrating over endothermic peak area in DTA curve, $\Delta H_f^m = 11$ kJ/mol[5]. η is dependent on temperature and meets Vogel-Fulcher's expression: $\eta = A\exp[B/(T - T_0)]$, For metallic glass alloys, the following expression is widely accepted[6,7]:

$$\eta = 10^{-3.3}\exp\left(\frac{3.34\,T_m}{T - T_g}\right) \quad (3)$$

Table 1 Computed η from Eqn.(3) and Eqn.(4)

Temperature	Eqn.(3)	Eqn.(4)
T_m	1.18	587.19
T_g	∞	9.94×10^{12}

Substituting the T_m and T_g of $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy into Eqn.(3), we obtained the values of η at T_m and T_g temperature listed in Table 1, which are 1.18 P and ∞ respectively. 1.18 P is too small for such strong glass forming alloy at its melting temperature, so that Eqn.(3) is not good suitable for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy. Hng *et al*[5] suggested η-T expression for $Zr_{66}Ni_9Al_9Cu_{16}$ alloy as follow:

$$\eta = 1.3\times10^{-5}\exp\left(\frac{14660}{T - 274.6}\right) \quad (4)$$

Using Eqn.(4) to evaluate the value of η at T_m and T_g temperature for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy, we obtain the η at T_m in order of 10^2 P, this η value is well consistent with strong glass forming ability for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy. Fig.6(a) and (b) are TTT curves from Eqn.(1) by using Eqn.(3) and Eqn.(4) respectively, from the TTT curves the critical cooling rates R_c are 5.8×10^3 K/s and 32.6 K/s. 10^3 K/s is too high to form bulk glass state alloy by using conventional method such as

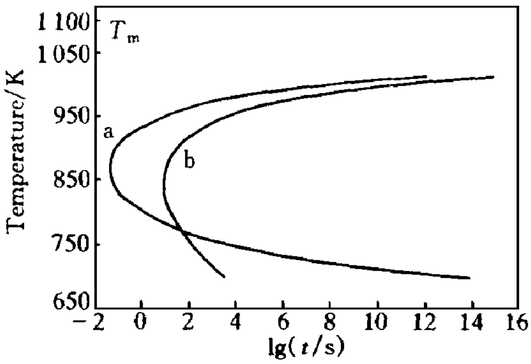

Fig.6 TTT curves for $Zr_{52.5}Ni_{14.6}$-$Al_{10}Cu_{17.9}Ti_5$ alloy a and b computed from Eqn.(1) by using Eqn.(3) and Eqn.(4) respectively

metallic mold casting. 32.6 K/s is more close to real R_c for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy.

The evaluation of R_c for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy above is very rough, because we take η-T expression for $Zr_{66}Ni_9Al_9Cu_{16}$ alloy as it for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy. What is more, Eqn.(1) model omits the effect of heterogeneous nucleation in the supercooled region.

Secondly, the critical cooling rate R_c for glass state formation can evaluate from thermal analysis data by empirical expression[8]:

$$\ln R_t = \ln R_c - \frac{b}{(T_L - T_{xc})^2} \quad (5)$$

where b is a constant which is relative to composition of the alloy and the thermal analysis processing. R_t is the heating or cooling rate for DTA. T_L and T_{xc} are determined from DTA curve and listed in Table 2. At $R_t = 0.167$ K/s, R_c obtained from Eqn.(5) is 13.4 K/s. This R_c value is in the same order as 32.6 K/s obtained by crystallization kinetic model, and more close to real R_c for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy. Such lower R_c makes it possible that bulk glass state alloy be formed by conventional model casting.

Table 2 DTA results of $Zr_{52.5}Ni_{14.6}$-$Al_{10}Cu_{17.9}Ti_5$ alloy

$R_t/(K\cdot s^{-1})$	T_L/K	T_{XC}/K
0.167	1106.33	1080.14
0.333	1108.71	1077.80

4.2 Real critical cooling rate R_c under this experimental condition

The metallic model casting provides the cooling rate of 400 K/s when the cylindrical sample's diameter is 1 mm, but quickly decrease to 120 K/s with increasing the sample diameter to 3 mm[9]. The critical cooling rate R_c for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy has been evaluated above to be smaller than 120 K/s, so that it is possible to produce bulk glass state $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy with diameter larger than 3 mm by metallic mold casting, but, it should not be too large because the cooling rate goes down sharply with increasing the sample's diameter.

In this paper, the melt injection method which can improve the cooling rate was used to produce bulk glass state alloy, the largest sample's diameter is between 6 mm and 8 mm for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy. Fig.4 shows the microstructure on longitudinal cross section of wedge-shaped samples on which glass phase is detected on tip side area, and crystal phase appears on the other side area. The length of glass phase area is about 20 mm for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy (alloy A in Fig.4), and the thickest glass area is about 3.5 mm. Based on the measurement of cooling rates in the center of wedge-shaped mold during casting, the points in the length of 10, 20 and 30 mm from tip point reach cooling rates of 171, 51 and 14 K/s respectively[10], so that the real critical cooling rate R_c for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy is 51 K/s which is slight larger than the values of 13.4 K/s and 32.6 K/s evaluated by empirical model and crystallization kinetic model respectively. The larger real R_c means that the GFA for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy in this experimental condition is smaller than the predictions by the empirical and kinetic models, and means more difficult to produce bulk glass state alloy than the predictions.

In Fig.4, we can find that the crystalline appears firstly in the center of the samples, not on their surface contacted with the inner surface of copper mold hole, which means the nucleates for crystallization come from the alloy itself, not from the mold cavity surface. So keeping purified alloy clean from oxides and other impurities could improve its GFA and form larger bulk glass state alloy. For comparison, $Zr_{65}Ni_{10}Al_{7.5}Cu_{17.5}$ alloy was used to produce wedge-shaped sample and shown lower GFA than $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy. The length of glass phase area is 18 mm, and the thickest area is about 3.1 mm shown in Fig.4(b). The addition of Ti on Zr-Ni-Al-Cu quaternary alloy improves its GFA, because Ti can form complexes in the liquid quinary alloy such as Ni_3Ti, Cu_2Ti and Ti_3Al etc, which can obstruct atoms long-term diffusion and stabilize the supercooled liquid alloy. Zr-Ni-Al-Cu quaternary alloy has been widely investigated and has a high GFA. Inoue has evaluated $Zr_{65}Ni_{10}Al_{7.5}Cu_{17.5}$ alloy with critical cooling rate of 1.5 K/s[11], such lower R_c is due to the high purity of the alloy and very low oxide content. In our experiment, the oxide content was not typically controlled, so that led to much higher critical cooling rates R_c for $Zr_{65}Ni_{10}Al_{7.5}Cu_{17.5}$ and $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloys.

5 CONCLUSIONS

(1) The pre-alloyed $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy is used to prepare bulk glass state samples with the largest diameter of 6 mm by melt injection method.

(2) By DTA and DSC analysis, the thermal transition temperatures for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy are examined as: melt temperature $T_m = 1106.33$ K, glass transition temperature $T_g = 630.61$ K, crystallization temperature $T_x = 709.90$ K, and supercooled liquid region $\Delta T_x = 79.29$ K.

(3) The critical cooling rate for forming glass state for $Zr_{52.5}Ni_{14.6}Al_{10}Cu_{17.9}Ti_5$ alloy is determined to be 13.4 K/s by empirical model and 32.6 K/s by crystallization kinetic model, such low R_c make it possible that bulk glass state alloy could be produced by conventional mold casting.

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(Edited by Zhu Zhongguo)