CRYSTALLIZATION KINETICS AND VISCOSITY OF $Cu_{47}Ti_{33}Zr_{11}Ni_8X_1$ (X=Si, Sn) METALLIC GLASSES

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Abstract. Crystallization kinetics of $Cu_{47}Ti_{34}Zr_{11}Ni_8$ and $Cu_{47}Ti_{33}Zr_{11}Ni_8X_1$ (X = Si, Sn) metallic glasses was investigated by the Johnson-Mehl-Avrami method. The Avrami exponent of 2.5~3.1 implies that the crystallization is governed by three-dimensional growth with an increasing nucleation rate. Viscosity measurements show that phase separation in amorphous phase and/or nanocrystallization occur near the glass transition region for the Si-containing metallic glass.

1. INTRODUCTION

The Cu-based metallic glasses have been reported to have high glass-forming ability [1,2] and high fracture strength over 2000 MPa [3,4] at room temperature. Recently, it has been reported in Cu-Ti-Zr-Ni alloys that small additions of Sn [5] or Si [6] can stabilize the undercooled liquid against crystallization. In addition, Si may facilitate the formation of nanocomposite-type microstructures [4], which significantly improve the mechanical properties. In this work, the effect of Si and Sn additions on the crystallization kinetics of the $Cu_{47}Ti_{34}Zr_{11}Ni_8$ alloy (named "base alloy" hereafter) is investigated by differential scanning calorimetry. Viscosity measurements upon heating are also carried out and correlated with the DSC results.

2. EXPERIMENTAL

Glassy ribbons of 25~30 μm thick were produced by melt-spinning with a wheel surface velocity of 30 m/s. All ribbons were confirmed to be fully amorphous [4]. Thermal analysis was performed using a Perkin-Elmer Diamond differential scanning calorimetry (DSC) at a heating rate of 20 K/min. Detailed DSC measurements description can be found in Ref. [7,8]. Viscosity measurements were carried out by parallel plate rheometry in argon atmosphere using a Perkin-Elmer TMA 7 under a force of 2.6 N at a heating rate of 20 K/min.

3. RESULTS AND DISCUSSION

Fig. 1 shows the isothermal DSC traces of the glassy ribbons at four different temperatures (T_x–20, T_x–25, T_x–30, and T_x–35K, where T_x is the crystallization temperature). All the isothermal DSC traces exhibit an exothermic peak after passing a certain incubation period (τ). The crystallization kinetics of the amorphous ribbons is analyzed using the well-known Johnson-Mehl-Avrami (JMA) theory [9]: $\ln\{-\ln[1-x_c(t,T)]\} = n\ln k + n\ln(t-\tau)$, where $x_c(t,T)$ is the volume fraction of crystallized phases after annealing time t, k a temperature-dependent kinetic parameter and n the Avrami exponent, which describes the crystallization mechanism. The JMA

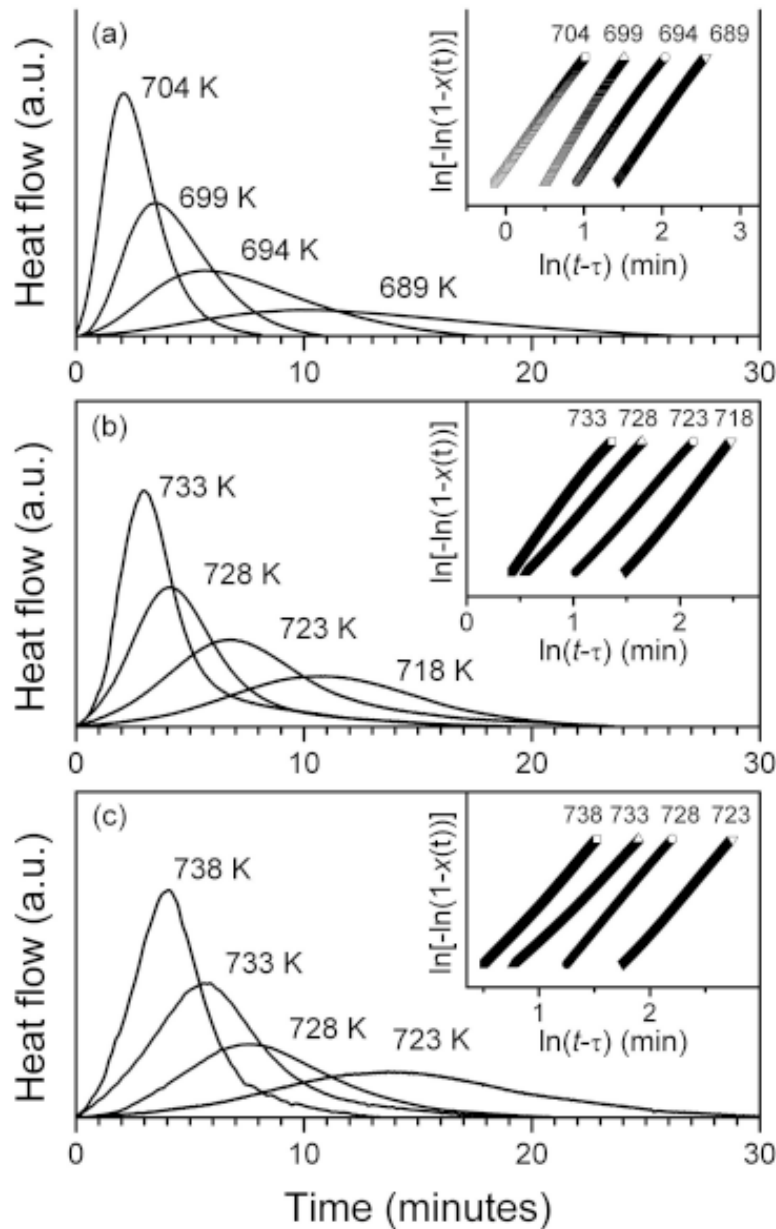Corresponding author: L.C. Zhang, e-mail: lczhangimr@gmail.com and laichang@uow.edu.au

Fig. 1. Isothermal DSC traces and the corresponding JMA plots (insets) for (a) base alloy: $Cu_{47}Ti_{34}Zr_{11}Ni_8$, (b) Si- and (c) Sn- containing glassy ribbons.

plots of $\ln\{-\ln[1-x_c(t,T)]\}$ vs. $\ln(t-\tau)$ for all the glassy ribbons in the range of $0.05 \leq x_c(t,T) \leq 0.60$ are shown in the insets (Fig. 1) for correctly reflecting the crystallization kinetics [10]. The data in this range are almost on a straight line with a correlation coefficient better than 0.999. The Avrami exponent n is calculated from the slopes of the fitted lines to be 2.5~2.8, 2.6~3.1 and 2.6~3.1 for the base alloy, the Si- and Sn-containing metallic glasses, respectively. These n values indicate that

the crystallization is governed by a nucleation rate that increases with time [10].

Fig. 2 displays the viscosity changes upon heating in the supercooled liquid region for all glassy ribbons. The base alloy and the Sn-bearing metallic glasses exhibit a typical continuous decrease of the viscosity in the supercooled liquid range (below T_x) [11]. In contrast, in the case of the Si-containing metallic glass, one can observe a distinct shoulder or a peak split. This kind of abnormal vis-
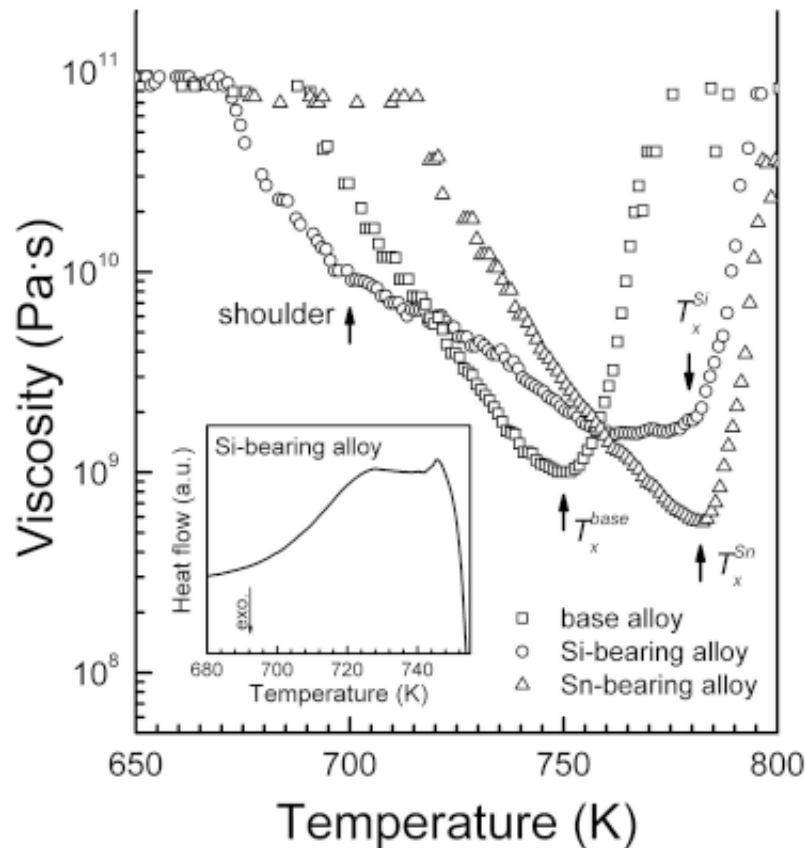
Fig. 2. Viscosity changes near the supercooled liquid region for the base alloy Cu$_{47}$Ti$_{34}$Zr$_{11}$Ni$_{8}$ and Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{8}$X$_{1}$ (X = Si, Sn) glassy ribbons. Inset: enlarged view of the DSC curve for the Si-bearing glass near the supercooled liquid region (heating rate: 20 K/min).

cosity behavior combined with the presence of a small exothermic heat flow recorded on the DSC scan (inset in Fig. 2) also in the supercooled liquid region suggest the existence of some local chemical inhomogeneities in the amorphous phase, which could easily lead to the formation of nanocrystals near the glass transition region upon heating [12]. Nanocrystallization during annealing below the glass transition temperature was recently reported in the Si-bearing amorphous powder based on the same composition as in the present study (Cu$_{47}$Ti$_{33}$Zr$_{11}$Ni$_{8}$Si$_{1}$) [13]. Similar behavior with a shoulder in the viscosity curves and a slight exothermic heat flow in the supercooled liquid region was observed in Cu-Zr-Y-Al metallic glasses and that was assumed to be due to the occurrence of phase separation in amorphous phase [12]. Phase separation in amorphous alloys has a significant influence on the crystallization process by destabi-

lizing metallic glasses and ultimately resulting in formation of fine nanocrystals upon annealing in the glass transition range [14]. Hence, the atypical viscosity vs. temperature curve recorded for the Si-bearing metallic glasses might be attributed to either phase separation and/or nanocrystallization near the glass transition region.

4. SUMMARY

The Avrami exponent of 2.5~3.1 implies that the crystallization is governed by three-dimensional growth with an increasing nucleation rate. The Si addition leads to an abnormal viscosity changes near the glass transition region and a small exothermic heat flow in supercooled liquid region, suggesting that phase separation and/or nanocrystallization near the glass transition region occurs.

ACKNOWLEDGEMENTS

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