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ARTICLE

Phase Separation and Microstructure Evolution of $Zr_{48}Cu_{36}Ag_8Al_8$ Bulk Metallic Glass in the Supercooled Liquid Region

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Abstract: The effect of annealing temperature on the microstructure evolution of $Zr_{48}Cu_{36}Ag_8Al_8$ bulk metallic glass was investigated by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). Results show that the as-cast $Zr_{48}Cu_{36}Ag_8Al_8$ alloy by rapid solidification exhibits a typical characteristic of an amorphous structure. After annealed at 703 K for 20 min, a homogeneous amorphous matrix is separated into two different glassy phases, namely, phase separation occurs. Because phase separation structure will compete with the amorphous matrix during isothermal annealing, this structure is easily decomposed and transformed into the crystalline phases $AlZr_2$ and $AlAg_3$ with annealing temperature increasing. The microstructure of $Zr_{48}Cu_{36}Ag_8Al_8$ bulk metallic glass undergoes the local structure transformation, phase separation and nano-crystallization transformation during heat treatment in the supercooled liquid region, which implies that the microstructure of $Zr_{48}Cu_{36}Ag_8Al_8$ bulk metallic glass is sensitive to the annealing temperature. In addition, the formation of phase separation will accelerate the formation of nano-crystals.

Key words: bulk metallic glass; phase separation; crystallization; isothermal annealing

The Cu-Zr based bulk metallic glasses (BMGs) have been regarded as a high potential in industrial applications due to their excellent glass forming ability, high-compressive fracture strength, excellent corrosion resistance, relatively low elements cost and environmentally friendly raw materials [1,2]. However, like other metallic glasses, they show a poor ductility at room temperature. Recently, it has been found that phase separation was formed during the process of solidification or during the reheating [3-5] of metallic glasses when two elements in the multicomponent alloys have a positive heat of mixing [6, 7]. Therefore, great attention has been given to the design of composite structure by phase separation to overcome the limit of the plasticity [8, 9], upon considering that phase separation can play an important role in controlling crystallization, glass-forming ability and microstructure in homogeneity [10, 11].

Several works showed that phase separation could appear in Cu-based BMGs containing Ag since Cu and Ag have a positive enthalpy of mixing. Oh et al. [10] reported that phase separation was detected in the as-cast $Zr_{43}Cu_{43}Al_7Ag_7$ by a three-dimensional atom probe. Zhang et al. [12] found that phase separation appeared in $Zr_{40}Cu_{40}Al_{10}Ag_{10}$ BMG which could be directly confirmed by TEM, while there was a homogenous and non-contrast pattern for the ribbon. Later, phase separation was also found in the recently discovered $Zr_{48}Cu_{36}Al_8Ag_8$ BMG in the glass transition region prior to crystallization [13].

Phase separation in metallic glasses is strongly dependent on the annealing process and sample preparation. Thus, the investigation on the relationship between the annealing temperature and the microstructure of metallic glass is meaningful not only in regard to fundamental research but also in practical applications. In the present work, the alloy chosen for this study was a recently reported $Zr_{48}Cu_{36}Al_8Ag_8$ bulk

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metallic glass (a maximum diameter of 25 mm)[2] to investigate the effect of phase separation on crystallization behaviors.

1 Experiment

The $Zr_{48}Cu_{36}Ag_8Al_8$ (at%) alloy was prepared by arc melting high purity metals in a Ti-gettered argon atmosphere, and cast into a copper mold to produce BMG rods with 5 mm diameter. All samples were isothermally annealed at a given temperature within the supercooled liquid region in vacuum. The as-cast and the annealed samples were examined by DX-2700 X-ray diffractometer with a Cu Kα radiation and transmission electron microscopy performed on Tecnai G2F30. Thermal analysis was conducted using differential scanning calorimetry (DSC) under N_2 atmosphere with the flowing rate of 100 mL/min. The sample mass was about 20 mg. The samples were heated at a heating rate of 20 K/min. The second run was used as a baseline, which was then subtracted from the first run to obtain the irreversible part of the heat flow signal.

2 Results and Discussion

2.1 Effect of annealing temperature on microstructure

Fig.1 shows the XRD patterns of both as-cast and annealed samples of $Zr_{48}Cu_{36}Ag_8Al_8$ alloy. It can be observed that the as-cast sample exhibits a single halo pattern, which is a typical characteristic of the amorphous structure. Another diffuse halo peak comes from the sample annealed at 703 K for 20 min, indicating that decomposition of amorphous matrix occurs before crystallization during isothermal annealing. Intermetallic compounds, $AlZr_2$ and $AlAg_3$, appear distinctly in amorphous matrix when the heating temperature is increased to 723 K. These results indicate the amorphous matrix during the reheating within the supercooled liquid region may decompose into two metallic glasses. However, there is no another diffuse halo peak appearing in 3 mm diameter rod, which is attributed to more ordered clusters formed under the condition of the lower cooling rate [5].

Fig.2 shows the DSC curves of the as-cast and annealed samples measured at the scanning rate of 20 K/min. For the as-cast sample, it can be clearly seen that there exists one exothermic peak at 775 K. The glass transition temperature (T_g) and crystallization onset temperature (T_x) measured from the DSC curve are 680 and 750 K, respectively. These data agree well with those data reported in the literature for this alloy [2]. After annealed at 703 K, continuous heating DSC curves show that two separated peaks appear at the main peak. It is shown that another phase appears in the annealed specimen. With the annealing temperature increasing, the exothermic peak at 750 K gradually disappears, and the area of second exothermic peaks at 775 K increases. It implies that phase separation decomposes into stable crystalline phase.

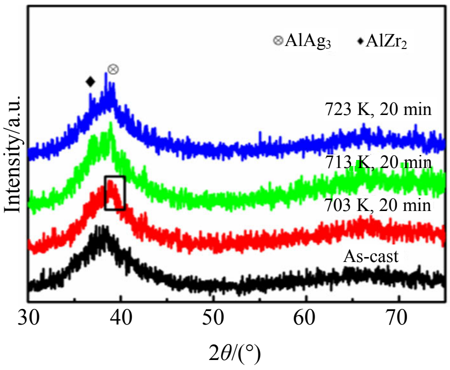

Fig.1 XRD patterns of the as-cast and annealed $Zr_{48}Cu_{36}Ag_8Al_8$ samples (the marked peak at 703 K is the "another diffuse halo peak")

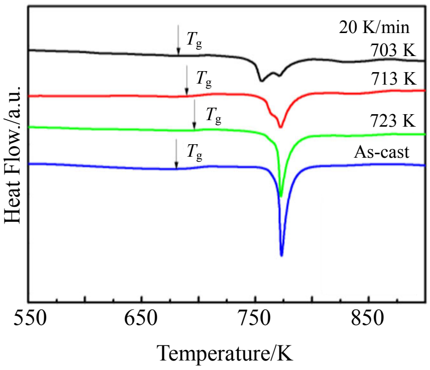

Fig.2 DSC curves of the as-cast and annealed $Zr_{48}Cu_{36}Ag_8Al_8$ bulk metallic alloy

2.2 Phase separation

Fig.3a presents the TEM images and the selected area electron diffraction (SAED) pattern of the as-cast $Zr_{48}Cu_{36}Al_8Ag_8$ bulk metallic glass. The SAED pattern does not show any diffraction spots on the diffuse ring in Fig.3a. No ordered structure is observed in Fig.3b, which proves that the as-cast sample is completely amorphous. Fig.4a shows the TEM images and SAED pattern of the $Zr_{48}Cu_{36}Ag_8Al_8$ bulk metallic glass annealed at 703 K for 20 min. The brighter and darker contrast in the TEM image is different from the as-cast microstructure in Fig.3.

The SAED pattern (inset Fig.4a) shows two halo rings, which demonstrates that a homogeneous glassy phase is separated into two different glassy phases during the isothermal annealing. Fig.4b shows the HETEM image of "A" region in Fig.4a and corresponding FFT (fast Fourier transformation) images. The FFT images of "b1" and "b3" regions show two halo rings and some diffraction spots appear in "b1" region. This phenomenon implies that the phase separation structure is easily transformed into the crystalline. However, it is noteworthy that HRTEM images of "b2" and "b3" regions both display disordered structure, but one halo ring occurs in "b2" region. The formation of phase separation structure competes with amorphous matrix during heat treatment, leading to the local composition difference and microstructure change.

When an initially homogeneous liquid melt is cooled across