

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 K α radiation and transmission electron microscopy performed on Tecnai G2F30. Thermal analysis was conducted using differential scanning calorimetry (DSC) under N₂ 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, AlZr₂ and AlAg₃, 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

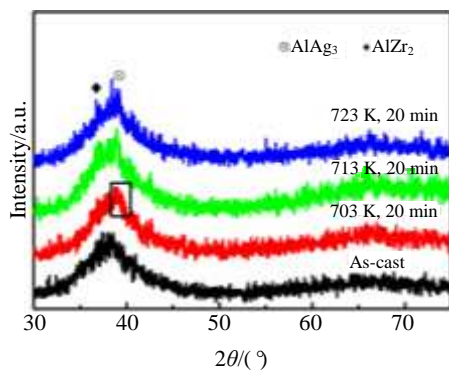


Fig.1 XRD patterns of the as-cast and annealed $Zr_{48}Cu_{36}Ag_8Al_8$ samples (the marked peak at 703 K is the “another diffuse halo peak”)

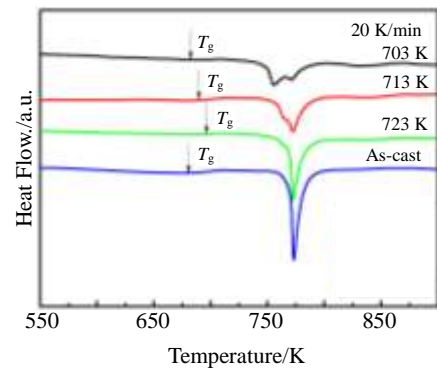


Fig.2 DSC curves of the as-cast and annealed $Zr_{48}Cu_{36}Ag_8Al_8$ bulk metallic alloy

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.

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

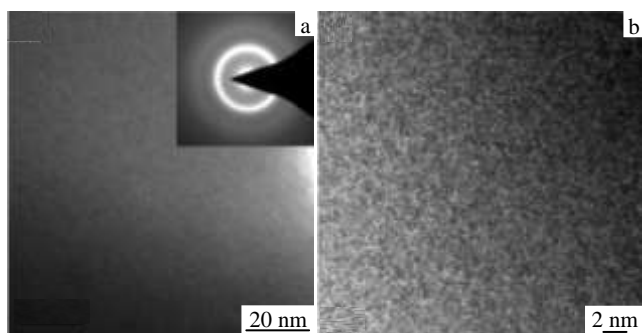


Fig.3 SAED pattern (a) and TEM image (b) of as-cast $Zr_{48}Cu_{36}Al_8Ag_8$ bulk metallic glass

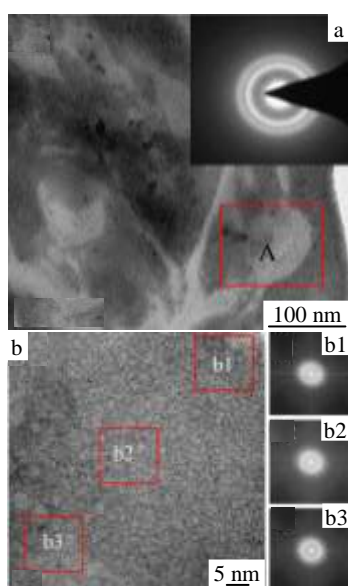


Fig.4 Microstructure of BMG sample annealed at 703 K for 20 min: (a) TEM image, (b) HRTEM image, the inset shows their corresponding FFT images of “b1”, “b2” and “b3” regions

its miscibility curve into the two-phase region and the two constituent elements in the alloy have a zero or positive heat of mixing, it is possible to form phase separation for BMG^[10,14]. In

the current work, phase separation occurs via post annealing, while it is not detected in the as-cast $Zr_{48}Cu_{36}Al_8Ag_8$ bulk metallic glass. Similar phenomenon was reported by Dmitri^[13]. But morphology of the phase separation structure is different from our result, which is attributed to the size and the microstructure of the phase separation regions depending on annealing temperature and cooling rate^[15]. In addition, the formation of phase separation depends on the ratio between Cu and Ag atoms^[16]. Consequently, phase separation can be more distinctly detected by TEM compared with the $Zr_{43}Cu_{43}Al_7Ag_7$ BMG, whereas it can be more difficultly detected compared with the $Zr_{40}Cu_{40}Al_{10}Ag_{10}$ BMG.

2.3 Crystallization behavior

To verify the effect of phase separation on crystallization, the crystallization behaviors in $Zr_{48}Cu_{36}Al_8Ag_8$ bulk metallic glass were further analyzed. The bright field image in Fig.5

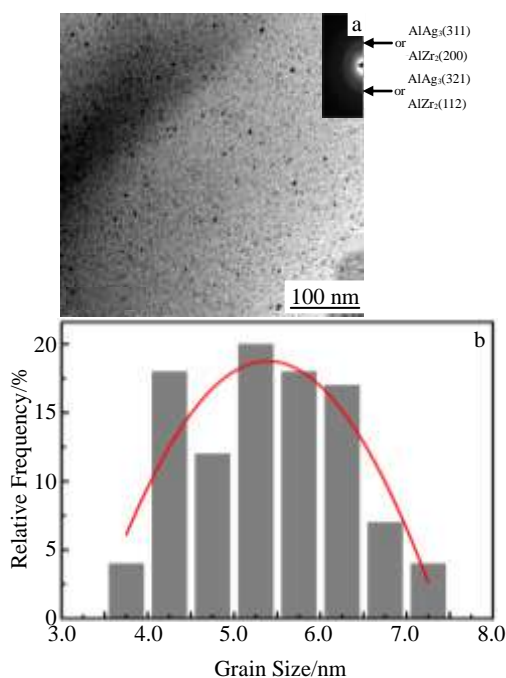


Fig.5 TEM image-SAED pattern (a) and its grain size distribution (b) for BMG sample annealed at 713 K for 20 min

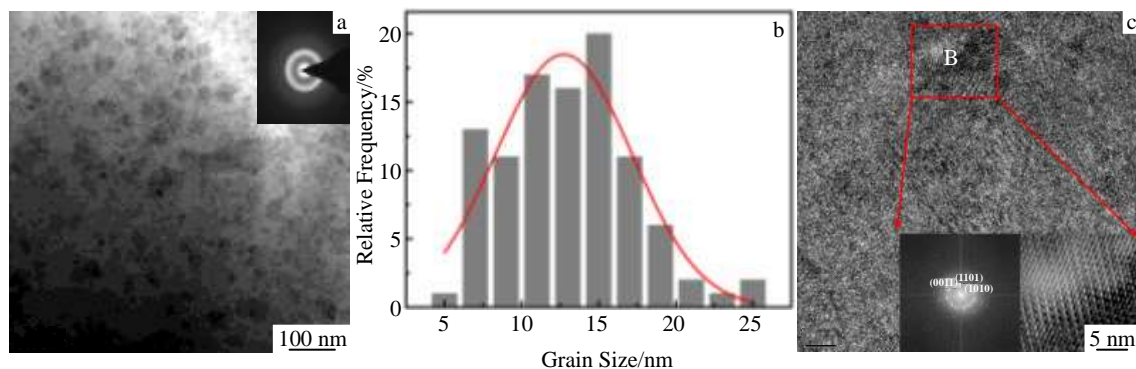


Fig.6 Microstructure of BMG sample annealed at 723 K for 20 min: (a) TEM image, (b) grain size distribution, and (c) HRTEM image, with the inset showing their corresponding FFT images of “B” region

shows ultrafine crystalline grain size is about 4 nm to 7 nm when the specimen is annealed at 713 K (see grain size distribution of Fig.5b). The SAED consists of several ring patterns but some bright spots appear in the diffuse ring, indicating a number of nano-crystalline are embedded in residual amorphous phase with random orientation. The crystalline particles are identified as AlZr_2 and AlAg_3 phase. When the temperature increases to 723 K, nano-crystals increase (see Fig.6a), and grain size distribution (Fig.6b) shows that average grain size increases to 7~16 nm. The outside weak diffuse ring disappears in SAED compared to that in Fig.4, which agree with the result of DSC. The HRTEM image in Fig.6c shows distinct lattice structure. The corresponding FFT image of a big nano-particle is confirmed as hexagonal AlZr_2 and the indexing of the diffraction patterns is shown in inset of Fig.6c. These results confirmed that phase separation structure easily transforms into the crystalline phase with the annealing temperature increasing. Moreover, the crystallization pathway can be changed by the modulation of the annealing temperature.

3 Conclusions

1) The microstructure of $\text{Zr}_{48}\text{Cu}_{36}\text{Ag}_8\text{Al}_8$ bulk metallic glass is strongly affected by annealing treatment. The phase separation occurs after isothermal annealing within the phase supercooled liquid region.

2) The formation of phase separation structure competes and coexists with amorphous matrix, leading to the local composition difference and microstructure change, which is attributed to the sensitization of this alloy to the temperature.

3) With annealing temperature increasing, this unstable structure is gradually transformed into stable crystalline AlZr_2 and AlAg_3 phases.

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过冷液态 $\text{Zr}_{48}\text{Cu}_{36}\text{Ag}_8\text{Al}_8$ 块体非晶合金的相分离及组织演变

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摘要: 通过 X 射线衍射(XRD)、差示扫描量热法(DSC)和透射电子显微镜(TEM)研究了退火温度对 $\text{Zr}_{48}\text{Cu}_{36}\text{Ag}_8\text{Al}_8$ 金属玻璃微观结构演化的影响。结果表明, 快速凝固获得的样品为典型的非晶态结构。当样品在 703 K 保温 20 min 时, 均一的非晶基体相分离成 2 种非晶合金, 即, 发生相分离。由于相分离结构与非晶基体在等温退火过程是竞争的关系, 这个结构很容易向晶化态进行转变, 形成 AlZr_2 和 AlAg_3 相。 $\text{Zr}_{48}\text{Cu}_{36}\text{Ag}_8\text{Al}_8$ 金属玻璃的微观结构在过冷液相区等温退火过程中经历了局部结构转变, 相分离以及纳米晶转变, 这个过程意味着 $\text{Zr}_{48}\text{Cu}_{36}\text{Ag}_8\text{Al}_8$ 金属玻璃的微观结构对退火温度十分敏感。此外, 相分离的形成可以加速纳米晶的形成。

关键词: 块体非晶合金; 相分离; 晶化; 等温热处理

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