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Formation and phase evolution of liquid phase-separated metallic glasses with double glass transition, crystallization and melting

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ABSTRACT

$Zr_{57}Co_{27}Al_{16}$ and $La_{57}Co_{27}Al_{16}$ alloys with excellent glass-forming ability (GFA) were adopted to synthesize new phase-separated bulk metallic glasses (BMGs) upon rapid solidification. $(Zr_xLa_{1-x})_{57}Co_{27}Al_{16}$ ($x = 0.2$, 0.4, 0.6, and 0.8) melts separate into ZrCo-rich and La-rich liquids upon cooling due to the existence of a miscibility gap in Zr-La liquids. The intrinsic and extrinsic mechanisms for the formation of phase-separated alloys under different casting conditions were analyzed in detail. The GFA of the studied alloys changes in the following order: $Zr_{57}Co_{27}Al_{16} > La_{57}Co_{27}Al_{16} > Zr_{11.4}La_{45.6}Co_{27}Al_{16} > Zr_{22.8}La_{34.2}Co_{27}Al_{16} > Zr_{34.2}La_{22.8}Co_{27}Al_{16} > Zr_{45.6}La_{11.4}Co_{27}Al_{16}$. The quaternary Zr-La-Co-Al phase-separated metallic glasses (MGs) are shown to experience double glass transition, crystallization and melting events, which could be regarded as possible model materials to study the glassy transition and structural relaxation behavior of BMGs.

1. Introduction

In the past decades, one of composite materials with core-shell-type, dual-layer-type, or sandwich-type structures synthesized based on metallic alloys with liquid phase-separation has been considered as potential materials for advanced bearings in automotive applications [1–3]. However, relatively poor mechanical properties of these phase-separated alloys, such as hardness, strength, corrosion resistance, and wear resistance, cannot satisfy increasing requirements for industrial application. It is therefore necessary to search for alternative phase-separated alloys or to modify their microstructures. In recent years, it has been shown that materials obtained upon quenching of metallic melts into an amorphous state, so-called metallic glasses (MGs), show many desirable properties such as high mechanical strength, extended elastic limit and high hardness and excellent wear resistance and corrosion resistance [4–7]. By carefully controlling alloy compositions, phase-separated bulk metallic glasses (BMGs) with good mechanical properties were successfully fabricated [8–18]. If a liquid phase-separated system contains two liquids with individual good glass-forming ability (GFA) or with individual self-assembling eutectic compositions, two-phase BMGs could be obtained [8–25]. It is also expected that development of micro- and nano-phase separated BMGs can be one of the methods for obtaining ductile BMGs since nano- or micro-scale structural heterogeneities in a glassy matrix can effectively impede rapid propagation of shear bands and induce their multiplication, and ultimately prohibit the abrupt rupture of BMGs [4–7,26–28].

Furthermore, recently much attentions have been paid to the structural relaxation in BMGs, especially for β-relaxation [29–32]. β-relaxations in La-based BMGs, being more pronounced than in Zr-based BMGs, are associated with systems where all the atomic pairs have large similar negative values of enthalpy of mixing, while positive values of enthalpy of mixing suppress β-relaxations [32]. Therefore, if a series of BMGs can contain both of La-based and Zr-based amorphous phases and their component proportion ratios are adjustable, it could be feasible to study the change tendency of the β-relaxations with changing structural inhomogeneity. Furthermore, the α-relaxation has been proposed to be directly related

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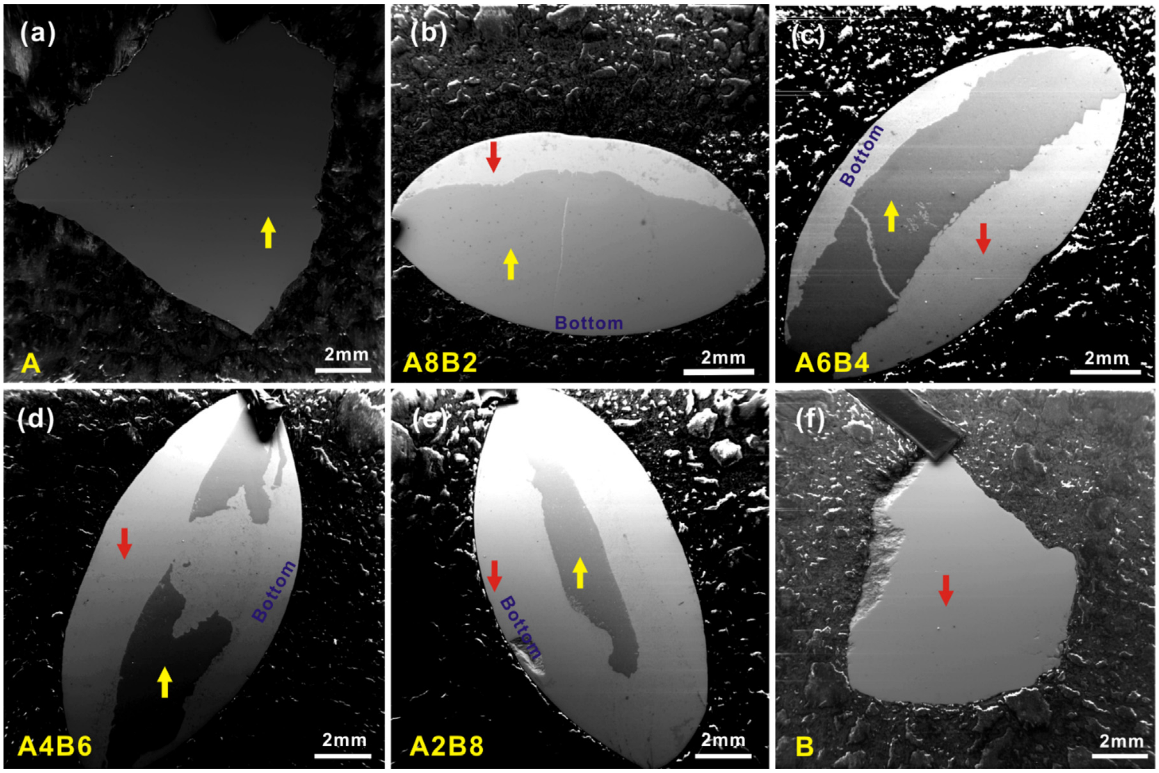

Fig. 1. OM images of the as-cast A_xB_{10-x} (x = 0, 2, 4, 6, 8, and 10) master ingots; Insets: enlarged OM pictures of phase-separated crystals.

to viscous flow and the glass transition and be regarded as the central feature of glassy physics [33–36], which also exhibits a compositional dependence. Then the glass transition and α-relaxation of La-rich amorphous phase should be affected by a second amorphous phase.

Based on such purpose above, we successfully fabricate Zr-La-based MGs based on the concept of liquid–liquid phase separation. In present work, phase-separated alloys based on $Zr_{57}Co_{27}Al_{16}$ and $La_{57}Co_{27}Al_{16}$ were studied. The base compositions were chosen due to their excellent GFA [37–44]. Besides, Zr and La process a positive heat of mixing (13 kJ/mol) [45], which was assumed to result in a liquid–liquid miscibility gap [1]. The liquid phase-separated $(Zr_xLa_{1-x})_{57}Co_{27}Al_{16}$ (x = 0.2, 0.4, 0.6, and 0.8) metastable alloys were prepared upon rapid solidification. In order to understand the phase-separation during solidification, the composition dependence of the microstructure, and glass-forming ability Zr-La-Co-Al alloys were in detail investigated under different casting conditions.

2. Experimental

$Zr_{57}Co_{27}Al_{16}$ and $La_{57}Co_{27}Al_{16}$ master alloys (further denoted as alloys A and B, respectively) were prepared by arc-melting appropriate amounts of the constituting elements (at least purity 99.9%) under a Ti-gettered argon atmosphere. Master alloys were remelted at least three times for good homogenization. $(Zr_xLa_{1-x})_{57}Co_{27}Al_{16}$ (x = 0.2, 0.4, 0.6, and 0.8) master ingots with a weight of approximately 5 g were fabricated by arc melting A and B master alloys with the ratio of 2:8, 4:6, 6:4, and 8:2, being indexed as A_2B_8, A_4B_6, A_6B_4, and A_8B_2, respectively. The prepared alloys were cast into rods with a diameter of 2 mm using an injection casting machine (custom-made in Japan, Beihang University) under an argon atmosphere. The corresponding ribbons were obtained by a melt-spinning device with a thermodetector (custom-made in China, Shanghai University). Casting temperatures (T_{cast}) for the ribbons with the thickness of 35 ± 5 μm and the width of 1.8 ± 0.8 mm were roughly estimated to be 1323 K–1473 K. Microstructure and phase formation of the as-cast samples were characterized using an optical microscope (OM, Olympus), an X-ray diffraction in reflection geometry (XRD, X'Pert Pro diffractometer, Cu radiation), and a field emission scanning electron microscope (SEM, Zeiss Supra 55VP) equipped with an energy dispersive spectrometer (EDS). The glass transition, crystallization and melting events were detected by a differential scanning calorimetry (DSC, METTLER TOLEDO STA 449C) at a heating rate of 20 K/min.

3. Results

3.1. Phase formation and microstructures of the as-cast Zr-La-Co-Al master ingots

Fig. 1 displays OM images of the as-cast $(Zr_xLa_{1-x})_{57}Co_{27}Al_{16}$ (x = 0, 0.2, 0.4, 0.6, 0.8, and 1 at.%) cobblestone-shaped ingots. The ingots A ($Zr_{57}Co_{27}Al_{16}$) and B ($La_{57}Co_{27}Al_{16}$) are homogenous at a macroscopic scale (Figs. 1(a) and (f)). However, severe phase segregation with a core-shell type, dual-layer type or sandwich type structure is observed in the A_xB_{10-x} (x = 2, 4, 6, and 8) master ingots (Fig. 1(b–e)). It was found some tiny gray particles precipitate in the white regions while the gray regions contain some fine white precipitates based on SEM measurements (for clarity only selected results are shown in Fig. 2(a)). EDS micrographs (Fig. 2(b–e)) reveal that the gray regions are rich in Zr and Co, while the white ones are dominated by La. Besides, the white particles (marked by yellow dotted circles) precipitating in ZrCo-rich regions are La-rich, while the dominating elements in the gray particles (marked by blue circles) in La-rich regions are Zr and Co, implying the occurrence of liquid phase-separation during solidification. For La- or ZrCo-rich regions, some dendrites and intermetallic compounds seem to precipitate under relatively slow cooling of ∼4 K/s after arc-melting [46]. As shown by XRD patterns (Fig. S1 in the Supplementary data),