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Phase separation and microstructure evolution of rapidly quenched Gd–Hf–Co–Al alloys

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ABSTRACT

Phase separated metallic glasses were prepared in the Gd–Hf–Co–Al system by rapid quenching of the melt. Due to the strong positive enthalpy of mixing between the main constituent elements Gd and Hf (ΔH_{Gd-Hf} = +11 kJ/mol) a heterogeneous microstructure is formed consisting of two amorphous phases, which are Gd-enriched and Hf-enriched, respectively. The size of the phase separated regions varies from 0.1 μm to 5 μm, depending on alloy composition and cooling rate. Different types of microstructure, such as an interconnected structure or a droplet structure were obtained as a function of cooling rate. The microstructure of the phase separated metallic glasses is determined not only by their composition, the critical temperature, and the shape of the miscibility gap, but also by the viscosity and diffusivity of the melt.

1. Introduction

Since the first finding of liquid state phase separation in the La–Zr–Al–Ni–Cu system [1], the strategy to develop in situ glass–glass composites containing two compositionally different amorphous phases, were successfully developed in different alloy systems. Examples for such systems are Ti–Y–Co–Al [2], Ni–Nb–Y [3], Cu–Zr–Al–Y [4] and Gd–Ti–Co–Al [5]. These systems consist of element combinations with high glass-forming ability (GFA) on one hand, and a strong positive enthalpy of mixing between certain constituent elements (i.e. ΔH_{Nb-Y} = +30 kJ/mol, ΔH_{Ti-Y} = +15 kJ/mol, ΔH_{Zr-Y} = +35 kJ/mol and ΔH_{Gd-Ti} = +15 kJ/mol) [2–5] on the other hand. The requirement of adding an element with a positive enthalpy of mixing to any of the components of the alloy usually reduces the glass-forming ability and, therefore, rapid quenching of the melt is necessary in order to prepare a phase separated metallic glass. As well as in nano-structured and other conventional crystalline materials, the microstructure evolution affects the properties of phase separated metallic glassy alloys [6,7]. The characteristic types of microstructure of phase separated metallic glasses can be classified into a droplet-like or an interconnected structure, which develop by nucleation and growth or by spinodal decomposition, respectively [8]. An improvement of mechanical properties was found for some phase separated metallic glasses, which was attributed to the heterogeneities hindering the movement of shear bands [9,10]. Moreover, the phase separated structure has received attention as a useful way to fabricate porous metallic glassy material by selective dissolution of one of the constituent phases [11,12].

In this paper, we report on the composition and cooling rate dependence of the microstructure evolution in rapidly quenched $Gd_{55-x}Hf_xCo_{25}Al_{20}$ (x = 10, 20, 27.5, 35, 45 and 55 at.%) metallic glasses. The alloy compositions were chosen because they fulfil the prepositions to prepare phase separated metallic glasses. The ternary $Gd_{55}Co_{25}Al_{20}$ and $Hf_{55}Co_{25}Al_{20}$ alloys exhibit a rather high glass-forming ability and monolithic bulk glassy specimens of ~2 mm in diameter have been successfully produced [13–15]. Due to the large positive enthalpy of mixing between Gd and Hf (ΔH_{Gd-Hf} = +11 kJ/mol), decomposition of Gd–Hf–Co–Al melts into Gd-rich and Hf-rich phases during quenching is expected. We will show that besides the chemical composition also the cooling rate determines the morphology of the microstructure with respect to formation of a droplet-type or an interconnected-type structure.

2. Experimental

Pre-alloyed ingots of $Gd_{55-x}Hf_xCo_{25}Al_{20}$ (x = 0, 10, 20, 27.5, 35, 45, 55) were prepared by arc-melting in an argon atmosphere starting from elements with a purity of 99.9% or higher. To achieve homogeneity, the ingots were remelted 3 times and cast into a water-cooled Cu mold of cylindrical rod-shape with 5 mm diameter by suction casting. From these rod-shape pre-alloys, ribbon samples with 3–4 mm in width and 25–30 μm in thickness were fabricated by single-roller melt spinning

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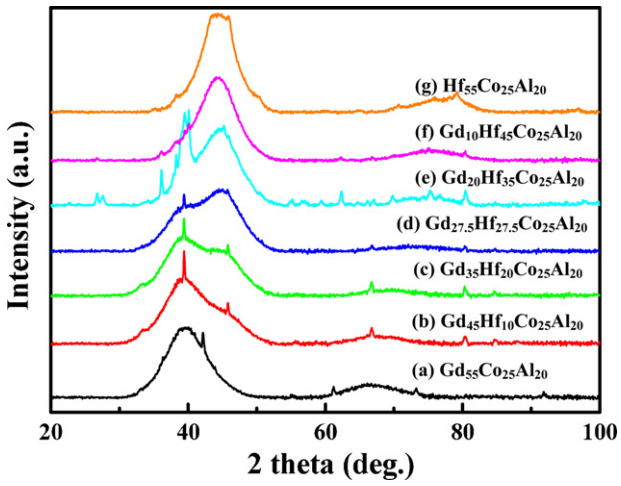

Fig. 1. XRD patterns of rapidly quenched $Gd_{55-x}Hf_xCo_{25}Al_{20}$ alloys (x = 0, 10, 20, 27.5, 35, 45 and 55).

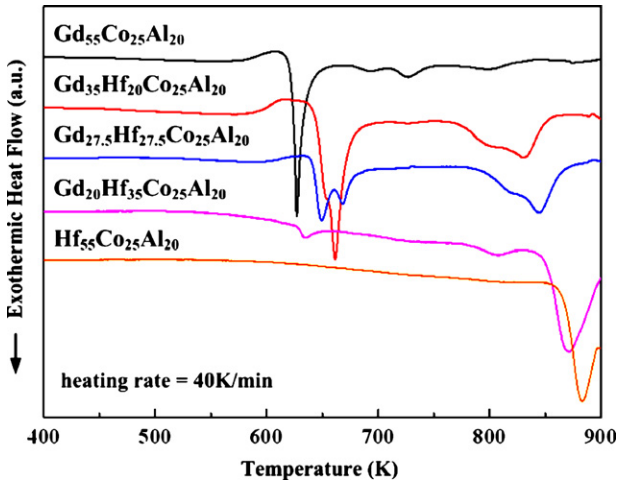

Fig. 2. DSC traces obtained for rapidly quenched $Gd_{55}Co_{25}Al_{20}$, $Hf_{55}Co_{25}Al_{20}$, $Gd_{35}Hf_{20}Co_25Al_{20}$, $Gd_{27.5}Hf_{27.5}Co_{25}Al_{20}$ and $Gd_{20}Hf_{35}Co_{25}Al_{20}$ ribbons with a heating rate 40 K/min. The exothermic peaks in the low temperature range correspond to crystallization of the Gd-rich amorphous phase, and the peaks at the high temperature range to that of the Hf-rich amorphous phase, respectively.

with quartz crucible in an argon atmosphere. The wheel speed and the casting temperature measured with a pyrometer were 30 m/s and 1600–1700 K, respectively. The structures of the ribbon samples were analysed by X-ray diffraction (XRD) with Co Kα radiation (Panalytical X'Pert Pro). To investigate the thermal stability, differential scanning calorimeter (Perkin Elmer DSC7) with a heating rate of 40 K/min was performed. A scanning electron microscope (SEM) (Gemini–Zeiss) equipped with an energy-dispersive spectrometer (EDX) was applied for microstructure observation and quantitative analysis of chemical compositions.

3. Results and discussion

The XRD patterns of as-quenched $Gd_{55-x}Hf_xCo_{25}Al_{20}$ (x = 0, 10, 20, 27.5, 35, 45 and 55) ribbons are shown in Fig. 1. The broad diffuse patterns indicate that these as-quenched ribbons are mainly amorphous phase (Fig. 1(a)–(g)). Sharp diffraction peaks indicate that also some crystalline phases such as Gd_2Co_2Al are present for all alloys [16]. The unusual diffraction pattern for alloy with x = 55 at.% Hf in Fig. 1(g) is indicating superposition of amorphous matrix and cF96 Hf_2Co phase [15]. The appearance of two diffuse maxima for x = 10–45 at.% in Fig. 1(b)–(f) gives evidence for phase separation in these glasses. The first maximum around diffraction angles ($2\theta \approx 39.8^\circ$) corresponds to a Gd-rich phase and that at higher diffraction angles ($2\theta \approx 44.2^\circ$) to an Hf-rich phase, respectively. With increasing Hf-content, the intensity of the second diffuse maximum becomes larger and that of the first maximum decreases, which indicates the change in volume fraction of the respective phases with composition. From the area of the maxima determined by Gaussian fitting the volume fractions of the two amorphous phases were estimated. The obtained values are given in Table 1. Within the error limits a linear dependence is found. The two-phase glassy structure is also confirmed by DSC investigations. Fig. 2 shows the

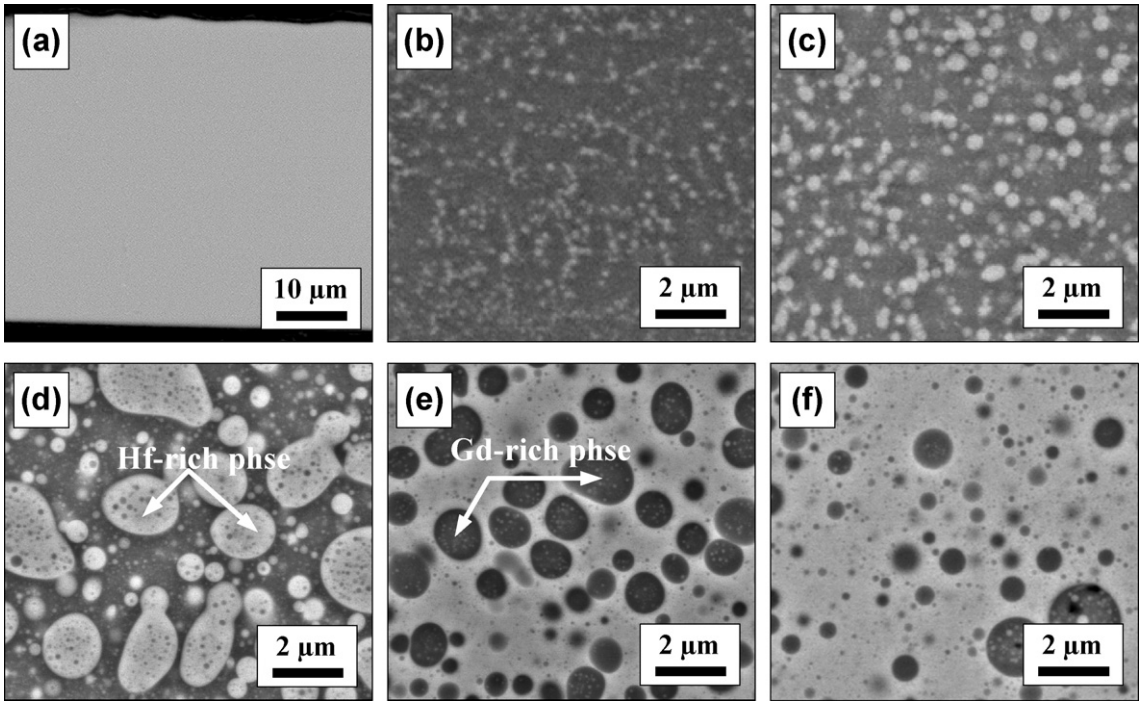

Fig. 3. Backscattered electron micrographs obtained from the cross-section of rapidly quenched (a) $Gd_{55}Co_{25}Al_{20}$, (b) $Gd_{45}Hf_{10}Co_{25}Al_{20}$, (c) $Gd_{35}Hf_{20}Co_{25}Al_{20}$, (d) $Gd_{27.5}Hf_{27.5}Co_{25}Al_{20}$, (e) $Gd_{20}Hf_{35}Co_{25}Al_{20}$ and (f) $Gd_{10}Hf_{45}Co_{25}Al_{20}$ ribbons.