Journal of Non-Crystalline Solids 445–446 (2016) 53–60

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Effect of annealing on the devitrification behavior and mechanical properties of rapidly quenched Ce-based glassy alloys

Dharmendra Singh [a], Devinder Singh [b], R.K. Mandal [c], O.N. Srivastava [a], R.S. Tiwari [a,*]

[a] Department of Physics, Nano–Science Unit, Banaras Hindu University, Varanasi 221005, India
[b] Department of Physics, Panjab University, Chandigarh 160014, India
[c] Department of Metallurgical Engineering, Indian Institute of Technology (Banaras Hindu University), Varanasi 221005, India

ARTICLE INFO

Article history:
Received 7 January 2016
Received in revised form 26 April 2016
Accepted 1 May 2016
Available online 20 May 2016

Keywords:
Metallic glasses
Devitrification
Nanocrystalline
Mechanical properties
Ce-based alloys

ABSTRACT

This study deals with the effect of controlled crystallization of melt spun $Ce_{75}Al_{25-x}Ga_x$ (x = 0, 2, 4 and 6 at.%) and $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ (x = 0, 1, 2 and 4 at.%) metallic glasses on the formation of nano-composites. It has been found that the substitution of Ga significantly affects the devitrification behavior of these alloys. The $Ce_{75}Al_{25-x}Ga_x$ alloys with x = 0 shows the formation of hexagonal phase ($AlCe_3$ type) while the alloys with x ≥ 2 give rise to the formation of tetragonal phase (Al_2CeGa_2 type). Contrary to this, for the $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ alloys, hexagonal phase of AlCeCu type for x = 0 transforms to hexagonal phase of Al_2Cu_3Ce type for x ≥ 1. The indentation behavior of nano-composites permitted us to understand the nature of microhardness, yield strength and strain hardening constant. They are compared for the above two alloy systems. The load dependent hardness values of annealed ribbons of $Ce_{75}Al_{19}Ga_6$ and $Ce_{60}Cu_{25}Al_{13}Ga_2$ alloys have been found to be ~2.80 GPa and ~2.96 GPa, respectively. The absence of cracks around the indentation area up to 200 g of load for $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ alloys suggests better capability to resist crack propagation in comparison to $Ce_{75}Al_{25-x}Ga_x$ alloys. Latter display cracks at 200 g load. The formation of shear bands around the periphery of the indenter has been observed. The number of visible shear bands in a given area for the $Ce_{75}Al_{25-x}Ga_x$ alloys is higher in comparison to those of $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ alloys. The values of yield strength and Meyer exponent of these alloys are also compared.

1. Introduction

Metallic glasses (MGs) of rare earth (RE) metals have attracted attention of scientific communities, because of their technologically interesting properties [1–5]. Binary RE-Al alloy systems have been investigated over a wide range of composition with respect to formation of MGs [3–7]. These glassy alloys have high glass forming ability, magnetic properties, better tensile strength, high fracture strength and good bending ductility [1,2,7–10]. The sluggish atomic rearrangements near glass transition temperature have made them ideal systems for the study of nucleation and growth mechanism [2,11]. RE-MGs seem to qualify as a candidate material for applications in optical storage media [12], micro-device manufacture [13] or as matrices in composites suitable for various functional properties [11,14]. MGs form shear bands at room temperature due to localized deformation induced by high pressure [15–17]. Indentation studies are conducted to measure the mechanical properties and elastic/plastic deformation responses of MGs and their composites [18–22]. MGs show higher strength and hardness when suitable mixtures of micro or nano scale crystalline, quasicrystalline or amorphous phases are present [23–30]. Out of the large number of RE-MGs known, Ce-based MGs have drawn recent attention due to its exceptionally low glass transition temperature (T_g) and unique properties such as heavy fermion behavior, thermoplastic near room temperature and excellent magneto-caloric effect [6,11,31,32]. Although the glass forming ability and thermal properties of Ce-based MGs have been investigated in detail, less attention has been paid to the study of devitrification behavior and mechanical properties of their partial or completely crystallized counterparts. For application of these materials, a detailed knowledge of the crystallization and kinetic behavior is thus very important. Recently, we have reported the effect of Ga substitution on the glass forming ability, thermal stability and indentation characteristics of $Ce_{75}Al_{25-x}Ga_x$ (0 ≤ x ≤ 6) and $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ (0 ≤ x ≤ 4) MGs [3,7]. Some of the recent studies have shown that Ga is normally substituted in place of Al [16–19]. Both Al and Ga are lying in the same group of the periodic table and having same valency (+3). Thus the substitution of Al by Ga does not change the valence electron concentration i.e. e/a ratio of $Ce_{75}Al_{25-x}Ga_x$ and $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ alloys for any compositions. The atomic size of Ga (1.41 Å) and Al (1.43 Å) are also comparable. We have observed phase separation of $Ce_{75}Al_{25}$ alloy after Ga substitution. The structural and microstructural characterization studies clearly demonstrated the coexistence of two amorphous phases [3]. In the case of

* Corresponding author at: Department of Physics, Banaras Hindu University, Varanasi 221005, India.
E-mail address: rstiwariphy@yahoo.com (R.S. Tiwari).

http://dx.doi.org/10.1016/j.jnoncrysol.2016.05.003
0022-3093/

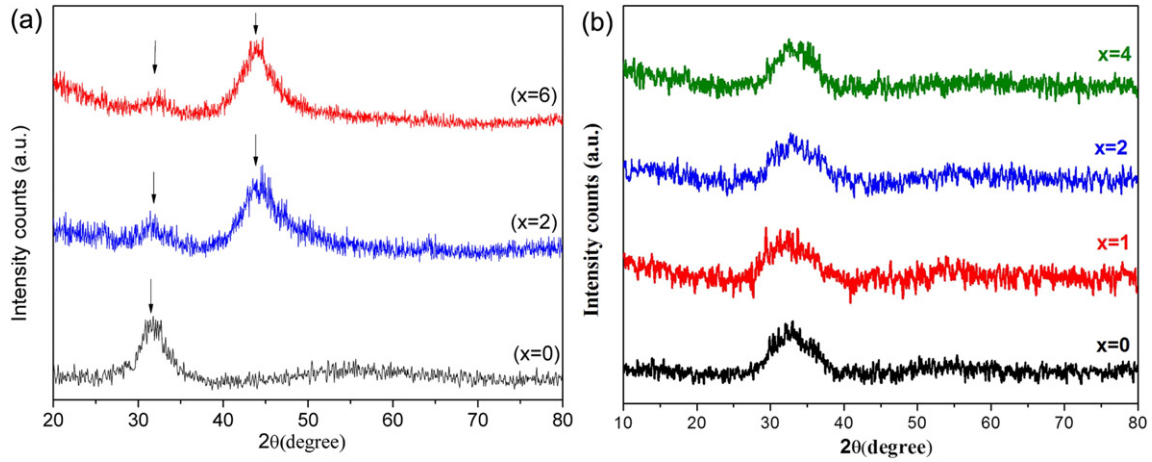

Fig. 1. XRD patterns of as-synthesized ribbons of (a) $Ce_{75}Al_{25-x}Ga_x$ (x = 0, 2 and 6) and (b) $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ (x = 0, 1, 2, 4) alloys. (Reprinted from references [3,7] with kind permission from Elsevier, Copyright 2014 and 2015, Elsevier).

Table 1
Values of T_g, T_x and ΔT_x for $Ce_{75}Al_{25-x}Ga_x$ and $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ alloys. The estimated error in the DSC measurement for the alloys is ±0.1 K.

$Ce_{75}Al_{25-x}Ga_x$				$Ce_{60}Cu_{25}Al_{15-x}Ga_x$			
x (at.%)	T_g(K)	T_x(K)	ΔT_x(K)	x (at.%)	T_g(K)	T_x(K)	ΔT_x(K)
0	458	494	36	0	386	468	82
2	388	477	69	1	385	473	88
4	370	477	107	2	384	471	87
6	345	486	141	4	383	469	86

T_g: glass transition temperature; T_x: onset crystallization temperature.
ΔT_x: supercooled liquid region.

$Ce_{60}Cu_{25}Al_{15}$ alloy, no such changes have been observed after Ga substitution [7]. This may be due to the presence of Cu in $Ce_{60}Cu_{25}Al_{15}$ alloy which have multi-valent states. The devitrification behavior and mechanical properties of resulting composites of $Ce_{75}Al_{25-x}Ga_x$ and $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ MGs have not been studied so far. This investigation deals with these aspects.

2. Experimental details

High purity Ce (99.9%), Cu (99.9%), Al (99.98%) and Ga (99.99%) were used for the preparation of alloy ingots of compositions $Ce_{75}Al_{25-x}Ga_x$ (x = 0, 2, 4 and 6 at.%) and $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ (x = 0, 1, 2 and 4 at.%) by melting the ingredients in the desired ratios in a silica crucible using a RF induction furnace. The ingots were re-melted several times to improve homogeneity. To convert the ingots into ribbons, they were placed in a silica nozzle tube with a circular orifice of ~1 mm diameter. These alloys were then melt spun onto a Cu-wheel rotating at a speed of 40 m/s. The ribbons were prepared by flowing Ar gas continuously. This was done to prevent oxidation of the ribbons after ejection from the nozzle. The length and thickness of the ribbons were ~1 to 3 cm and ~40 μm respectively. The ribbons of these alloys were then packed in a Ta foil which was sealed in a silica ampoule under vacuum for annealing experiment.

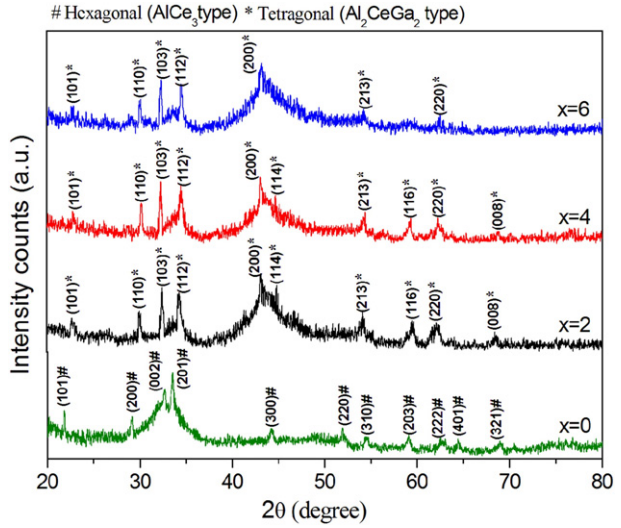

Fig. 2. XRD patterns of $Ce_{75}Al_{25-x}Ga_x$ (x = 0, 2, 4 and 6) ribbons annealed for 8 h.

The structural characterization was done by employing X-ray diffractometer (X'Pert Pro PANalytical diffractometer) with CuK_α radiation. The experimental conditions and parameters (scan speed 0.05°/s, etc.) were kept same for all diffraction studies performed on different samples. The thermal stability of the samples has been investigated by differential scanning calorimetry (DSC) at 20 K/min heating rate with the help of SHIMADZU DSC-60 under a continuous flow of high purity nitrogen. The estimated error in the DSC measurement for the alloys is ±0.1 K. Isothermal annealing of the ribbons was carried out in a vacuum (10^{-6} Torr) using a furnace with temperature control of ±5 °C. The ribbons were thinned using an electrolyte (70% methanol and 30% nitric acid) at 253 K. The thinned samples were then observed under transmission electron microscopy (TEM) using FEI: Technai $20G^2$ electron microscope. An energy dispersive X-ray analysis (EDX) was employed for the compositional analysis. Microhardness measurements of all the samples were done with the help of SHIMADZU HMV-2T microhardness tester at different loads. The ribbons were mounted on a cylindrical steel base with the help of glue. The tests were conducted up to a load till cracks around the indentation impression were observed. The standard diamond pyramid shape Vickers indenter with tip edge ~0.5 μm provided with the instrument was used.

3. Results and discussion

3.1. Structural and microstructural features

The $Ce_{75}Al_{25-x}Ga_x$ (x = 0–6 at.%) and $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ (x = 0–4 at.%) melt spun alloys were observed to be fully amorphous by means of X-ray diffraction (XRD) as well as by TEM studies [3,7]. For the sake of completeness, we have shown the XRD patterns of melt spun alloys (Fig. 1). The substitution of Ga results in the formation of two types of amorphous phases in $Ce_{75}Al_{25-x}Ga_x$ (x = 2–6) alloys (Fig. 1(a)). This may be due to phase separation in the alloys. This observation is in contrast to the $Ce_{60}Cu_{25}Al_{15-x}Ga_x$ alloys, where no such phase separation