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The role of Fe and Cu additions on the structural, thermal and magnetic properties of amorphous Al-Ce-Fe-Cu alloys

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ABSTRACT

Iron and copper are immiscible elements, but can be combined in the presence of a third element such as aluminium or cerium. We varied the additions of immiscible Fe and Cu (ratio y) in the stoichiometric $Al_{20.5}Ce_{41.5}(Fe_yCu_{1-y})_{38}$ alloys in order to trace their impact on the structure, microstructure, thermal properties and magnetism. By powder X-ray diffraction (PXRD), we found that Fe-rich alloys ($0.87 \leq y \leq 1$) do not completely hinder crystallisation and yield nanocrystalline precipitates. Cu-rich alloys completely vitrify for $0 \leq y \leq 0.74$ and exhibit a characteristic broad hump in PXRD patterns. DSC shows that Cu-rich alloys exhibit a noticeably lower crystallisation temperature T_x of about 510 K, liquidus temperature T_l at approximately 900 K and a more pronounced drop Δ of the heat flux at the glass transition temperature T_g. These criteria indicate that Cu-rich alloys are better glass formers. Transmission electron microscopy (TEM) shows that the specimens with $y = 0$ and $y = 0.34$ are composed of an amorphous matrix with minor impurities of CeO_2 nanocrystals, which can only be observed via transmission electron microscopy. However, these nanocrystals do not interfere with the formation of the glassy phase and are therefore inert. Magnetic measurements show that Fe-rich alloys possess higher magnetisation at maximum field ($M_{\max H}$), peaking at 3.3 and 3 emu/g for $y = 1$ and $y = 0.87$, respectively. From ferromagnetism in the latter two alloys, the behaviour turns to paramagnetism for $0 \leq y \leq 0.74$. Cryogenic measurements on SQUID show that the sample with $y = 0$ displays two different temperature regions at 2–50 K and 100–300 K. The first one exhibits nearly pure paramagnetic behaviour with $\Theta = -0.7$, while the second one shows a highly negative Weiss constant of $\Theta = -80.6$.

1. Introduction

Formation of metallic glasses (MG) has been under scientific investigation for more than five decades since the pioneering work of Klement, Willens and Duwez [1]. A series of Al-Ce-based MG around the eutectic composition 25:75 in at.%, is interesting due to its unusual physical properties [2–4], and very low glass transition temperature T_g compared to other metallic systems [5]. An intriguing phenomenon is amorphous polymorphism, which manifests with the increase of pressure. Transition from low density amorphous state to high density amorphous state occurs at 2 GPa [6], and can be detected by the shift to higher values of the momentum vector q associated with the maximum diffracted intensity as a result of densification [3]. This effect is ascribed to the delocalization of 4f electrons from 3^+ valence, but only to the extent whereby the energy landscape still remains within the stability range of a glassy structure [3]. A different situation is observed at substantially higher pressures of approximately 25 GPa. Al and Ce containing glassy alloys hereby undergo a devitrification, which results in crystallisation to face-centred cubic $Al_{25}Ce_{75}$ [7]. Pressure-induced delocalization of the 4f electron governs a collapse in the volume of Ce atom [8], which shrinks and thereby its size approaches that of Al. Subsequently, the two metals are brought within the Hume-Rothery limits for substitutional alloy formation [9] and crystalline nucleation occurs. Another peculiarity of Ce based glasses is their thermoplastic behaviour at very low temperatures. Some compositions exhibit a glass transition temperature as low as 80 °C [5,10], with a stable supercooled liquid region (ΔT_x) and with it, the ability of thermoplastic forming. The temperature of glass transition below 100 °C is the lowest among amorphous alloys, and it could turn out as an advantage for fundamental studies or carry significance for future applicative research [11].

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In this respect, it has been demonstrated that Ce-based amorphous alloys can be consolidated into centimetre-sized discs via pulsed electric current sintering in ΔT_x region, while still maintaining its glassy structure [12].

The term "immiscibility" can be used to define an effect, where thermodynamic driving forces oppose the intermixing of elements, so that little alloying is possible [13]. Immiscibility of some constitutive elements and its effect on glass formation in a multicomponent glassy alloy is an approach, which is not frequently considered in the literature. Heats of mixing (ΔH) for immiscible systems are positive, which manifests their disability of forming an intermetallic phase. A requirement for glass formation according to the set of empirical rules [14], however, states that ΔH should be negative in order to form strong glasses. Nevertheless, when some immiscible elements are introduced into a multicomponent alloy, these postulations tend to change. Microalloying additions of immiscible Nb to Cu-based glasses [15] provide an evidence that element pairs with positive ΔH in the correct concentration ratio can enhance the formation of glassy structures [15]. This effect is ascribed to a change in the local atomic environment, and is very sensitive to the composition. Fe and Cu exhibit a complete phase separation at room temperature [16], and also in liquid state at 1873 K, where ΔH remains positive with a value of about 10 kJ/mol [17]. Formation of an amorphous structure in binary Fe-Cu was reported via solid state transformation with ion beam mixing [18]. A series of alloys produced via sputter deposition, resulted in an amorphous structure in the ternary alloy of Fe-Cu-Ag as well [19]. Similarly, the combination of immiscible Fe and Cu has an important implication in the formation of aperiodic Al-Cu-Fe quasicrystals [20]. However, a systematic study of multicomponent metallic glasses depicting variable amounts of immiscible Fe and Cu is to the best of our knowledge not present in the literature.

In this work, we fix the concentration ratio $x = Ce/(Ce + Al)$ to 0.67, according to the findings of our previous study [12]. This choice is illustrated in Fig. 1 where we present simultaneously the position q_M of the maximum intensity in reciprocal space of the main diffraction peak, the full width at half maximum (FWHM $= q_R - q_L$, where the indices L and R denote the left and right sides at half maximum intensity of the main peak in q-space) and a measure of the asymmetry of this peak, which is given by $q_B - q_M$, where $q_B = (q_L + q_R) / 2$ is the position in q-space of the barycentre of the peak at half maximum. This measure is equal to 0 for a symmetric peak whereas it yields negative values if the peak is broadened on the side of low q values. It is observed that the position of the peak shifts smoothly towards lower values of q when the concentration of Ce increases from 31 at.% to 62 at.%, which traces the replacement of the smaller aluminium atoms by larger Ce ones. Meanwhile, the peak is broader and significantly less symmetric at low Ce contents (< 40 at.%) whereas it keeps almost unchanged in symmetry from 41.5 at.% and above. This is basically the reason why we have selected this composition or equivalently a ratio $x = 0.67$ for the present study. Henceforth, we start from a composition with good glass forming ability, and extend the investigation to the variation of the $y = Fe/(Fe + Cu)$ ratio. The system $Al_{20.5}Ce_{41.5}(Fe_yCu_{1-y})_{38}$ (at.%) is studied with respect to structure, microstructure, thermal properties and magnetism.

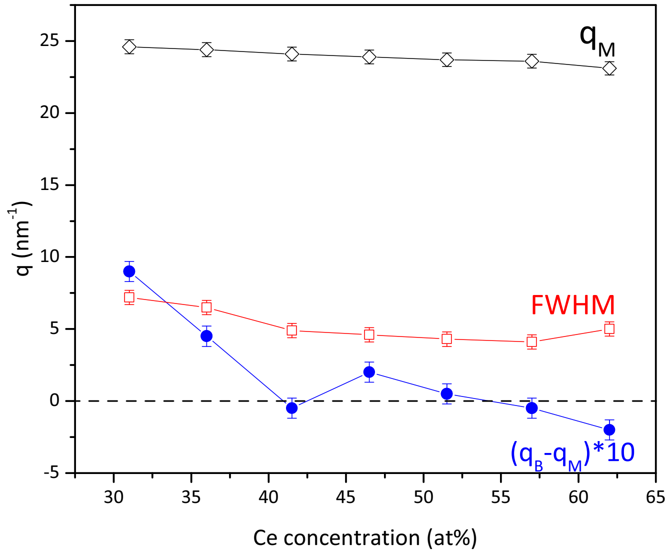

Fig. 1. Variation with Ce concentration of the position in q-space of the maximum diffracted intensity (open lozenges), full width at half-maximum of the most intense diffraction peak (open squares) and symmetry index (solid dots) as defined in text (and multiplied by 10 to make the figure easier to read). Error bars denote the uncertainty of data determination and lines connecting the data points are guide for the eyes only.

2. Experimental

Specimens were prepared by weighing appropriate amounts of 99.9% Al chunks (Sigma-Aldrich), 99.9% Ce ingot (Aldrich), 99.98% Fe ingot (PI-KEM) and $\geq$ 99.9% Cu shots (Sigma-Aldrich). Alloying was performed in an arc-melting furnace (Edmund-Buehler), with multiple turning and melting cycles in order to ensure the alloying of all the pieces. Weight loss after the arc melting never exceeded 1 wt%. Further, the ingots were processed in a single roller melt spinner (Edmund-Buehler). The alloy was inductively melted and ejected onto the surface of a copper cooling wheel, rotating at circumferential speed of 25 m/s. This procedure was accomplished in 700 mbar of 99.999% Ar. For the powder X-ray diffraction (PXRD) characterization, comminuted melt-spun ribbons were used to prepare powder batches by means of crushing in a mortar and manual crushing. PXRD measurements were performed with an Empyrean diffractometer (PANalytical) in Bragg-Brentano geometry, using Cu radiation (wavelength $\lambda = 0.15406$ nm). Zero background Si holders were used to load the powdered samples. Analysis of the patterns included background subtraction in order to correct the data for the high background in the case of Cu-rich alloys. Differential scanning calorimetry (DSC) measurements were performed on a Jupiter 449 simultaneous thermal analysis (STA) instrument (Netzsch) using a TG/DSC-cp sample holder and highly conductive Pt crucibles with Al_2O_3 liners. Calibration of temperature and sensitivity was performed with In, Bi, Zn, Al and Au standards. The accuracy in temperature readings is better than 3 K. Specimens for DSC analysis were prepared from crushed ribbons with a mass of $\approx$ 22 mg stacked into the crucibles to ensure good contact with the bottom of the crucible. Thermal measurements were performed in an inert atmosphere of 99.999% Ar (flow rate 50 ml/min) and in the temperature range from 310 K to 1273 K, with a heating rate of 20 K/min. Magnetic measurements were carried out on a vibrating sample magnetometer (VSM) (MicroSense), up to the maximum applied field of 18 kOe using a step of 100 Oe. We used point-by-point mode, where the field is increased and steadied in one-step, followed by the measurement of magnetisation. Specimens were prepared of crushed ribbons ($\approx$ 100 μg), which were fixed in the plastic holder. For magnetic measurements at cryogenic temperatures, we used a superconducting quantum interference device (SQUID), model MPMS3 (Quantum Design), operated in DC mode. The programme to measure the thermal dependence of magnetisation featured a temperature interval from 2 to 300 K at the applied field of 5 kOe. M(H) loops were measured at a maximum field of 70 kOe and at temperatures of 2 K, 10 K and 100 K. Phase composition and crystallinity of the samples were investigated by transmission electron microscopy (TEM), using a 200 kV JEM-2100 instrument (Jeol), equipped with an energy-dispersive X-ray (EDX) spectrometer (Jeol). Special care was taken to avoid excessive heat evolution during sample preparation: a single ribbon was fixed onto the Mo-support disc with Ag-adhesive paint. Sample prepared this way was further thinned until being transparent for electrons using precision ion polishing system (PIPS, model 691, Gatan). Initially $\approx$ 30 μm thick