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Glass transition and crystallization of Al–Ni–La based metallic glasses studied by temperature modulated DSC

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ABSTRACT

Crystallization behavior and glass transition phenomenon of $Al_{89}Ni_6La_5$, $Al_{87}Ni_6La_7$ and $Al_{87}Ni_5La_7M_1$ (M = Ag, Cu) metallic glasses have been studied by temperature modulated differential scanning calorimetry (TMDSC). A clear glass transition of these glasses, which could not be detected in conventional differential scanning calorimetry (DSC), even at higher heating rates, was observed through TMDSC measurements. All these glasses undergo two-stages of crystallization on heating. The precipitation and growth of fcc-Al in $Al_{89}Ni_6La_5$ and bcc-metastable phase in other alloys are responsible for the first stage of crystallization. The glass transition phenomenon in these alloys except $Al_{87}Ni_6La_7$, could not be detected in DSC because the signals are overlapped with the relatively large heat release from the primary crystallization. This was confirmed from the TMDSC measurements. These measurements were necessary for the development of new nanocrystalline/amorphous composite materials.

1. Introduction

Al-based metallic glasses have received a significant attention since their discovery, by Inoue et al. [1] and He et al. [2], due to their inherent scientific and technological importance. An enormous amount of work has been accounted towards the understanding of the structure [3,4], crystallization kinetics [5,6] and glass forming abilities [4,7] of these materials. The amorphous alloys form over a wide concentration range in the Al corner depending on the content of transition metals and rare-earth elements. The transformation of amorphous alloys to the fully crystalline state follows composition-dependent pathways [8]. Although these glasses are believed to be amorphous in their as-quenched condition by conventional X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies, the existence of cluster/concentration fluctuations from the small angle neutron scattering [8] and three-dimensional atom tomography experiments was reported [9]. Many of the reported alloys that transform to α-Al upon devitrification fail to depict a clear glass transition temperature (T_g) in conventional differential scanning calorimetry (DSC) studies [2,4,5], though they appear to be amorphous based on XRD and TEM evidences. Though DSC is an important thermal analysis tool, which has already been used for several decades, it is often difficult to interpret the heat flow data from DSC experiments if multiple processes are involved over the same temperature region. Tg is not revealed in conventional DSC. This may be due to (i) The enthalpy change due to Tg is small, (ii) the temperaure if Tg phenomenon is within the temperature of the first crystallization stages [4,5]. Besides some of the Al-based glasses, other amorphous alloys such as $Nd_{60}Fe_{30}Al_{10}$ [10] and $Mg_{75}Ni_{10}Nd_{15}$ [11] do not show any signature of T_g in DSC heating scans, even at higher heating rates. The absence of T_g may also be explained that during quenching, while preparing Al-based amorphous alloy in the form of ribbons, some significant number of small clusters may be formed. On heating, those clusters above the critical nucleation size grow even at lower temperatures. As a result, T_g is hidden underneath the first crystallization peak. Thus, direct evidence of the formation of a vitreous state in these alloys is still amiss. Now the question arises, are these alloys without resolvable T_g in DSC truly amorphous? In order to answer the question temperature modulated differential scanning calorimetry (TMDSC) experiments were performed. From modulated DSC (MDSC) experiment on an Al–Y–Fe glass, Wu et al. [12] reported that onset of the primary crystallization peak coincided with the glass transition. Bokeloh et al. [13] also performed MDSC measurements on a series of Al–Y–Fe glass and reported the shifting of onset temperatures with annealing treatments.

The glass transition upon heating is a reversible process in which heat is absorbed to accommodate the heat capacity increase during the transition, while crystallization is a non-reversible exothermic process which releases heat. In DSC, the sample is either heated isochronally or isothermally in order to measure heat flow into or out of the sample. TMDSC is a development of conventional heat flux DSC that allows the sample temperature to be modulated sinusoidally about a constant ramp so that the temperature, T, at a time, t, is

$$T = T + \beta t + A\sin\omega t$$

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where T_o is the initial (or starting) temperature, β is the heating rate, A is the amplitude of the modulation and ω is the angular frequency of modulation ($\omega = 2\pi/\rho$, where ρ is the modulation period) [11,14]. The resulting instantaneous heating rate dT/dt varies sinusoidally about the average heating rate. The apparatus measures the amplitude of the instantaneous heat flow and the average heat flow (HF), called the total heat flow, and then by carrying out a suitable Fourier deconvolution of the measured quantities the heat capacity (C_P) component of the total HF, i.e., the reversible heat flow (RHF) can be separated from the kinetic component of the total HF, i.e., the non-reversible heat flow (NHF). The RHF is determined as the arithmetic difference between total HF and the NHF. Actually, glass transition is marked by an abrupt change in heat capacity at the glass transition temperature which will only be displayed on the RHF. On the other hand, crystallization and enthalpy relaxation will only appear on the NHF. Therefore, TMDSC has the capability to separate the glass transition occurrence from crystallization and relaxation transformations for the metallic glasses.

In this work, we report the TMDSC, along with conventional DSC, TEM and XRD analyses to characterize the glass transition and primary crystallization for $Al_{89-x}Ni_6La_{5+x}$ (x = 0,2) and $Al_{87}Ni_5La_7M_1$ (M = Ag or Cu) metallic glasses.

2. Experimental procedures

Alloy ingots of compositions $Al_{89-x}Ni_6La_{5+x}$ (x = 0, 2) and $Al_{87}Ni_5La_7M_1$ (M = Ag or Cu) were prepared by alloying pure components (purity: 4N/3N) by induction melting under a purified argon atmosphere (purity: 99.99%), taking care that the melt was well inductively stirred to ensure good chemical homogeneity. In order to obtain rapidly solidified ribbons, the ingots were re-melted in an alumina-coated quartz crucible and then ejected through an orifice, at a temperature of 1100 °C, onto a rotating Cu wheel (diameter 300 mm and thickness 38 mm, rotating speed 40 m/s) in argon atmosphere. The structure of the as-melt-spun was investigated by XRD and TEM. The TEM as-melt-spun samples were prepared, by ion milling or by jet thinning using a solution of 30% nitric acid and 70% methanol at 230–240 K and 12 V. The crystallization behavior of the ribbons was studied by DSC and TMDSC. The DSC was calibrated by using pure In and Zn standards, giving an accuracy of ±0.3 K for the temperature and ±0.02 mW for the heat flow measurements. The continuous heating DSC studies were conducted at heating rates 10–40 K/min. In all cases, a second scan was used as a base line. The TMDSC experiments were carried out on a modulated DSC instrument (TA Instruments Inc, USA) using a refrigerated cooling system or an Ar-gas cooling system with a N_2-gas DSC cell purge. The TMDSC scans were conducted at an underlying heating rate of 1 or 5 K/min up to a temperature of 573 K. Oscillation amplitude of 0.2 K and a modulation period of 60 s were used for the sample masses of 3–10 mg.

3. Results and discussion

3.1. X-ray diffraction results of as-melt-spun ribbons

The ribbons prepared from ingots are 2–3 mm wide, 30 ± 5 μm in thickness and several meters long. Fig. 1 shows the representative XRD patterns of $Al_{89-x}Ni_6La_{5+x}$ (x = 0,2) and $Al_{87}Ni_5La_7M_1$ (M = Ag or Cu) alloys on the air-cooled side. The pattern revealed that all the as-melt-spun ribbons are fully amorphous on the wheel side as well as on the air-cooled side. The samples showed a distinct broad diffuse maximum centered on sin θ/λ = 0.208 nm^{-1} (2θ = 37.5°), which is a characteristic of a glassy phase. The representative TEM micrograph from as-melt spun $Al_{89}Ni_6La_5$ ribbons is shown in Fig. 2. The TEM micrograph and the corresponding selected area diffraction (SAD) pattern also support that the as-melt-spun ribbons are amorphous in the as melt-spun condition as no crystalline contrast is found.

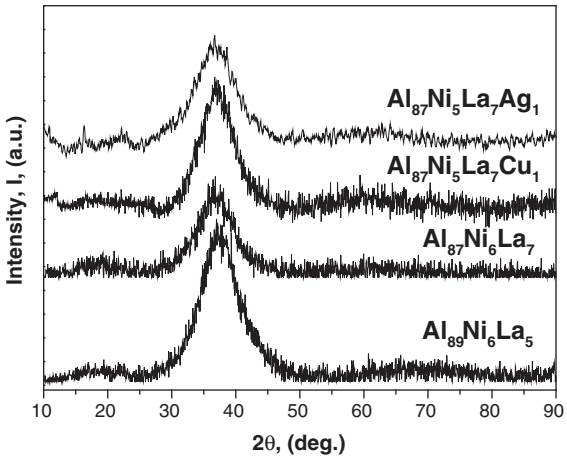

Fig. 1. X-ray diffraction patterns of $Al_{89-x}Ni_6La_{5+x}$ (x = 0, 2) and $Al_{87}Ni_5La_7M_1$ (M = Ag or Cu) alloy ribbons on the air-cooled side.

3.2. Conventional DSC results of as-melt-spun ribbons

Fig. 3 shows the continuous heating DSC curve of amorphous $Al_{89-x}Ni_6La_{5+x}$ (x = 0,2) and $Al_{87}Ni_5La_7M_1$ (Ag or Cu) alloys at a constant heating rate 40 K/min. The alloys showed two exothermic peaks corresponding to the crystallization which are attributed to the formation of different phases. In order to identify the phases formed at different stages of crystallization, samples were heated up to the end of corresponding crystallization stages and then after cooling to room temperature XRD pattern was recorded (figure not shown). In $Al_{89}Ni_6La_5$ alloy the first crystallization stage is due to the formation of fcc-Al and the second crystallization stage is due to the formation of Al, Al_3Ni, $Al_{11}La_4$ phases whereas for the remaining alloys the first crystallization stage is due to the formation of metastable bcc-phase containing significant amount of La [8] which transformed to stable Al, Al_3Ni and $Al_{11}La_4$ phases during the second stage of crystallization. The position of heat events on the temperature axis changes with alloy compositions. The first peak temperature of the crystallization event increases and the second peak temperature decreases with the increase of La content (Fig. 3a and b). This indicates that the amorphous alloy is more stabilized with the increase of La content. There are definite differences in the peak temperature of the first crystallization (T_{x1p}) as well as the second crystallization (T_{x2p}) stages. It was observed that T_{x1p} of the $Al_{87}Ni_6La_7$ alloy is higher and T_{x2p} is lower than that of Ag- or Cu-containing alloys. From Fig. 3 it can be calculated that ΔT_x ($T_{x2p} - T_{x1p}$) is greatest for

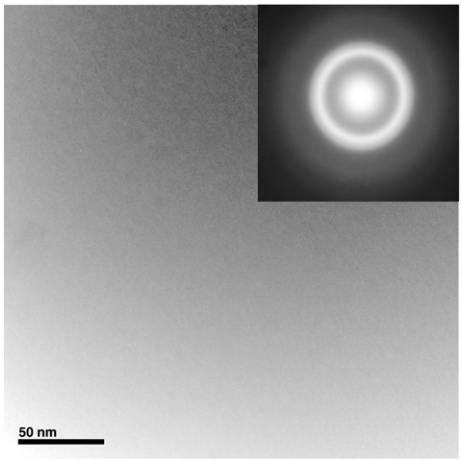

Fig. 2. The TEM bright field images of $Al_{89}Ni_6La_5$ melt-spun ribbons. The inset shows the corresponding SAD pattern.