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Effect of substituting elements on thermal stability and glass-forming ability of an Al-based Al–Ni–Er metallic glass

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ABSTRACT

Addition of a small amount of La and Co enhances the stabilization of supercooled liquid and glass-forming ability (GFA) of an $Al_{85}Ni_7Er_8$ metallic glass. The $Al_{85}Ni_5Co_2Er_6La_2$ alloy exhibits large supercooled liquid region of 40 K, high GFA with a critical thickness of 450 μm, and the viscosities on the order of 10^7–10^9 Pa s in the supercooled liquid state. The Al-based glassy nano-scale patterns were formed by imprinting, indicating its good thermoplastic formability. The possible mechanism for the improvement of the supercooled liquid stability of the Al–Ni–Er alloy by addition of La and Co elements was discussed in terms of the crystallization behavior.

1. Introduction

Al-based metallic glasses (MGs) have attracted increasing interest due to their ultrahigh specific strength, high toughness and good corrosion resistance [1–5], which are promising for applications as a new type of structural materials in the fields of aerospace and micro-electro mechanical systems (MEMS), *etc.* However, it is significantly challenging to fabricate Al-based bulk metallic glasses (BMGs) because of their relatively low glass-forming ability (GFA) [3]. The first batch of Al-based BMGs up to 1 mm in critical size were developed recently [4,5], but their GFA and the stability of supercooled liquid are still far lower than those of other BMGs [6].

The thermoplastic formability is one of the most useful characteristic for MGs due to the Newtonian viscous flow in the supercooled liquid state [6–8]. The large-scale BMGs can be fabricated in the frame of thermoplastic forming by consolidating the glassy powders through hot working and shape forming techniques [9,10]. On the other hand, the thermoplastic processing has been developed to make micro- and nano-devices for MGs, which are expected to enter commercial production [6,8,11]. The MGs suitable for thermoplastic processes should simultaneously possess low glass transition temperature (T_g), large supercooled liquid region ($\Delta T_x = T_x - T_g$, T_x: crystallization temperature), adequate GFA, and low viscosity in the supercooled liquid state [12]. From a processing point of view, it is desirable to possess a large ΔT_x which means excellent stabilization of supercooled liquids and gives access to a low viscosity, which in turn facilitates thermoplastic formability. A low T_g implies a low processing temperature since it facilitates processing. Production costs are reduced as a consequence of a low T_g by minimizing the heating and cooling cycles and the thermal cycling of the mold, which limits mold materials and mold lifetime. Although the reported Al-based MGs have low T_g below 573 K, they exhibit narrow ΔT_x and low GFA, some alloys even don't show distinct glass transition before crystallization [3,13–18], which make them difficult to use the thermoplastic processing [12].

A large number of Al-based MGs have been developed based on Al–TM–RE (TM = Transition Metal, RE = Rare Earth Metal) ternary alloy systems in the past three decades. Among them, the Al–Ni–RE ternary alloys have a relatively good stabilization of supercooled liquid and high GFA, while their ΔT_x are seldom larger than 30 K [3,13–19]. Louzguine et al [19] reported that the ΔT_x value of

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the Al–Ni–RE alloys strongly depends upon the electronegativity of RE. The lower electronegativity difference between RE and Al elements will probably lead to a larger ΔT_x. It is also known that micro-alloying with suitable element and similar element substitutions can increase the atomic packing density and complicate the precipitated phases during crystallization, which are beneficial to improve the stability of supercooled liquid and GFA of the MGs [20,21]. In the present work, considering the low electronegativity difference of Er (electronegativity: 1.24) to Al (electronegativity: 1.61) in RE elements, An Al-based Al–Ni–Er alloy was selected as the base one, and the effects of the substitution of Co for Ni and La for Er on the thermal properties as well as GFA were investigated. It was found that the addition of a small amount of Co and La significantly increases the ΔT_x and GFA, and decreases the viscosity in the supercooled liquid state. The mechanism for the enhancement of the ΔT_x was discussed in terms of the crystallization behavior of the Al-based MGs.

2. Experimental methods

Alloy ingots of Al-(Ni, Co)-(Er, La) were prepared by arc-melting a mixture of pure Al (99.999 mass %), Ni (99.99 mass %), Co (99.99 mass %), Er (99.9 mass %) and La (99.9 mass %) metals under a high purified argon atmosphere. The ingots were re-melted at least 4 times to ensure chemical homogeneity. The total mass loss was less than 0.2 mass %. The ribbons of different thicknesses were spun using a melt-spinning method. The wedge-shaped samples were prepared through injection copper mold casting to explore the critical size for glass formation [15]. To examine the primary crystallization products, the melt-spun ribbons were sealed into a quartz tube evacuated to 2×10^{-3} Pa, isothermally annealed for 600 s at different temperatures, and then quenched into water. The sample structure was examined by X-ray diffraction (XRD; D8 Focus, Bruker) with Cu $K\alpha$ radiation and optical microscopy. The thermal parameters, namely T_g, T_x, and liquidus temperature (T_l) of the alloys was examined by differential scanning calorimetry (DSC; Q-20, TA Ins.) and differential thermal analyzer (DTA; SDT Q-400, TA Inc.) at a heating rate of 0.67 and 0.33 K/s, respectively. The thermal stability was investigated in both isochronal and isothermal mode by DSC. The isochronal DSC measurements were conducted from 373 to 773 K at heating rates ranging from 0.17 to 0.67 K/s. The isothermal DSC measurements were carried out at temperatures between 526 and 558 K. The ribbons were first heated to the desired annealing temperature at a heating rate of 0.67 K/s and then held isothermally for a certain period of time. A thermomechanical analyzer (TMA; Q-400, TA Ins.) was employed to measure the temperature dependence of the apparent viscosity for the ribbon samples at a heating rate of 0.33 K/s and with an applied load is 1 N. The dimension of ribbon samples is about 6.0 mm in length, 1.5 mm in width and 0.025 mm in thickness. The samples were put in a chamber inserted in the TMA and filled with a purified argon gas to avoid the oxidation. An imprinting test was performed using a nano-imprinter (NM-0501-T, Meishokiko Corporation) in a vacuum state of 1×10^{-2} Pa. The imprinting temperature, applied pressure, and duration time for imprinting is 543 K, 100 MPa, and 70 s, respectively. The heating and cooling rates for the imprinting experiments are about 3.3 K/s. The imprinting surfaces morphology was observed with a scanning electron microscope (SEM, Hitachi S-4800).

3. Results and discussions

All melt-spun samples were confirmed to have a fully amorphous by XRD measurements in the present study. Fig. 1 shows the DSC and DTA curves of the Al-(Ni, Co)-(Er, La) MGs. The T_g, T_x and T_l are marked with arrows. The alloys all exhibit a clear endothermic glass transition followed by a supercooled liquid region, and then three exothermic peaks due to crystallizations (see Fig. 1a). Addition of 2 at.% La enhances the stabilization of supercooled liquid by an indication of 28 and 34 K for the ΔT_x of $Al_{85}Ni_7Er_8$ and $Al_{85}Ni_7Er_6La_2$ alloys, respectively. Substitution of 2 at.% Co for Ni in the $Al_{85}Ni_7Er_6La_2$ alloy further increases the ΔT_x to 40 K. Fig. 1b shows that addition of 2 at.% La reduces the T_l of the base alloy, whereas further addition of 2 at.% Co to $Al_{85}Ni_7Er_6La_2$ slightly increases the T_l. Based on the data shown in Fig. 1, the GFA indicators such as reduced glass transition temperature T_{rg} ($T_{rg} = T_g/T_l$) [22], γ ($\gamma = T_x/(T_l + T_g)$) [23] and S value ($S = \Delta T_x/(T_l - T_g)$) [12] of the alloys were calculated (*see* Table 1). All the indicators increase with Co and La additions, suggesting an enhancement of the GFA.

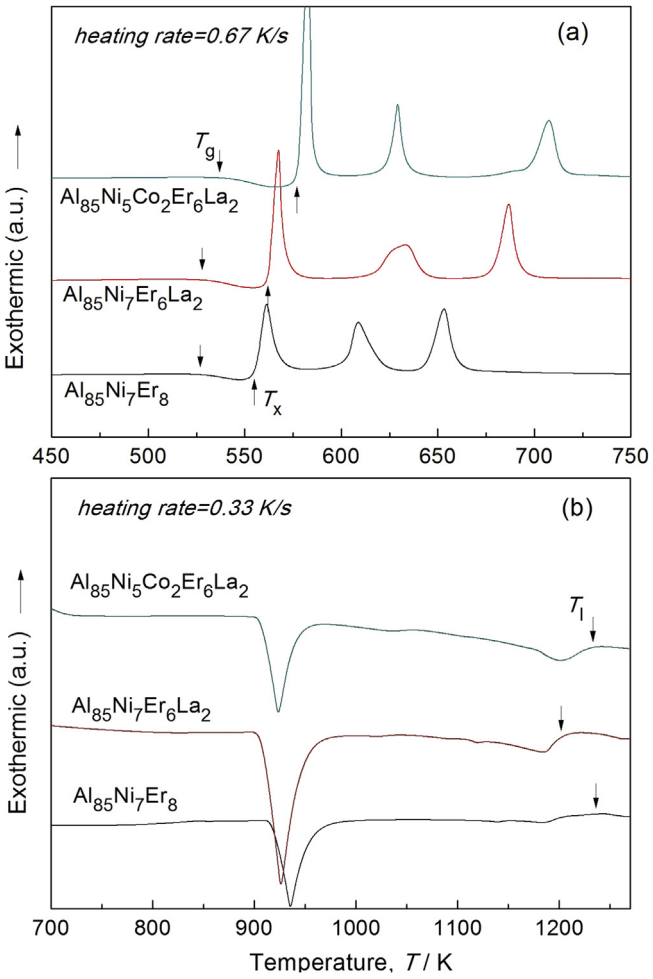

Fig. 1. DSC (a) and DTA (b) curves of $Al_{85}Ni_7Er_8$, $Al_{85}Ni_7Er_6La_2$ and $Al_{85}Ni_5Co_2Er_6La_2$ MGs.

Fig. 2 shows the optical images of the as-cast wedge-shaped samples for the three investigated alloys. Three distinct regions representing the fully amorphous (I), amorphous plus crystalline (II), and crystalline regions (III), respectively, can be clearly distinguished. The amorphous critical thickness (t_c) of each sample is determined corresponding to the boundary between the fully amorphous and amorphous plus crystalline regions (marked by the black lines in Fig. 2) [15], which is 0.45 mm for the $Al_{85}Ni_5Co_2Er_6La_2$ alloy, 0.40 mm for $Al_{85}Ni_7Er_6La_2$ alloy and 0.30 mm for the base alloy. It can be inferred that the addition of La and Co improves the GFA of the alloys.

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