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Maximum Glass-forming Ability Obtained at an Off-eutectic Composition Within a La-al-(Cu, Ni) Pseudo-ternary Eutectic System

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Abstract: Glass formation was investigated for the $La_{100-x}Al_{0.412x}(Cu,Ni)_{0.588x}$(x = 30-56.3) alloys. The optimum Glass Forming Ability (GFA) with full glassy rods of 12 mm in diameter was obtained at an off-eutectic composition $La_{62}Al_{15.7}(Cu,Ni)_{22.3}$, by copper mold casting, while a full glassy rod of only 1.5 mm in diameter was obtained at the $La_{66}Al_{14}(Cu, Ni)_{20}$ eutectic alloy. A strong dependence of GFA on the composition was observed for these alloys. It has been found that the GFA does not correlate well with the extent of the supercooled liquid region (ΔT_x) and is even not related closely to the reduced glass transition temperature T_{rg}.

Key words: Bulk metallic glasses, glass forming ability, eutectic, La-based alloy

INTRODUCTION

Glass formation basically is avoiding detectable crystallization[1-10]. Based on theoretical work on crystal nucleation in undercooled liquid metals, Turnbull[1] proposed that the glass-forming tendency should increase with the reduced glass transition temperature, T_{rg}, which was defined by T_g/T_l. Here, T_g is the glass transition temperature and T_l is the liquidus temperature. Later works of Uhlmann[2] and Davies[3] on the crystallization of undercooled liquids further identified this dimension-less parameter as a crucial figure of merit in determining Glass Forming Ability (GFA). As T_g is generally less dependant on the composition, while T_l has the lowest value at eutectic composition, T_{rg} reaches the maximum at the eutectic composition, i.e., the best glass formation should be located around the eutectic composition[1,4-7]. On the other hand, Inoue[8] and his coworkers found that most of their multi-component bulk glass formers have large extent of supercooled liquid region ΔT_x ($\Delta t_x = T_x - T_g$, T_x is the onset temperature of the first crystallization event). Although this quantity has been generally regarded as the thermal stability of the metallic glasses[3], it has been used successfully in finding many bulk metallic glasses[8]. This study, shows our experimental findings that the composition for the optimum glass formation in the multi-component La based La-Al-(Cu,Ni) pseudo ternary eutectic system is actually at an off-eutectic composition. Furthermore, the GFA in this alloy system does not correlate with the ΔT_x and even not well with T_{rg}.

MATERIALS AND METHODS

The master alloys of $La_{100-x}Al_{0.412x}(Cu,Ni)_{0.588x}$ (x = 30-56.3) were prepared by arc melting the constituent elements, La (99.9%), Al (99.9%), Ni (99.98%) and Cu (99.999%) under a Ti-gettered argon atmosphere, in which Cu and Ni always have equal amount. The ingots were cast by pouring the molten alloys into a set of copper molds with diameters of 5 to 12 mm with length up to 60 mm. The samples with diameters less than 5 mm were prepared by suction casting in the copper molds. The resulting samples were sectioned transversely, mounted and polished for observation by Scanning Electron Microscopy (SEM). The degrees of amorphicity of all samples were examined by X-ray Diffractometry (XRD) and Differential Scanning Calorimetry (DSC). For measuring T_g and T_x, ribbon sample was also prepared by a single roller melt-spinner in an argon atmosphere. The onset melting temperature T_m (solidus temperature) and the offset melting temperature T_l (liquidus temperature) were measured by DSC with a heating rate of 40 K min^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows T_l and T_m as a function of Al content in the $La_{100-x}Al_{0.412x}(Cu,Ni)_{0.588x}$ alloys and indicates that the eutectic is at $La_{66}Al_{14}(Cu,Ni)_{20}$ (x = 34) with eutectic temperature at around 675 K (In the Fig. 1, T_m was used instead of T_l for the eutectic alloy). After locating the eutectic composition, we have studied the GFA of these alloys and its correlation with their T_{rg} and ΔT_x. SEM micrographs of the cross sections of the central parts of the 12 mm diameter cast rods demonstrating a

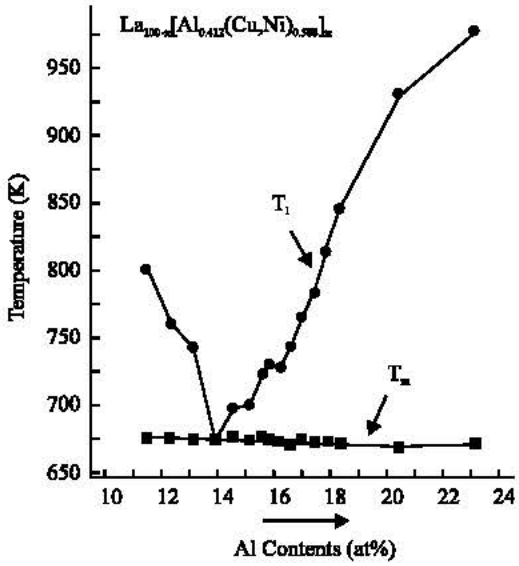

Fig. 1: Solidus temperature T_m and liquidus temperature T_l as a function of Al content in the $La_{100-x}[(Cu,Ni)_{0.588}Al_{0.412}]_x$ (x = 28-56.3) alloy series

microstructure of a dendritic crystalline phase distributed in an amorphous matrix for the eutectic $La_{66}Al_{14}(Cu,Ni)_{20}$ alloy (Fig. 2a) and a featureless microstructure for the $La_{62}Al_{15.7}(Cu,Ni)_{22.3}$ alloy (Fig. 2b) consistent with it being fully amorphous. The insets of Fig. 2 show the corresponding XRD patterns on the sections of 12 mm diameter rods. The inset of Fig. 2a shows a broad diffraction maximum with some crystalline sharp peaks. The dendritic crystalline phase has been identified previously as hcp La[11]. The inset of Fig. 2b only shows a broad diffraction maximum, no crystalline peaks were observed, indicating that the 12 mm diameter rod is full amorphous. Further studies confirm that only 1.5 mm diameter full glassy rods can be formed by copper mold casting for the eutectic alloy $La_{66}Al_{14}(Cu,Ni)_{20}$ alloy.

DSC curves for the fully amorphous state of the as-spun ribbons showing that the crystallization behavior changed from multiple crystallization events to a single event as the La content decreased and the value of ΔT_x increased to a maximum of 76 K (Fig. 3). The values of ΔT_x exhibit maximum at about 17 at% Al. The $La_{62}Al_{15.7}(Cu,Ni)_{22.3}$ alloy with a critical diameter of 12 mm has a ΔT_x value of 38 K only (Fig. 3). The critical (limiting) size increased sharply from 1.5 mm at the eutectic composition $La_{66}Al_{14}(Cu,Ni)_{20}$ to 12 mm for an off-eutectic alloy around $La_{62}Al_{15.7}(Cu,Ni)_{22.3}$ (x = 38) and then decreased sharply again to 1.5 mm at $La_{56.3}Al_{18}(Cu,Ni)_{25.7}$ (x = 43.7) (Fig. 3b).

The GFA of La-Al-Cu-Ni-(Co) based alloys has been studied extensively during the past decade[8,12-14]. The best manifestation of GFA for the quaternary La-Al-Cu-Ni

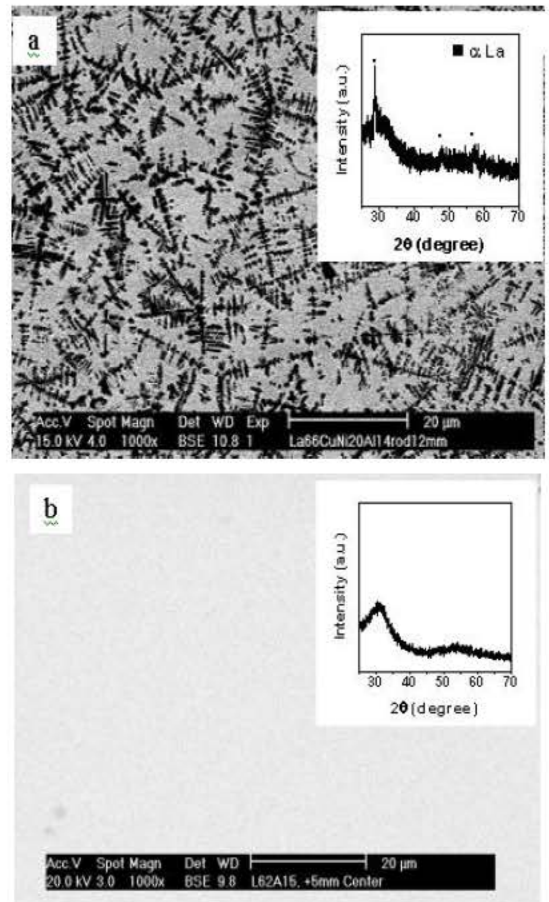

Fig. 2: SEM micrographs showing composite of hcp α-La in amorphous matrix (a) and fully amorphous (b) in the center of 12 mm rods of $La_{66}(Cu,Ni)_{20}Al_{14}$ and $La_{62}(Cu,Ni)_{22.3}Al_{15.7}$ alloys, respectively. The insets are the XRD patterns on the sections of 12 mm diameter rods

alloys was a 7 mm diameter rod of $La_{55}Al_{25}Cu_{10}Ni_{10}$ alloy obtained by high pressure die-casting and this diameter was further improved to 9 mm in a quinary $La_{55}Al_{25}Cu_{10}Ni_5Co_5$[13]. The amorphous $La_{55}Al_{25}Cu_{10}Ni_{10}$ and $La_{55}Al_{25}Cu_{10}Ni_5Co_5$ alloys have values of ΔT_x of 88 and 98 K, respectively[13], which are much larger than those for the current alloys. Therefore, within one eutectic system of La-Al-(Cu, Ni) pseudo ternary alloys, large values of ΔT_x have no direct correlation with the optimum GFA, similar results were also obtained in the Be containing Zr-based alloys[10].

Furthermore, the correlation between T_{rg} and GFA for the present alloys is also weak. As shown in Fig. 3b, most of T_{rg} are above 0.5. However, the highest T_{rg} of 0.60 corresponds to the GFA of 1.5 mm for the eutectic alloy,

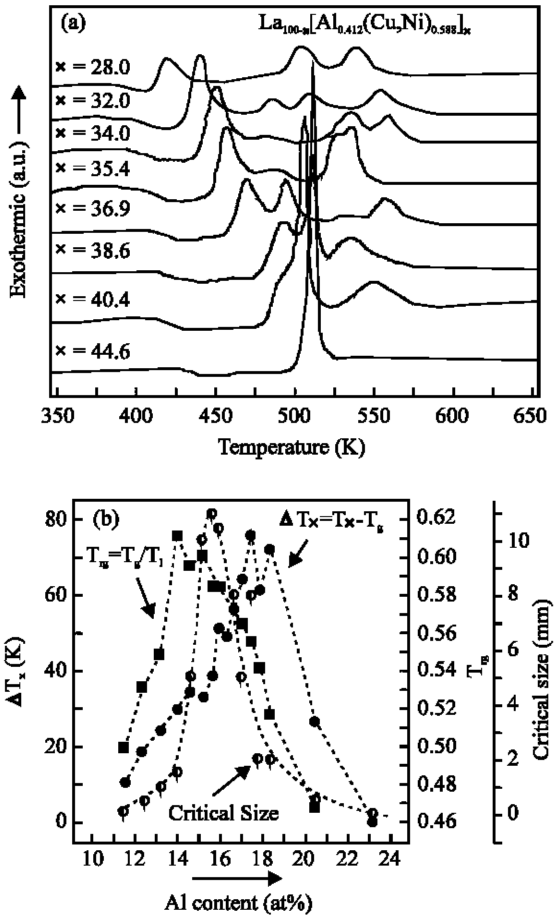

Fig. 3: a: DSC curves of $La_{100-x}[(Cu,Ni)_{0.588}Al_{0.412}]_x$ (x = 28-56.3) alloys. b: limiting diameter for glass formation as a function of Al content in the $La_{100-x}[(Cu,Ni)_{0.588}Al_{0.412}]_x$ (x = 28-56.3) alloy series and T_{rg} and ΔT_x as a function of Al content in the alloys

while a slight lower value of T_{rg} 0.58 corresponds to GFA of 12 mm at an off-eutectic composition.

The steady state nucleation rate I can be expressed as[1,5]:

$$I = \frac{k_n}{\eta}\exp[\frac{-b\alpha^3\beta}{T_r\Delta T_r^2}] \quad (1)$$

The η can be expressed by a Vogel-Fulcher form[1]:

$$\eta = \eta_0 \exp(\frac{A}{T_r - T_{rg}}) \quad (2)$$

Substitute Eq. 2 in 1, we can have:

$$I = \frac{k_n}{\eta_0}\exp(\frac{A}{T_{rg} - T_r} - \frac{b\alpha^3\beta}{T_r\Delta T_r^2}) \quad (3)$$

Here, k_n is a constant (typically about 10^{23} N.m), $\alpha\beta^{1/3}$ for metals, $b = 16\pi/3$ for spherical nucleus. $T_r = T/T_l$, $\Delta T_r = 1 - T_r$, T_l and T are the equilibrium crystallization (liquidus) and actual absolute temperature, respectively. η_0 and A are materials constants. According to Turnbull[1], $\eta_0 = 10^{-3.3}$ Poise (1 Poise = 0.1 Ns m^{-1}) and A = 3.34. From Eq. 3 Turnbull concluded that the higher the T_{rg} is, the higher the glass forming ability is. In particular, liquids with T_{rg} = 2/3 would practically crystallize only within a narrow temperature range, thus they easily could be undercooled to the glass state. However, it is obvious that η_0 and A also have strong effect on nucleation rate I and on GFA. The melt viscosities at T_l are very roughly uniform (a few centiPoise) for metals[15]. But it becomes increasingly higher for the glass forming alloys, probably because the alloys become more complex and the melt viscosity at T_l becomes more variable especially at eutectics with extreme depressions of melting temperature[16,17], in much the same way as that of inorganic glass-forming liquids[15,17]. The slopes of the liquidus lines obtained from Fig. 1 are about 30 K/at%, indicating a very sharp depressing melting temperature in our present system. Thus it is possible for an off-eutectic alloy, with a higher melt viscosity to have a better GFA, particularly when their T_{rg} is close to each other like in the present alloy system (0.6 and 0.58). Furthermore, glass formation is also believed to be a competitive process between the formation of glass and the growth of crystals[18] and the eutectic will be different with the thermodynamic eutectic under the higher cooling rate than the equilibrium cooling. Under this consideration, it is also possible that the optimum GFA is located at an off-eutectic composition[19].

CONCLUSIONS

In conclusion, the best GFA in eutectic system of La-Al-(Cu,Ni) pseudo-ternary alloys is at an off-eutectic composition, $La_{62}Al_{15.7}(Cu,Ni)_{22.3}$ and full glassy rods of 12 mm in diameter were obtained by copper mold casting. The alloy has a small extent of supercooled liquid region. A strong dependence of GFA on the base element in these alloys was observed.

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