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Influence of Cu addition on the glass transition behavior of LaCe-based metallic glasses

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ABSTRACT

The effect of Cu content on glass transition behavior of $(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25-x}Cu_x$ (x = 0, 5, 10, 15, 20, 25) metallic glasses was measured by high-rate and high-precision differential scanning calorimetry. It is observed that the glass transition temperature (T_g) decreases with the increase of the Cu content. The fragility (m) increases first and then decreases with the increasing of Cu content, with a maximum $m = 63.6$ for x = 10. A correlation is confirmed between the enthalpy of mixing fragility. These results suggest that metallic glasses with desirable supercooled liquids characters can be designed by alloying elements with suitable mixing enthalpy.

1. Introduction

The fragility m is one of the key parameters to characterize the properties of the supercooled liquid, i.e. the arrangement of atoms close to glass transition temperature T_g, which is defined as [1,2].

$$m = \left.\frac{d\log\eta}{dT/T_g}\right|_{T=T_g} \quad (1)$$

The viscosity is given by $\eta = \eta_0 \cdot \exp[E(T)/RT]$, where η_0 is a constant, $E(T)$ is the energy barrier, R is gas constant. The fragility of supercooled liquids is influenced by the nature of chemical bonds. For example, glass-forming liquids can be divided into three general categories: strong (oxide glasses), intermediate (metallic glasses) and fragile (polymers). The viscosity of "strong" glass formers exhibit linear-like dependence on temperature, while the viscosity of "fragile" glass formers change much faster at low temperatures close to glass transition temperature.

For fundamental research, there are extensive studies on the influence of fragility in glass transition phenomenon, glass forming ability and mechanical properties. For example, there is a negative correlation between glass forming ability (GFA) and m [3–5]. There are various correlations between mechanical properties of MGs m [6–10]. It is reported that the m exhibits positive relation with T_g [11,12]. For applications, the thermal plastic deformability of supercooled liquid allows processing metallic glasses into complex shapes [13–16]. A suitable fragility allows large favorable temperature ranges for thermal plastic deformation. Studying the evolution of fragility along with the change of chemical compositions of metallic glass is helpful not only for studying physical mechanisms but also for designing new metallic glasses.

Fast-rate differential scanning calorimetry (DSC) is capable of heating/cooling at rate up to 10^4 K/s [17,18]. It allows measuring the phase change dynamics at extremely fast conditions, such as the glass transition kinetics, crystallization kinetics, and melting behaviors [17–21]. The crystal-growth kinetics can be determined over a wide range of heating rates [21–23]. A solid-solid transition via the metastable melting is discovered at ultrafast heating [24]. The fast heating capacity of high-rate DSC allows exploring new phenomena in supercooled liquids of metallic glasses.

In this letter, the glass transition kinetics of $(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25-x}Cu_x$ (x = 0, 5, 10, 15, 20, 25) metallic glasses were investigated by Flash DSC 1 (Mettler-Toledo). Substituting Co by Cu atoms can dramatically decrease the glasses transition temperature. Besides, the effect of Cu on m was further evaluated by Vogel-Fulcher-Tammann (VFT) equation.

2. Material and methods

Alloy ingots of $(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25-x}Cu_x$ (x = 0, 5, 10, 15, 20, 25) (at.%) was prepared by arc melting the pure elements (> 99.5 wt.%)

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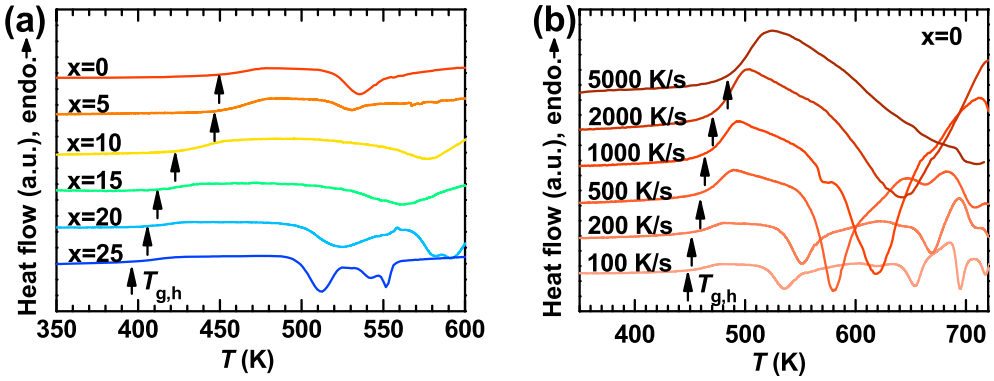

Fig. 1. (a) DSC traces of $(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25-x}Cu_x$ (x = 0, 5, 10, 15, 20, 25) at heating rate ϕ_h = 100 K/s. The glass transition temperatures are marked by arrows. (b) DSC traces of $(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25}$ at heating rates from 100 K/s to 5000 K/s.

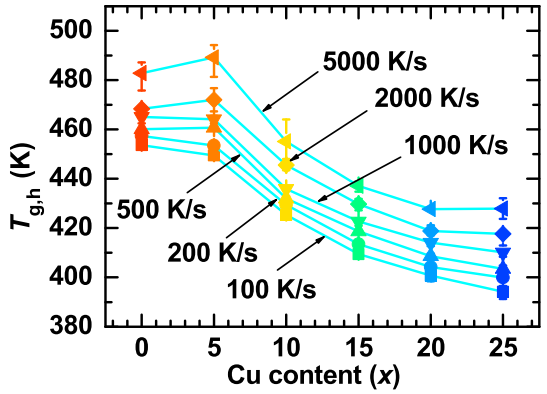

Fig. 2. The T_g of $(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25-x}Cu_x$ (x = 0, 5, 10, 15, 20, 25) at different heating rates from 100 K/s to 5000 K/s.

protected under an atmosphere of high-purity Ar gas. The master alloy was then remelt in a quartz tube and injected on a fast spinning copper roller (tangent speed ~40 m/s) to obtain metallic glass ribbons. A small piece of sample (mass is ~100 ng) was cut from the ribbon under an optical microscope. The small sample was then transferred to the sample chip for DSC measurement under an optical microscope. The glass transition temperature was measured by Flash DSC1 at heating rates ranging from 100 K/s to 5000 K/s.

3. Results

DSC traces of $(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25-x}Cu_x$ (x = 0, 5, 10, 15, 20, 25) at heating rate ϕ_h = 100 K/s were also given, as shown in Fig. 1a. The glass transition temperature (T_g) decrease from 453 K to 394 K when Cu content increases. To determine the glass transition kinetics, DSC curves at heating rates (ϕ) from 100 K/s to 5000 K/s was measured. The data of $(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25}$ is shown in Fig. 1b as an example. The T_g increase from 453 K to 482 K with the increase of the heating rates.

Table 1
The VFT fitting parameters of $(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25-x}Cu_x$ (x = 0, 5, 10, 15, 20, 25) alloys.

Composition	ln*B*	*D*	T_0 (K)
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25}$	23.39	7.11	327.49
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{20}Cu_5$	21.33	6.58	320.11
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{15}Cu_{10}$	19.93	4.01	336.13
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{10}Cu_{15}$	22.83	5.16	320.01
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_5Cu_{20}$	36.67	30.51	204.7
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Cu_{25}$	28.24	18.02	223.06

The glass transition temperatures measured at different heating rates are shown in Fig. 2. It is found that the glass transition kinetics of the LaCe-metallic glasses is sensitive to the Cu content. T_g decreases fast at around x = 10% for higher heating rates ($\phi_h \geq 100$ K/s), this phenomenon is not observed at ϕ_h = 0.33 K/s [25]. This denotes an abnormal behavior of supercooled liquid behavior at higher temperatures.

The non-linear relationship between T_g and lnϕ was illustrated in Fig. 3a. The solid curves are fitting results by VFT equation [26].

$$\ln\phi = \ln B - \frac{DT_0}{T - T_0}, \tag{2}$$

where B is a constant, D is the strength parameter, and T_0 is the asymptotic value of T_g at infinitely slow cooling and heating rate [26,27]. The best fitting results of parameters (B, D, T_0) are list in Table 1.

The m can be calculated by VFT fitting parameters [1].

$$m = \frac{DT_0T_g}{(T_g - T_0)^2 \ln 10}, \tag{3}$$

T_g is the value measured at heating rate of ϕ_h = 20 K/min. The m exhibits strong composition dependent character, with a maximum m = 63.6 for x = 10. It is interesting that the largest critical diameter d_{cr} was also found at about x = 10 [28]. A larger m suggests this composition is easier to reconstruct the arrangement of atoms. This

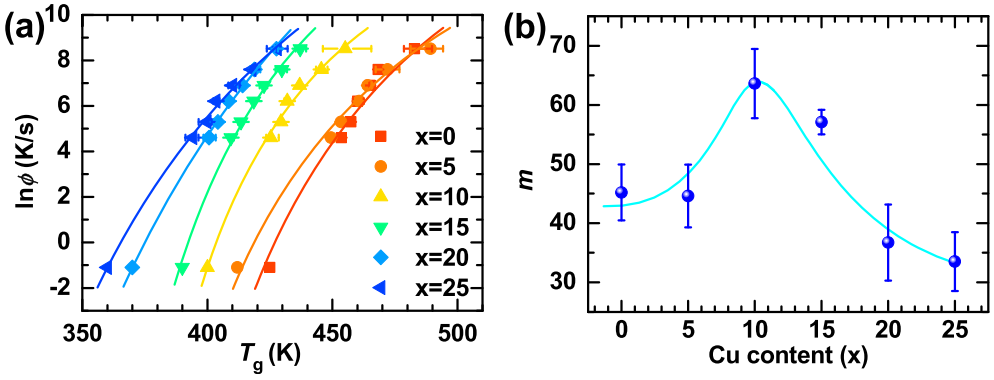

Fig. 3. (a) The heating rate dependence of glass transition temperatures T_g for $(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25-x}Cu_x$ (x = 0, 5, 10, 15, 20, 25) glassy specimens. The solid curves are fitting results of VFT equation. (b) Fragility m versus atomic fraction of copper.

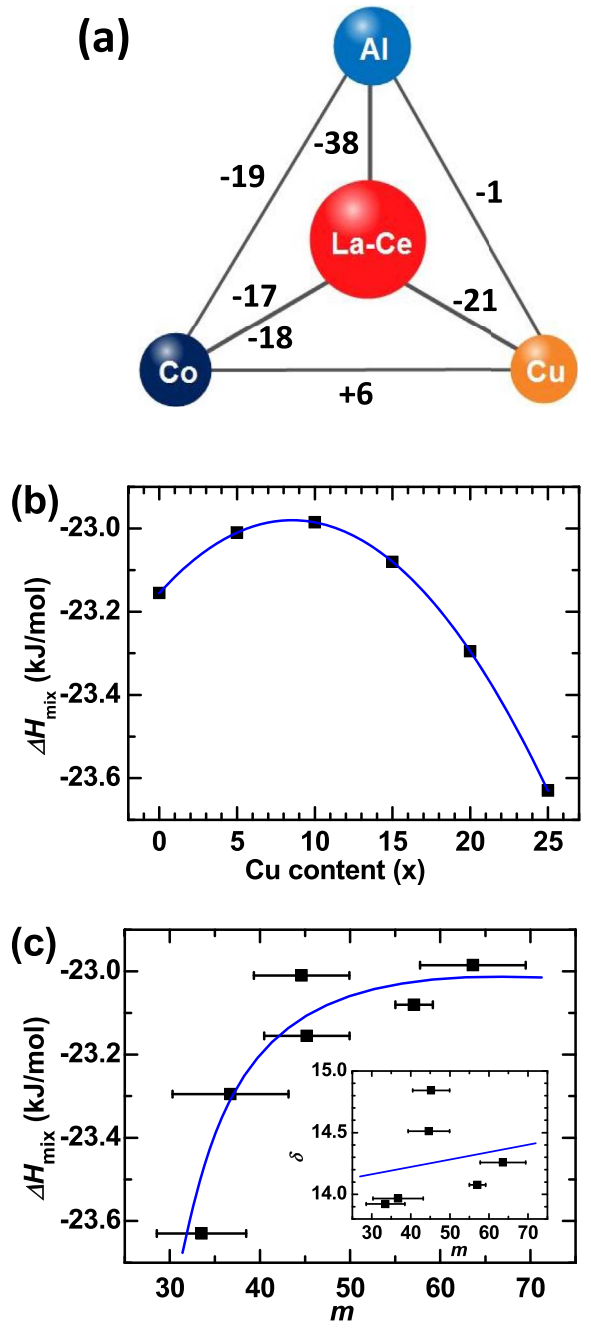

Fig. 4. (a) The enthalpy of mixing for the different elements. (b) The chemical composition dependent enthalpy of mixing. (c) The relationship between ΔH_{mix} and m. Inset is δ versus m.

Table 2
The enthalpy of mixing ΔH_{mix}, mismatch entropy normalized by Boltzmann constant $\delta = |\Delta H_{mix} \times S_\delta/k_B|$, and fragility m.

MGs	ΔH_{mix} (kJ/mol)	δ	m
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{25}$	−23.16	0.641	45.1
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{20}Cu_5$	−23.01	0.631	44.6
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{15}Cu_{10}$	−22.99	0.620	63.6
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{10}Cu_{15}$	−23.08	0.610	48
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_5Cu_{20}$	−23.30	0.600	36.7
$(La_{0.5}Ce_{0.5})_{65}Al_{10}Cu_{25}$	−23.63	0.589	33.5

phenomenon conflicts with the result that supercooled liquids with low m should exhibit greater GFA than high m [3–5,29]. But this is similar with polymer glasses that usually exhibit large glass forming ability and large fragility [30], which suggests that there may be chain-like bonds in this metallic glasses [31].

4. Discussions

Chemical influence on glass forming ability (GFA), mechanical properties and relaxation behaviors has been extensively researched [32–37]. Substituting Co by Cu atoms in La−Ce−Al−Co−Cu systems reaches a largest glass-forming diameter d_{cr} up to 32 mm [28]. Replacing Fe by Ni atoms in Fe−Ni−P−C systems enhanced the compressive plasticity [38]. Chemical compositions also influence the β relaxation behaviors [37]. A linear relationship is found between E_α/E_β and m [37,39]. Modifying chemical compositions can change the atomic interaction strength, which is well-characterized by the enthalpy of mixing [32]. Large enthalpy of mixing is related to good glass-forming ability [40]. It is probably a good parameter to explain the findings here. The enthalpy of mixing is defined as [32],

$$\Delta H_{mix} = 4 \sum_{A \neq B} \Delta H_{AB} c_A c_B, \quad (4)$$

where ΔH_{AB} means the enthalpy of mixing between elements A and B, c_A and c_B are the concentration of the elements A and B, respectively. The ΔH_{mix} of alloys (unit: kJ/mol) [32] are shown in Fig. 4a. The calculated ΔH_{mix} of all glassy specimens are listed in Table 2. ΔH_{mix} reaches a maximum at about composition point $(La_{0.5}Ce_{0.5})_{65}Al_{10}Co_{15}Cu_{10}$, which is in accordance with a maximum of m. Fig. 4b shows ΔH_{mix} versus m. It is shown that a metallic glass with larger negative ΔH_{mix} exhibits stronger supercooled liquid character. Large negative ΔH_{mix} means strong atomic bonding, which can make atoms difficult to move. Considering the weak interactions between Cu and Co ($\Delta H_{Cu\text{-}Co} = +6$ kJ/mol), Cu and Al ($\Delta H_{Cu\text{-}Al} = -1$ kJ/mol), the change of m can be attributed to the atomic diffusion of Cu. To research the mechanism of m further, the mismatch entropy was calculated, as list in Table 2. A parameter involving mismatch entropy, $\delta = |\Delta H_{mix} \times S_\delta/k_B|$, was proposed in Ref. [41] to understanding the change in fragility. However, this parameter has a scattered relation with m for this LaCe-based MGs. These results suggest that the fragility of metallic glass-forming liquids can be designed by alloying elements with suitable enthalpy of mixing with other components.

5. Conclusions

The chemical influences on glass transition kinetics in LaCe-based MGs are studied using a high-precision high-rate DSC. The alloy with 10% Cu exhibits the largest m, which is correlated with the large enthalpy of mixing. These results suggest that the fragility of metallic glass-forming liquids can be designed by alloying elements with suitable enthalpy of mixing with other components.

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