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Letter

Effect of Si addition on glass forming ability and thermal stability of Al–Fe–La alloys

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ABSTRACT

The effect of Si substitution for Al on the glass forming ability (GFA) and thermal stability of melt-quenched $Al_{88-x}Fe_6La_6Si_x$ ($x = 0, 0.5, 1–4$) alloys has been investigated systematically by using X-ray diffraction (XRD), differential scanning calorimetry (DSC) and viscometer. Results show that the addition of Si enhances the thermal stability and GFA of Al–Fe–La alloys, and the alloy containing 1 at.% Si has the best thermal ability, but the GFA of which is not best, the alloy containing 2 at.% Si has the best GFA. However, when Si content is beyond 2 at.%, the addition of Si reduces the GFA and thermal stability of the alloys. It is also found that the addition of Si influences the crystallization behaviors of the alloys, transforming from two-step crystallization process to three-step crystallization process.

1. Introduction

Al-based amorphous alloys exhibit outstanding mechanical properties such as high tensile strength with respect to their density [1]. Because of these excellent performances, Al-based amorphous alloys are attractive materials for structural applications. So far, the researches on the formation, structure and properties of Al-based amorphous alloys have been focused on Al–ETM–LTM (ETM: IV–VI group transition metal, LTM: VII–VIII group transition metal) and Al–RE–TM (RE: rare earth metal, TM: transition metal) ternary alloys because these alloys have higher glass forming ability (GFA) and better mechanical strength [2]. Inoue summarized the results of glass formation in the multicomponent alloys and proposed three empirical rules, which claimed that the alloys satisfying the three empirical rules have special atomic configuration [3]. In general, the GFA tends to increase as more components are added to alloys. That is called the "confusion principle" [4], which implies that a larger number of components in an alloy system destabilize the competing crystalline phases which may form during cooling. Liu and Lu reported that experimental evidences indicated that alloying additions of small atoms with atomic radius <0.12 nm (such as B and Si) or large atoms with radius >0.16 nm (such as Y and Sc) were most effective in enhancing glass forming ability [5]. Jun et al. investigated the effect of Be on glass forming ability and thermal stability of $(Al_{85}Ni_7Y_8)_{100-x}Be_x$ ($x = 0–6$ at.%) amorphous alloys in order to understand small atomic size effect in Al–TM–RE alloy system and found that the addition of 2 at.% Be enhanced the thermal stability of the $Al_{85}Ni_7Y_8$ alloy but did not practically enhance glass forming ability [6]. Recently, effects of Ce and Mm (misch metal: Ce, La, Nd, Gd, Sm and Pr) additions on the glass forming ability of Al–Ni–Si metallic glass alloys [7] and effect of Pr addition on glass forming ability of Al–Ni–Zr metallic glass alloy [8] have also been studied. However, no attention was paid to the effect of Si on the GFA and thermal ability of Al-based amorphous alloys.

Al–La–M (M = Fe, Co, Ni or Cu) amorphous alloys containing more than 80 at.% Al have good bend ductility, which can be completely bent by 180° without fracture, and no appreciable crack is observed even in the severely deformed area. In addition, the compositional ranges in which Al–La–M (M = Fe, Co or Ni) alloys can form single amorphous phase by melt spinning are relatively wide [9], indicating the alloys have high GFA. So in this paper, we added the small atom, Si, to Al–Fe–La alloys and studied the effect of Si substituting for Al on the GFA and thermal ability on Al–Fe–La alloy system.

2. Experimental

The samples of $Al_{88-x}Fe_6La_6Si_x$ ($x = 0, 0.5, 1–4$) used in this work were prepared by arc-melting the mixture of pure ingots of Al (99.9 mass%), Fe (99.96 mass%), La (99.5 mass%) and Si (99.9 mass%) in an argon atmosphere. Alloy ingots were remelted several times in order to homogenize alloy compositions. The ribbons of $Al_{88-x}Fe_6La_6Si_x$ ($x = 0, 0.5, 1–4$) were prepared by a single-roller melt-spinning technique under a partial argon atmosphere, the thickness of which is about 30–40 μm.

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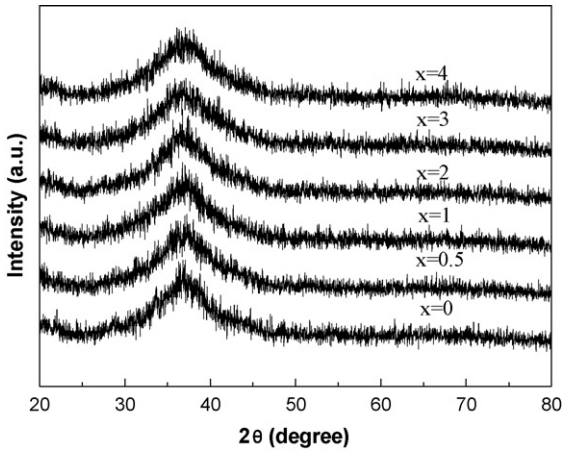

Fig. 1. XRD patterns of $Al_{88-x}Fe_6La_6Si_x$ (x = 0, 0.5, 1–4) amorphous alloys.

The diameter of the copper roller is 350 mm, and the circumferential speeds are 29.3 and 27.5 m/s.

The amorphous structure of the ribbons was examined by X-ray diffraction (XRD). The experiment was performed using a D/max-rB diffractometer with Cu Kα radiation. The thermal analysis of the melt-spinning ribbons was performed using a Netzsch DSC404 calorimeter under an argon atmosphere at a heating rate of 20 K/s.

Viscosity measurements were accomplished in a high vacuum atmosphere with an oscillating viscometer. Firstly, the samples of Al–Fe–La alloys, which were sealed in a vacuum of 10^{-3} Torr, were overheated to 250 K above liquidus temperature for 4 h. Then, the samples were cooled to the required temperature before the viscosity measurement was carried out by a torsional oscillation viscometer for high-temperature melts. Every Al–Fe–La sample was placed in an alumina crucible. (In this work, the crucible is columniform. The aspect ratio of the crucible is as follows: the inner diameter is 28 mm; the outer diameter is 32 mm; the height is 62 mm.)

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-quenched $Al_{88-x}Fe_6La_6Si_x$ (x = 0, 0.5, 1–4) ribbons at the same cooling rate of 29.3 m/s. Typical broad peaks are obtained for the samples at about 2θ = 36–38° and no distinct diffraction peaks corresponding to crystalline phases are observed, indicating fully amorphous structures.

Fig. 2 shows the differential scanning calorimetry (DSC) curves of $Al_{88-x}Fe_6La_6Si_x$ (x = 0, 0.5, 1–4) amorphous alloys. T_x (the onset crystallization temperature) and T_m (the onset melting temperature) are marked by arrows in the DSC curves. There is no distinct glass transition (T_g) before crystallization of these amorphous alloys. This may be due to some small fraction of crystallites

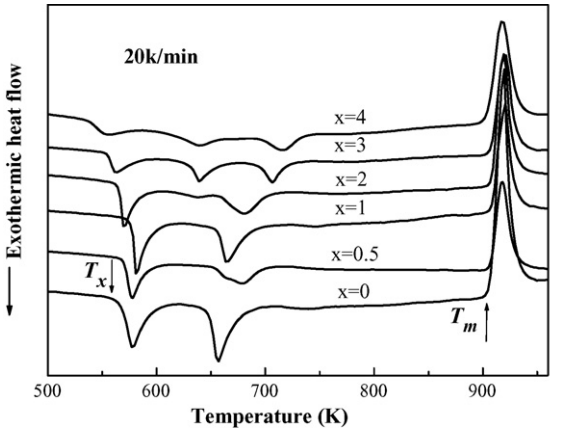

Fig. 2. Differential scanning calorimetry (DSC) curves of melt-spun $Al_{88-x}Fe_6La_6Si_x$ (x = 0, 0.5, 1–4) ribbons at a heating rate of 20 K/min.

Table 1
The related parameters of the $Al_{88-x}Fe_6La_6Si_x$ amorphous alloys

Alloys	T_x (K)	T_m (K)	$T_{rx} = T_x/T_m$	$\Delta T_m = T_m - T_x$ (K)
$Al_{88}Fe_6La_6$ (x = 0)	568	908	0.625	340
$Al_{87.5}Fe_6La_6Si_{0.5}$ (x = 0.5)	570	908	0.628	338
$Al_{87}Fe_6La_6Si_1$ (x = 1)	578	908	0.636	330
$Al_{86}Fe_6La_6Si_2$ (x = 2)	564	909	0.621	345
$Al_{85}Fe_6La_6Si_3$ (x = 3)	555	908	0.611	354
$Al_{84}Fe_6La_6Si_4$ (x = 4)	540	905	0.597	365

which may form initially during rapid cooling. The DSC curves of $Al_{85}Fe_6La_6Si_3$ and $Al_{84}Fe_6La_6Si_4$ alloys exhibit three exothermic peaks, respectively, indicating that structural transformation takes place in three single steps. However, for other Al–Fe–La amorphous alloys, the curve of each alloy shows a two-step crystallization process. In other words, the addition of Si influences the crystallization behaviors of Al–Fe–La amorphous alloys, transforming from two-step crystallization process to three-step crystallization process.

The thermal parameters of the samples such as T_x and T_m of $Al_{88-x}Fe_6La_6Si_x$ (x = 0, 0.5, 1–4) alloys are listed in Table 1. We also calculated ΔT_m ($\Delta T_m = T_m - T_x$) and T_{rx} ($T_{rx} = T_x/T_m$) of $Al_{88-x}Fe_6La_6Si_x$ (x = 0, 0.5, 1–4) alloys, the results are listed in Table 1. From Table 1, it can be seen that T_x increases from 567.5 to 577.6 K with the increase of x from 0 to 1, demonstrating a higher thermal ability [7,10]. However, when $x > 1$, T_x decreases from 577.6 to 539.8 K. So the thermal ability of $Al_{87}Fe_6La_6Si_1$ is best. Moreover, when x = 1, the value of ΔT_m is the smallest of all the amorphous alloys, in reverse to the change of T_x. Also, it can be noticed that the change of T_{rx} is consistent with that of T_x, i.e. $Al_{87}Fe_6La_6Si_1$ amorphous alloy has the highest value of 0.636 in all the alloys. It can be clearly seen the inter-relationship of T_x, T_{rx} and ΔT_m in Fig. 3. Inoue [11] has proposed T_x/T_m and ΔT_m as the criterions of the GFA. In this argument, it is proved that in some amorphous alloy systems larger T_x/T_m and lower ΔT_m usually correspond to better GFA. Based on the data listed in Table 1, these criterions suggest that the $Al_{87}Fe_6La_6Si_1$ amorphous alloy has the best GFA. But the result is different from that of the viscosity.

Generally speaking, the value of viscosity is larger, the GFA is better. The viscosity of $Al_{88-x}Fe_6La_6Si_x$ (x = 0, 0.5, 1–4) amorphous alloys was measured using an oscillating viscometer. Fig. 4 shows the experiment viscosity data for Al–Fe–La–Si alloys at high temperatures. It can be seen clearly that the value of viscosity for $Al_{86}Fe_6La_6Si_2$ alloy is largest, which implies this alloy has the best GFA. Xia et al. proposed a calculable parameter ε, defined as a negative ratio of mixing entropy to mixing enthalpy, to evaluate the GFA of metallic glasses from the viewpoint of a competition of disordering against ordering [12]. They found that the likely formation area of bulk metallic glass could be conservatively restricted within

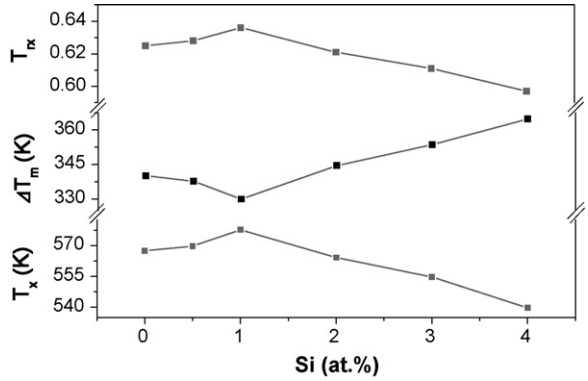

Fig. 3. Inter-relation of T_{rx}, T_x and ΔT_m of $Al_{88-x}Fe_6La_6Si_x$ (x = 0, 0.5, 1–4).