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Fragility and glass forming ability of Al-Ni-Ce alloy melts①

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Abstract: The fragility of Al-Ni-Ce alloy melts with three kinds of different compositions, Al85Ni10Ce5, Al85Ni8Ce7, Al85Ni5Ce10(mole fraction, %), was studied using oscillating-vessel viscometer and differential scanning calorimetry. Their fragility parameters obtained from experiments and theoretic calculation are: 238, 228 and 335 respectively. The results indicate that these three kinds of Al-Ni-Ce alloy melts are very fragile liquids, which kinetically show strong non-Arrhenius behaviour in the Angell plot, so they have poor glass forming ability (GFA). The alloy melt Al85Ni5Ce10 has the largest fragility parameter among the three alloy melts. In the preparation of rapidly quenched amorphous ribbons, Al85Ni10Ce5 and Al85Ni8Ce7 can gain amorphous ribbons when the rotate speed of the roller reaches 800 r/min, while for Al85Ni5Ce10 it must exceed 1 000 r/min.

Key words: fragility parameter; viscosity; amorphous; glass forming ability; Al-Ni-Ce alloy
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1 INTRODUCTION

Since Angell put forward the conception of the liquid's fragility, the fragility of liquid has been widely studied in many materials. Fragility has become an important parameter of material's physical characters. The liquids of materials can be divided into two groups: fragile and strong[1], or three categories: strong, intermediate and fragile[2, 3]. It was found that there is a close relation between the fragility and the glass forming ability. The more fragile a liquid is, the poorer its GFA is. As the amorphous materials have good performances in many aspects and are used widely, the study on their fragility has important theoretical and realistic significance.

Up to now, there are many studies on fragility of polymers, organic compounds and some ternary, quaternary, quinary bulk metallic glass (BMG) former alloys, which are often Zr, La, Pt, Au and the like transition metals based alloys. Few studies have been done on Al metal based alloys. In this study, the viscosity measurement was performed on the alloys at high temperature using oscillating-vessel viscometer, the viscosity in the supercooled liquids area was calculated with the Vogel-Fulcher-Tammann (VFT) equation[4, 5] and compared with the differential scanning calorimetry (DSC) measurements of the rapidly quenched amorphous ribbons.

2 EXPERIMENTAL

Elemental Al (99.9% in purity), Ni (99.7% in purity) and Ce (99.5% in purity) were used to prepare the alloys with the nominal compositions of Al85Ni10Ce5, Al85Ni8Ce7 and Al85Ni5Ce10 (mole fraction, %). The charges were melted in a graphite crucible using a medium frequency induction electric furnace under an inert argon atmosphere, and then were cast into ingots with iron chill moulds. The thick rods were machined into samples of d 27 mm × 48 mm for the measurement of high-temperature viscosity. The thin rods (2 - 3 cm) were used to prepare amorphous ribbons.

The viscosity measurements were carried out with a torsional oscillation viscometer for high-temperature melts[6, 7]. The kinematic viscosity of the liquid sample can be calculated by the Shvidkovskii equation [7]

$$\upsilon = \frac{I^2(\delta - T\delta_0/T_0)^2}{\pi(MR)^2 T W^2} \tag{1}$$

where

$$W = 1 - \frac{3}{2}\Delta - \frac{3}{8}\Delta^2 - a + (b - c\Delta)\frac{2nr}{H}$$

where $\Delta = \delta/2\pi$, and a, b and c are constants; r is the radius of the vessel; H is the height of the liquid sample in the vessel; n is the number of solid planes contacted horizontally by the liquid sample (i.e. in the case of a vessel having its lower end closed and its upper surface free, $n = 1$, if the vessel encloses the fluid top and bottom, $n = 2$). M represents the mass of the liquid sample, I is the momentum of inertia of the suspended system, δ is the logarithmic damping decrement, T is the periodic time of the oscillations, while the subscript "0" refers to an empty vessel. The dynamic viscosity η can be calculated us-

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ing the following formula: $\eta = v\rho$, where ρ is the density of the sample.

The amorphous ribbons were prepared using a single roller melt spinning apparatus. The prealloyed thin rods were remelted by high-frequency induction heating and then melt-spun onto a spinning copper roller with a diameter of 350 mm in a controlled inert argon atmosphere. The thickness of the amorphous ribbons is 0.03 − 0.05 mm. For Al85Ni10Ce5 and Al85Ni8Ce7, amorphous ribbons can be prepared at the rotating speed of 800 r/min, while for Al85Ni5Ce10 the rotating speed must exceed 1 000 r/min. The specimens of amorphous ribbons were analyzed by XRD and the thermal properties of amorphous ribbons and crystals were measured by a high-temperature Netzsch DSC404 system.

3 RESULTS

Fig. 1 shows the viscosity measurement results for liquids of Al85Ni10Ce5, Al85Ni8Ce7 and Al85Ni5Ce10 with oscillating-vessel viscometer.

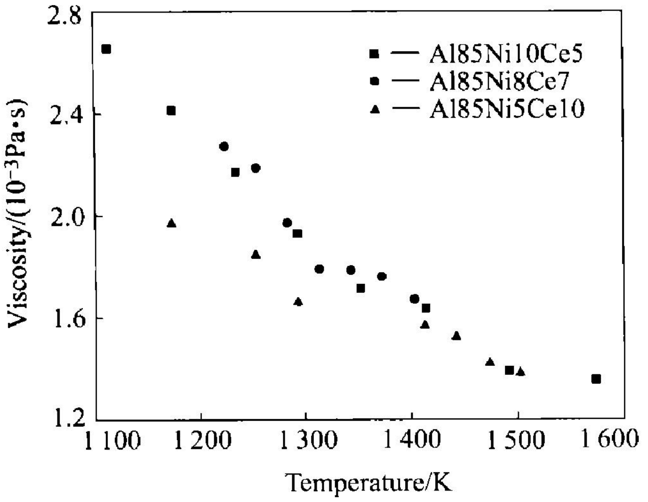

Fig. 1 Viscosity of liquid Al85Ni10Ce5, Al85Ni8Ce7 and Al85Ni5Ce10

Arrhenius relation can fit the viscosity over melting point:

$$\eta = \eta_0 \exp(E/RT) \quad (2)$$

where η_0 is the viscosity parameter relation to the nature of the liquid, E is an activation energy and R is the gas constant. In order to fit conveniently, A is used instead of E/R, and A can be seen as an activation energy or a scale of the activation energy. Then Eqn. (2) can be rewritten as

$$\eta = \eta_0 \exp(A/T) \quad (3)$$

The measured data of viscosity were fitted with Eqn. (3). The fitted parameters η_0 and A are listed in Table 1.

The three amorphous ribbons of Al-Ni-Ce alloy were analyzed in a DSC at a continuous heating rate of 20.0 K/min. The DSC results are shown in Fig. 2. The glass transition point (T_g), which is indicated by the gradual increase of the specific heat capacity in the DSC scan[8], can be gotten. A comparison of DSC curves of the crystal at the same continuous heating rate of 20.0 K/min is given in Fig. 3. And the melting point (T_m) is gained. The values of T_g and T_m are listed in Table 2.

For some supercooled liquids, such as SiO_2 and GeO_2, which have a three-dimensional tetrahedral network structure, the Arrhenius law (Eqn.

Table 1 Fitted parameters of Al85Ni10Ce5, Al85Ni8Ce7 and Al85Ni5Ce10

Alloy	η_0/(10^{-3}Pa·s)	A/K
Al85Ni10Ce5	0.240 31	2 690.625
Al85Ni8Ce7	0.181 52	3 084.595
Al85Ni5Ce10	0.426 22	1 804.952

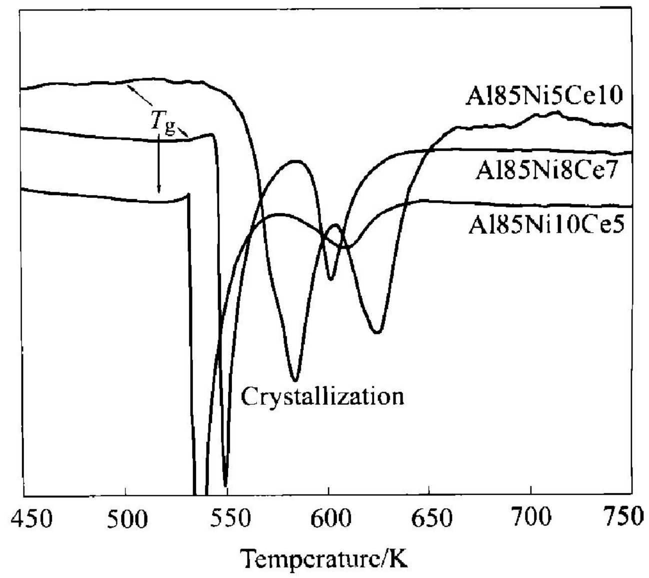

Fig. 2 DSC curves of amorphous ribbons of Al-Ni-Ce alloy at heating rate of 20.0 K/min

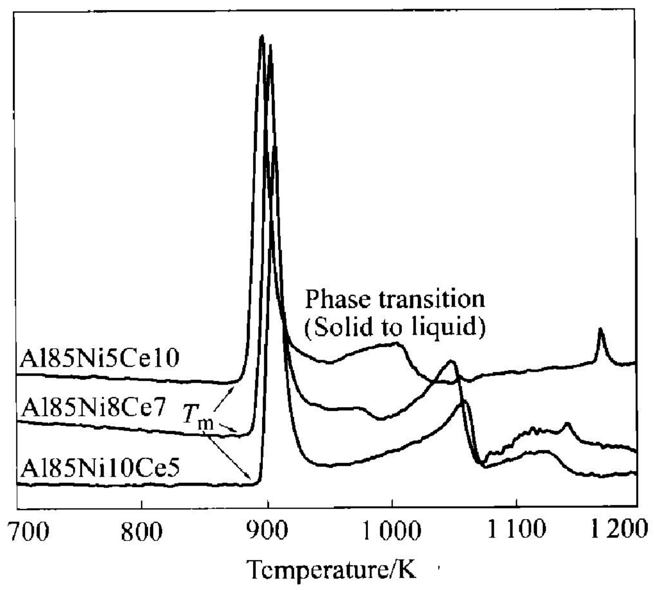

Fig. 3 DSC curves of crystals of Al-Ni-Ce alloy at heating rate of 20.0 K/min

Table 2 T_m and T_g of Al-Ni-Ce alloys

Alloy	T_g/K	T_m/K
Al85Ni10Ce5	519	889
Al85Ni8Ce7	535	881
Al85Ni5Ce10	502	873

(2)) can be used to fit $\eta(T)$ over the entire temperature range between T_m and T_g[9]. All other glass-forming liquids exhibit varying degrees of departure from Arrhenius behaviour[10]. But all equilibrium viscosity data obtained in the supercooled liquid can be described well with the Vogel-Fulcher-Tammann (VFT) relation[4, 10]:

$$\eta = \eta_0 \exp[B/(T - T_0)] \quad (4)$$

where η_0, B and T_0 are fitting parameters and T is the temperature. η_0 can be gotten from the fitting results by Eqn. (3). Although the change of viscosity is different between high temperature liquid and supercooled liquid, generally, at the critical point T_m the change of viscosity is continuous. And the transition point is defined as the point where $\eta = 10^{12}$ Pa·s[2, 11]. Two relations can be gained as:

$$\eta_m = \eta_0 \exp[B/(T_m - T_0)] \quad (5)$$

$$\eta_g = \eta_0 \exp[B/(T_g - T_0)] \quad (6)$$

where η_m can be gained from the fitting results by Eqn. (3), and $\eta_g = 10^{12}$ Pa·s. The parameters B and T_0, obtained from Eqns. (5) and (6), are listed in Table 3.

Table 3 Parameters B and T_0 of Al-Ni-Ce alloy

Alloy	B/K	T_0/K
Al85Ni10Ce5	1 222.7	485.0
Al85Ni8Ce7	1 340.9	498.0
Al85Ni5Ce10	814.8	479.0

There are two forms of dynamic fragility parameter. One is the D^* in VFT form described by the Vogel-Fulcher-Tammann relation[2, 12]:

$$\eta = \eta_0 \exp[D^* T_0/(T - T_0)] \quad (7)$$

and the other is put forward by B 9 hmer et al[3, 13, 14], which is defined as

$$m = \left. \frac{\mathrm{d}\lg \tau(T)}{\mathrm{d}(T_g/T)} \right|_{T = T_g} \quad (8)$$

where $\tau(T)$ is a characteristic temperature-dependent relaxation time. Since the viscosity is proportional to a structural relaxation time, m can be estimated by replacing $\tau(T)$ with $\eta(T)$ in Eqn. (8). Then, the fragility parameter can be obtained as the steepness of the slope of the viscosity curve at T_g[10].

Putting the VFT relation of viscosity into Eqn. (8), then one gets[10]

$$m = \frac{BT_g \lg e}{(T_g - T_0)^2} \quad (9)$$

From Eqn. (9) and the parameters B, T_g and T_0, the value of the fragility parameter can be gotten. The obtained fragility parameter of Al85Ni10Ce5, Al85Ni8Ce7 and Al85Ni5Ce10 are 238, 228, 335, respectively. All values have been rounded to the nearest integer.

4 DISCUSSION

In Fig. 4 the viscosities of three kinds of Al-Ni-Ce alloys are compared with other glass forming liquids in a fragility plot[1]. The fragility concept was proposed to classify materials according to the temperature dependence of their kinetics in liquid and supercooled liquid state. In the fragility plot the logarithm of viscosity data are normalized to the transition temperature, T_g, where the viscosity is found to be 10^{12} Pa·s[1, 2, 12]. Liquids, such as SiO_2, whose viscosities exhibit Arrhenius behavior and remain high in the molten state, are termed as strong liquids. Fragile liquids, in contrast, have low melt viscosities and exhibit a dramatic change in viscosity as the temperature is close to T_g[15].

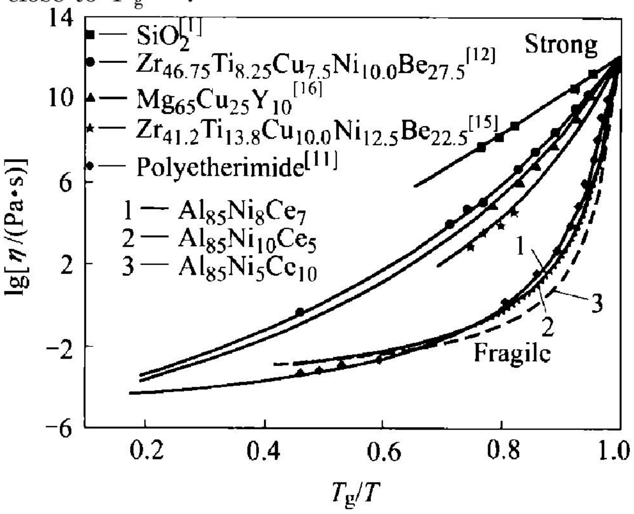

Fig. 4 Comparison of fragility of Al-Ni-Ce alloys with bulk metallic glasses and non-metallic "strong" and "fragile" glasses

According to Fig. 4, this three kinds of aluminium based alloys are very fragile liquids, the glass forming abilities (GFA) are poor. They GFAs are consistent with the results concluded from the nucleant ratio dependence of the normalized temperature T_{rg}, $T_{rg} = T_g/T_m$. When $T_{rg} \leqslant 1/2$, within a quite wide temperature range the nucleant ratio is so high that there is no probability to form glass; when $T_{rg} \geqslant 2/3$, the nucleant ratio is so low that glass can form under a very low cooling rate; when $T_{rg} \approx 1/2$, the cooling rate must reach 10^6 K/s if one wants to obtain glass. The T_{rg} temperatures of the three alloys are: 0.58

(Al85Ni10Ce5), 0.61 (Al85Ni8Ce7), 0.57 (Al85Ni5Ce10) respectively, which are between 1/2 and 2/3.

5 CONCLUSIONS

1) The fragility parameters of Al-Ni-Ce alloy melts with three kind of different composition, Al85Ni10Ce5, Al85Ni8Ce7, Al85Ni5Ce10, were studied using oscillating-vessel viscometer and differential scanning calorimetry. Their fragility parameters were obtained from experiments and theoretic calculation. These alloy melts and their fragility parameters (all values have been rounded to the nearest integer) are: Al85Ni10Ce5, 238; Al85Ni8Ce7, 228; Al85Ni5Ce10, 335, respectively. The results indicate that these three kind compositions of Al-Ni-Ce alloy melts are very fragile liquids that, kinetically, show strong non-Arrhenius behaviour in the Angell plot. And they have poor glass forming ability (GFA).

2) In the three alloy melts Al85Ni5Ce10 has the largest fragility parameter (m = 335), its GFA is worse than the others. This can be proved in the preparation of rapidly quenched amorphous ribbons. Al85Ni10Ce5 and Al85Ni8Ce7 can gain amorphous ribbons when the rotating speed reaches 800 r/min, while for Al85Ni5Ce10 it must exceed 1 000 r/min.

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