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Effects of TM on stability of structure corresponding to prepeak of amorphous $\text{Al}_{90}\text{TM}_5\text{Ce}_5$ Alloys^①

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[Abstract] X-ray diffraction and DSC were used to investigate the crystallization process of amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ and $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys, and the stability of the structure corresponding to the prepeak. Both these amorphous alloys are crystallized by two stages. The stability of the structure corresponding to the prepeak has a large difference. The structure corresponding to the prepeak for amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloy is more stable than the amorphous matrix. However, it is not stable for amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys during the first crystallization stage. The prepeak position of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys is very close to that of amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys. It is estimated that the prepeak is also due to diffraction peak broadening caused by very fine quasi-crystalline structure and the structural unit is an icosahedral quasi-crystalline structure with Ni as the central atom. The large difference of the stability of the structure corresponding to the prepeak is likely caused by different stability of the quasi-crystalline structure.

[Key words] amorphous $\text{Al}_{90}\text{TM}_5\text{Ce}_5$ alloy; prepeak; stability; crystallization

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1 INTRODUCTION

The amorphous alloys in Al-TM-RE systems with aluminum content up to 90% have been found to have extraordinary high strength combined with good ductility^[1,2]. Furthermore, it has been found that a homogeneous dispersion of fcc Al particles within the amorphous matrix after heat treatment can significantly increase the tensile strength combining with good bending ductility as compared with those for the amorphous single phase alloys with the same composition^[3,4]. The DSC results of the amorphous Al alloys usually exhibit two or three crystallization peaks. The first peak, the primary crystallization peak, is caused by the precipitation of Al nano-particles in the residual amorphous matrix. Usually, the formation of nanocrystals with excellent mechanical properties in Al-based alloys is not made directly by quenching but rather by overquenching to generate a fully amorphous state and thus the glass phase is then partially devitrified to produce a nanometer-scale dispersion of Al crystallites in a glassy matrix because the annealing process is easily controllable^[5]. In order to tailor the microstructures and the related properties, a clear understanding of the devitrification behavior of Al-based glasses is needed. The replacement of Ni by Fe increases the thermal stability of the amorphous Al-based alloys, which is ultimately interpreted by the fact that Fe has stronger interaction with Al than Ni, however, the

mechanism of the enhancement of the thermal stability of the amorphous alloys is still not clear^[6]. Studying crystallization process has provided substantial knowledge about crystal nucleation and growth, and the thermal stability of an amorphous phase. However, the crystallization behavior of the present amorphous alloy system is not completely understood yet. In our work, prepeaks are found in the amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ and $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys, the small angle information of the X-ray diffraction pattern during crystallization process and the effects of the TM elements on the stability of the structure corresponding to the prepeak are investigated.

2 EXPERIMENTS

Ingots of Al-Ni-Ce and Al-Fe-Ce alloys with nominal composition were prepared by arc melting the mixture of high purity(99.99%) Al, Ni(or Fe) and(99.9%) Ce in an argon atmosphere. Amorphous ribbons were prepared by a single roller melt-spinning technique under a partial argon atmosphere. The diameter of the copper roller is 35 cm, with a typical circumferential velocity of 40 m/s. The ribbons are about 2 mm in width and 25 μm in thickness.

The structure of the ribbon samples was examined by X-ray wide-angle diffraction(XRD) with Cu K_α radiation($\lambda = 0.1542\text{ nm}$) coupled with a graphite monochromator in the diffraction beam. The scattering

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intensity measured in arbitrary unit could be converted into the coherent scattering intensity per atom in electron units, using the generalized Krogh-Moe-Norman method^[7] with the atomic scattering factor including the anomalous dispersion factor^[8]. Compton scattering was also corrected using the values given by Cromer and Mann^[9]. Then, the total structure factor $S(Q)$ was obtained from the scattering intensity, where $Q = 4\pi \sin \theta / \lambda$ is the magnitude of the scattering vector and λ is the wavelength^[7]. A parabolic-like function $f(x) = ax^2 + bx^3$, in which b is often much smaller than a , was used to fit the small-angle part of $S(Q)$ ^[10]. Thermal analysis was performed using a Netzsch DSC-404 system under a pure argon atmosphere at heating rate of 10 °C/min.

3 RESULTS

Fig. 1 (a) and Fig. 2 (a) show the XRD patterns of the as-quenched $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ and $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ ribbons, respectively. The broad diffuse peaks indicate that both the as-quenched

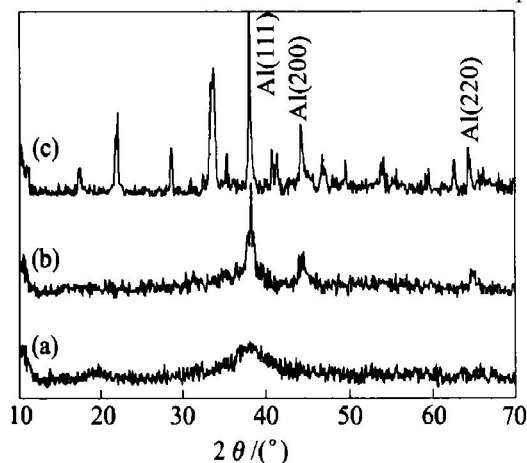


Fig. 1 X-ray diffraction patterns of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys at different temperatures
(a) $-25\text{ }^{\circ}\text{C}$; (b) $-230\text{ }^{\circ}\text{C}$; (c) $-360\text{ }^{\circ}\text{C}$

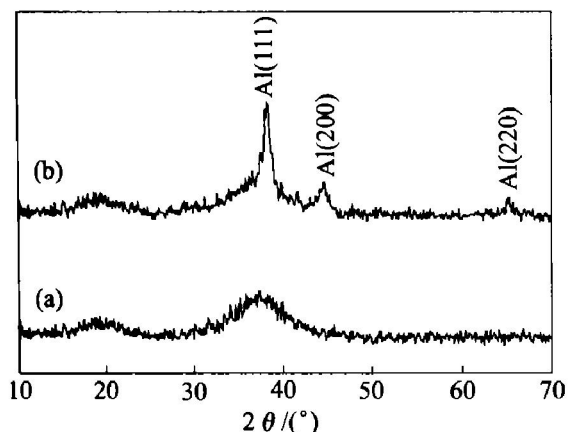


Fig. 2 X-ray diffraction patterns of amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys at different temperatures
(a) $-25\text{ }^{\circ}\text{C}$; (b) $-260\text{ }^{\circ}\text{C}$

$\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ and $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ ribbons are amorphous. The most intriguing feature is the existence of the prepeak, which is located at nearly $2\theta = 20^{\circ}$ for $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ amorphous alloys and at around $2\theta = 19.5^{\circ}$ for $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ amorphous alloys. The total structure factors of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys are shown in Fig. 3. The main peak is located at around 27 nm^{-1} . It can also be seen that a prepeak exists in the structure factors of amorphous alloys. The statistic error in the position of the peak has been evaluated by the method developed by Egami^[11] and the error in the position of the prepeak is relatively large due to its broad shape. The prepeak position is 14.0 nm^{-1} , with the statistic error about $\pm 0.5\text{ nm}^{-1}$. In the previous work^[12~14], the prepeak has been found existing in the total structure factors of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ amorphous alloys and locates at around 13.8 nm^{-1} . The prepeak position of $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ amorphous alloys is very close to that of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ amorphous alloys.

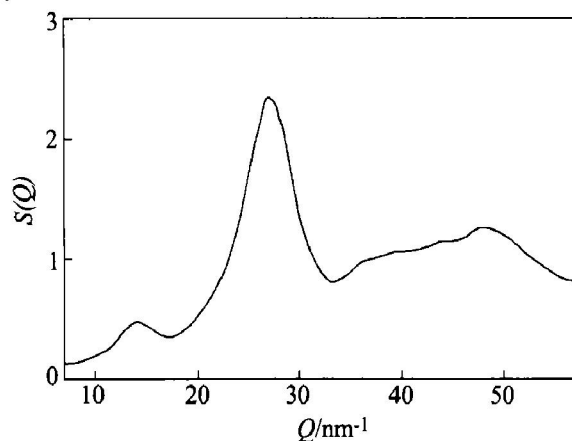


Fig. 3 Total structure factors of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys

Fig. 4 shows the DSC curves of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ and $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys, respectively. Two exothermic peaks are observed in each DSC curve. The first exothermic peak is very weak at low temperature and no glass transition is found. The second peak is at high temperature with strong exothermic peak. The crystallization onset temperature is about $110\text{ }^{\circ}\text{C}$ for the amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys and about $165\text{ }^{\circ}\text{C}$ for amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys. The crystallization onset temperature of the amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys is much higher than that of the amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys.

X-ray diffraction patterns at different temperatures of the amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys are shown in Fig. 1 (b) and (c). At $230\text{ }^{\circ}\text{C}$, after the first crystallization peak temperature, the prepeak disappears and fcc Al phase appears, at $360\text{ }^{\circ}\text{C}$, several intermetallic compounds indicated as Al_3Ni and $\text{Al}_{11}\text{Ce}_3$ phases are

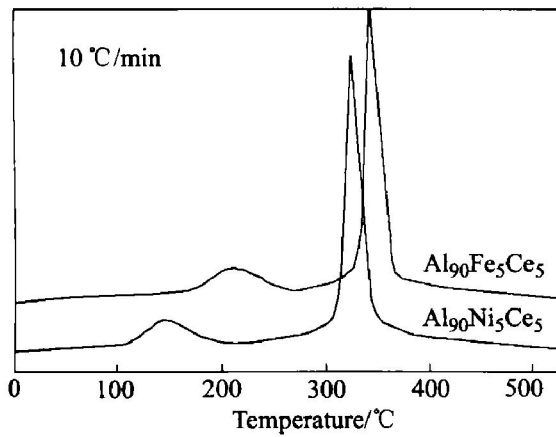


Fig. 4 DSC curves of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ and $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys

formed. Fig. 2(b) shows the XRD patterns of amorphous alloys at 260 °C after the first crystallization peak temperature for amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys, it can be seen the fcc Al phase appears; however, the prepeak still exists in the XRD pattern, which is different with the amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys.

4 DISCUSSION

From Fig. 4 and Fig. 2(b), during the first crystallization stage for the amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys, fcc Al phase appears, the prepeak still exists in the XRD pattern. It indicates that the structure corresponding to the prepeak is more stable than the amorphous matrix. From Fig. 4 and Fig. 1(b), during the first crystallization stage for the amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys, fcc Al phase appears; however, the prepeak also disappears. It indicates that the structure corresponding to the prepeak is not stable during the first crystallization process for amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys. Accordingly, the stability of the structure corresponding to the prepeak is strongly related to the TM elements in the amorphous $\text{Al}_{90}\text{TM}_5\text{Ce}_5$ alloys. The structure corresponding to the prepeak of amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys is more stable than that of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys during the first crystallization process.

The prepeak shows that the chemical short-range order (or the structural unit) and the medium-range order (or the cluster) caused by strong chemical bonds exist in the amorphous alloys^[13, 14]. In the amorphous Al-Fe-Ce and Al-Ni-Ce alloys, both Al-Fe and Al-Ni have a strong chemical bonding due to s, p, d hybridization of Al and TM^[15, 16]. However, the stability of the structure corresponding to the prepeak has a large difference in amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ and $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys. In amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys, it is considered that the pre-

peak is due to diffraction peak broadening caused by very fine quasi-crystalline structure (0.5~2 nm), the structural unit size can be estimated according to a formula, $R = 2\pi/Q_p$, where Q_p is the prepeak position, and the structural unit is an icosahedral quasi-crystalline structure with Fe as the central atom^[13, 14]. The prepeak position of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys is very close to that of $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ amorphous alloys. Icosahedral quasi-crystal $\text{Al}_{86}\text{Ni}_{14}$ had been prepared by rapid quenching from the melt^[17]. Decagonal quasi-crystal was also reported in the Al_6Ni alloy^[18]. The decagonal quasi-crystal is believed to develop at slower solidification velocities than those required for the icosahedral phase and the decagonal quasi-crystal phase nucleates frequently on surfaces of growing dendrites of the icosahedral phase. Al-Ni icosahedral quasi-crystal and Al-Fe icosahedral quasi-crystal have the similar diffraction pattern and very close lattice parameter^[17]. Ce can increase quenching effect in Al based alloys and can form large volume fraction of icosahedral phases^[19]. Furthermore, Al-Fe and Al-Ni have almost the same bonding length. Therefore, it is estimated that the prepeak is also due to diffraction peak broadening caused by very fine quasi-crystalline structure and the structural unit is an icosahedral quasi-crystalline structure with Ni as the central atom for amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys. The stability of the icosahedral quasi-crystalline phase decreases with increasing concentration of 3d electron and the stability of Al-Ni icosahedral quasi-crystalline phase is much lower than that of the Al-Fe icosahedral quasi-crystalline phase^[17]. Al-Ni and Al-Fe icosahedral quasi-crystalline phase decompose at about 150 °C and 380 °C, respectively, with heating rate 20 °C/min^[17]. The crystallization temperature will shift to a little slower value at slower heating rate. This value is close in the range of the first exothermic peak in DSC curves for amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys. In addition to the stronger Al-Fe interaction than that of Al-Ni^[9] and the same Al-Ce pairs, the Fe-Ce interaction were deduced to be stronger than that of Ni-Ce pairs from the stability analysis of amorphous alloys^[20]. Therefore, the large difference of the stability of the structure corresponding to the prepeak is likely caused by the different stability of quasi-crystalline structure.

As shown in Fig. 4, the crystallization onset temperature of amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloy is much higher than that of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloy. Although they both have strong chemical bonding since they have the similar chemical bonding length which is much shorter than the sum of atomic metallic radius, their crystallization onset temperature has a large difference, about 55 °C. The enhanced chemical short-range order can in-

crease the stability of the amorphous matrix by inhibiting Al diffusion^[5]. As discussed above, the stability of the structure corresponding to the prepeak is strongly different during crystallization process. Since the structure corresponding to the prepeak of amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys is stable, it can inhibit Al diffusion during crystallization. Therefore, the large difference of the crystallization onset temperature is likely caused by the different stability of the structure corresponding to the prepeak during crystallization process.

5 CONCLUSIONS

1) The crystallization onset temperature of amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys is much higher than that of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys.

2) The structure corresponding to the prepeak for amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys is stable during the first crystallization stage. However, it is not stable for amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys.

3) The prepeak position of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys is very close to that of amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys. It is estimated that the prepeak for amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ alloys is due to diffraction peak broadening caused by very fine quasi-crystalline structure and the structural unit is an icosahedral quasi-crystalline structure with Ni as the central atom.

4) The large difference of the stability of the structure corresponding to the prepeak of amorphous $\text{Al}_{90}\text{Ni}_5\text{Ce}_5$ and $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys is likely caused by different stability of the corresponding quasi-crystalline structure. The higher crystallization onset temperature for amorphous $\text{Al}_{90}\text{Fe}_5\text{Ce}_5$ alloys is likely due to the more stable structure corresponding to the prepeak.

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