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Effects of quenching conditions on crystallization behavior of amorphous $Al_{90}Ni_5Ce_5$ alloys①

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Abstract: X-ray diffraction and DSC were used to investigate the crystallization behavior of amorphous $Al_{90}Ni_5Ce_5$ alloys at different quenching temperatures. All the amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at different temperatures crystallize by two stages. The first stage corresponds to FCC Al phase precipitating from the amorphous matrix. The crystallization onset temperature increases with increasing quenching temperature. The quenching temperature also influences the isothermal behaviors. At low quenching temperatures, the FCC Al precipitation is only through grain growth. At high quenching temperatures, the FCC Al precipitation is through growth of quenched-in Al nuclei and nucleation and growth of new crystallites. The reason that the crystallization onset temperature varies with quenching temperature is likely as that the quenched-in Al nuclei decreases with increasing temperature.

Key words: amorphous alloy; quenching condition; crystallization
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1 INTRODUCTION

Aluminum-based alloys produced by rapid solidification have great potential for elevated temperature applications. A group of amorphous alloys with aluminum content up to 90% (mole fraction), possessing excellent strength, have been discovered in several Al-TM-RE systems[1-3]. The as-quenched amorphous alloys are ductile and also exhibit other mechanical properties such as high hardness, wear and corrosion resistance[4-5]. Partial devitrification of these metallic glasses produces a very high density of FCC Al nanocrystals(10－20 nm) embedded in an amorphous matrix with excellent physical properties, such as high specific strength, good ductility, enhanced fracture strength and superior corrosion resistance[6-8]. It is necessary to study the glassy state so as to explain the transformation from a glassy state to a nano-cystalline state. In order to explain the unusual glass forming ability, the atomic structures of Al-based amorphous alloys have been investigated by neutron scattering[9], X-ray scattering[10] and EXAFS[11]. These studies have mainly focused on the statistical function, or the radical distribution function(RDF), which cannot reflect the strong local compositional and geometrical order and the micro-inhomogeneous structure of the amorphous alloys. The formation of metallic glasses by the melt spinning technique is strongly dependent on the processing parameters. One of the most important technical parameters is the quenching temperature, which can modify the viscosity of the melts[12]. However, the effects of the quenching temperature on the amorphous structure are lack. It has been reported that the quenching temperature can influence the micro-inhomogeneous structure in Al-Fe-Ce system[13-15]. In this work, we investigate the devitrification behavior of the amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at different temperatures.

2 EXPERIMENTAL

Ingots of Al-Ni-Ce alloys with nominal composition were prepared by arc melting the mixture of high purity Al, Ni and 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 was 35 cm, with a typical circumferential velocity of 40 m/s. The ribbons were about 2 mm in width and about 25 μm in thickness.

The amorphous structure of the ribbon samples was examined by X-ray diffraction(XRD) with Cu K_α radiation (λ= 0.154 2 nm) coupled with a graphite monochromator in the diffraction beam. Thermal analysis was performed using a Netzsch DSC-404 system under a pure argon atmosphere.

3 RESULTS AND DISCUSSION

The amorphous structure of the as-quenched $Al_{90}Ni_5Ce_5$ ribbons was examined by X-ray diffraction. Fig. 1

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shows the XRD patterns of the as-quenched $Al_{90}Ni_5Ce_5$ ribbons quenched at 1 175 ℃, 1 300 ℃ and 1 425 ℃, respectively. All the XRD patterns only contain broad diffuse peak. The broad diffuse peak indicates that the as-quenched ribbons at different quenching temperatures are all amorphous. The broad diffuse peak locates at nearly $2\theta = 38.2°$. According to the Ehrenst relation $R_{nn} = \lambda/1.626\,7 \times \sin\theta$, the broad peak position corresponds to the nearest neighbor distance 0.289 7 nm, which agrees well with values calculated from atomic diameter[16].

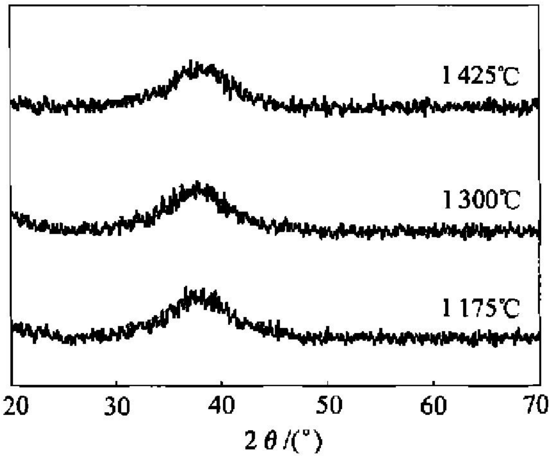

Fig. 1 XRD patterns of as-quenched $Al_{90}Ni_5Ce_5$ alloys quenched at 1 175 ℃, 1 300 ℃ and 1 425 ℃ respectively

Fig. 2 shows the DSC curves of amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at different temperatures. Two exothermic peaks are observed in each DSC curve. The first exothermic peak is very weak at low temperature. The second peak is at high temperature with strong exothermic peak. It can be seen that the second exothermic peak temperature is nearly not varied with quenching temperature. The crystallization onset temperature t_x and the first exothermic peak temperature t_{p1} are shown in Table 1. It is found that both the crystallization onset temperature t_x and first peak temperature t_{p1} increase as quenching temperature increases.

Table 1 Crystallization onset temperature, t_x, and first exothermic peak temperature, t_{p1} of amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at different temperatures

Quenching temperature	t_x/ ℃	t_{p1}/ ℃
1 175 ℃	102	128
1 300 ℃	114	145
1 425 ℃	144	176

X-ray diffraction patterns at different elevated temperatures of amorphous $Al_{90}Ni_5Ce_5$ alloy quenched at 1 300 ℃ are shown in Fig. 3. The thermal treatment were

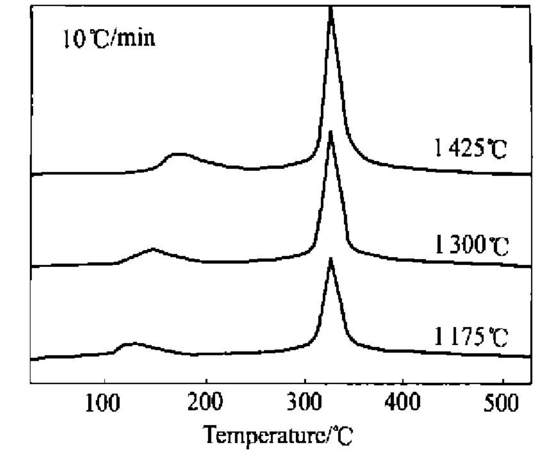

Fig. 2 DSC curves of amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at different temperatures

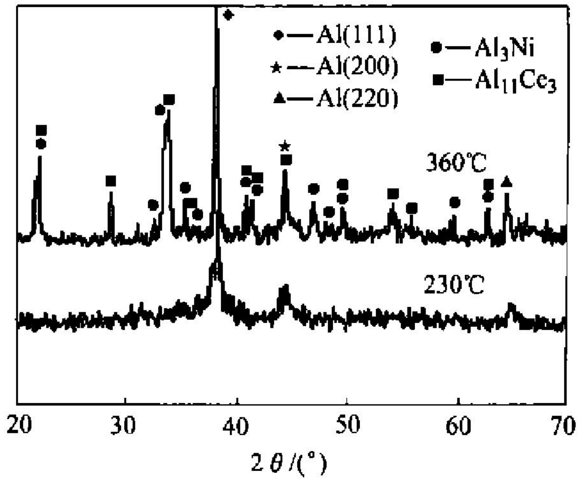

Fig. 3 XRD patterns of different temperatures of amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at 1 300 ℃

carried out by heating the samples at 10 ℃/min. At 230 ℃, after the first crystallization peak temperature, FCC Al phase appears. At 360 ℃, several intermetallic compounds indicated as Al_3Ni and $Al_{11}Ce_3$ phases are formed. Amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at 1 175 ℃ and 1 425 ℃ have the similar behaviors. From the analysis of these figures, the crystallization of amorphous $Al_{90}Ni_5Ce_5$ ribbons is by two stages.

A: amorphous $\longrightarrow$ α(Al) + amorphous′

B: amorphous′ $\longrightarrow$ α(Al) + Al_3Ni + $Al_{11}Ce_3$

It indicates that α(Al) phase precipitates from the amorphous matrix at the first crystallization stage.

Isothermal DSC was used to examine the precipitation behavior of the α(Al). The isothermal DSC curves obtained nearly at the onset temperature of the primary crystallization peak. Fig. 4 shows the isothermal DSC scans of amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at different temperatures. From the analysis of these curves, further information on the crystallization process and on

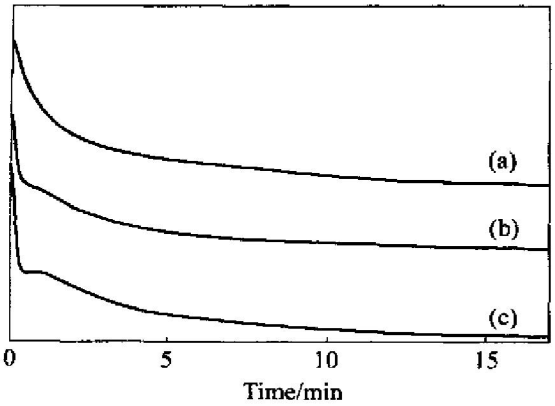

Fig. 4 Isothermal DSC curves
(a) —At 95 ℃ for amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at 1 175 ℃;
(b) —At 105 ℃ for amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at 1 300 ℃;
(c) —At 135 ℃ for amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at 1 425 ℃

the difference of their thermal stability can be revealed.

As shown in Fig. 4(a), for the amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at 1 175 ℃, a monotonically decreasing exothermic DSC signal can be observed. However, in Fig. 4(b) and (c) for amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at 1 300 ℃ and 1 425 ℃, respectively, an exothermic peak superimposed with this monotonical signal appears, the peak being more evident for Fig. 4(c).

According to the analysis by Inoue[17], a monotonically decreasing exothermic signal is only due to grain growth. That is, the FCC Al phase precipitates only through the growth mechanism without any nucleation stage from the amorphous matrix. The absence of nucleation stage for amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at 1 175 ℃ is due to the pre-existence of Al nuclei in the as-quenched amorphous structure. On the other hand, for amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at 1 300 ℃ and 1 425 ℃, the existence of two overlapping processes is proposed[18]: growth of quenched-in nuclei (decreasing of DSC signal), and nucleation and growth of new crystallites (explaining the presence of the exothermic peak) both induced during the isothermal heat treatment. It indicates that the amorphous alloys quenched at lower temperatures contain higher density of quenched-in Al nuclei.

It has been reported that the quenching conditions can not influence the crystallization onset temperature in Fe-B systems[19]. The crystallization onset temperature strongly relates to the amorphous structure after relaxation. The amorphous alloys are relaxed to the ideal glass structure before crystallization. Therefore, that the crystallization onset temperature is not correlated with quenching conditions in Fe-B system. However, in Ni-Zr system[20], the crystallization temperature increases with quenching temperature. The amorphous alloys quenched at low temperatures contain more chemical short-range order. That is, there are more local configurations close to intermetallic compound $NiZr_2$ so that less diffusion is required to form nuclei, which leads to the lower crystallization temperatures at low quenching temperatures. In the investigated amorphous $Al_{90}Ni_5Ce_5$ alloys, the quenching temperature influences the crystallization onset temperature. A relatively high density of quenched-in nuclei in amorphous $Al_{90}Ni_5Ce_5$ alloys quenched at low temperatures is consistent with their low crystallization quenching temperature. Therefore, that the crystallization onset temperature increases with increasing quenching temperature in amorphous $Al_{90}Ni_5Ce_5$ alloys is caused by the decreasing density of quenched-in nuclei.

4 CONCLUSIONS

1) The amorphous alloys quenched at different temperatures crystallize by two stages. The first stage corresponds to FCC Al precipitating from the amorphous matrix.

2) The quenching temperature influences the isothermal behaviors. At low quenching temperature, the FCC Al precipitation is only through grain growth. At high quenching temperatures, the FCC Al precipitation is through growth of quenched-in Al nuclei and nucleation and growth of new crystallites.

3) The crystallization onset temperature increases with increasing quenching temperature. It is likely caused by that the density of quenched-in Al nuclei decreases with increasing quenching temperature.

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