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Effect of quenching condition on micro-inhomogeneous structure of Al-Fe-Ce amorphous alloy①

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Abstract: The microstructures of liquid and amorphous $Al_{90}Fe_5Ce_5$ alloys were studied by X-ray diffraction (XRD), and the crystalline behavior of the amorphous alloy was also investigated by differential scanning calorimetry (DSC). The distinct pre-peaks were found on the structure factors of the liquid and amorphous alloys. The quenching temperature affects the pre-peak area, but does not affect its position. The reduction of quenching temperature decreases the crystallization temperature and the activation energy of the Al-Fe-Ce amorphous alloy. Quenched from 1 050 ℃, a novel structure with a fine dispersion of Al nanophase particles homogeneously distributed in the amorphous matrix was obtained. And the sensitivity of the Al-Fe-Ce amorphous alloy to the quenching temperature reflects the micro-inhomogeneity of the melt.

Key words: Al-Fe-Ce; amorphous alloys; micro inhomogeneous structure; quenching temperature
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1 INTRODUCTION

The effects of quenching temperature on Fe-based metallic glasses close to the eutectic region have been studied by Luborsky[1] and Brower[2]. They found that different quenching temperatures could cause some physical properties (such as electrical resistance and magnetism) changing obviously. Manov[3] tried to interpret this phenomenon by the free volume model, but there were still some difficulties to overcome. In fact, metallic glasses quenched from different temperatures correspond to different atomic structures, but little work has been done in this field. People often lay particular stress on the cooling rate[4] and the metallic glasses close to the eutectic region which are single phase homogeneously in liquid state, neglecting quenching temperature[5]. The structural information at small angles is often ignored, however, the presence of a pre-peak at smaller angles can be attributed to the strong correlation between different atoms, which has the characteristic of medium-range order (MRO)[6]. This MRO structure appears frequently in covalent glasses[7], but seldom in metallic ones. In this paper, we choose the Al-Fe-Ce amorphous alloy with Al content of 90% (mole fraction) as the research object to investigate the effects of liquid structure and quenching temperature on the chemical short-range order (CSRO) and crystalline behavior of the amorphous alloy.

2 EXPERIMENTAL

Ingots of the Al-Fe-Ce alloy were obtained by high purity elements in an arc furnace under argon atmosphere. Amorphous ribbons were prepared by the single roller melt-spinning technique under a partial argon atmosphere. The typical circumferential velocity is 30 m/s. The ribbons were 2 ~ 3 mm in width and 20 μm in thickness.

Using a Netzsch DSC-404 system under a pure argon atmosphere, thermal analysis was performed. The structure of liquid and amorphous alloys have been investigated with X-ray wide-angle diffractometer (Mo K_α radiation), the wavelength λ is 0.071 nm. The scattering intensity measured in arbitrary units can be converted into the coherent scattering intensity per atom in electron units, using the generalized Krogh-Moe-Norman method[8]. Then, the Ashcroft-Langreth structure factor $S(Q)$ can be obtained from the scattering intensity, where $Q = (4\pi/\lambda)\sin\theta$ is the magnitude of the scattering vector. And the factor $S(Q)$ has been normalized.

3 RESULTS

Fig.1 and Fig.2 show the total structure factors of liquid $Al_{90}Fe_5Ce_5$ alloy, and those of amorphous $Al_{90}Fe_5Ce_5$ alloy quenched from different temperatures respectively. The pre-peak position ($Q = 13.8$ nm^{-1}) and the first peak position ($Q = 26.5$ nm^{-1}) are constant, having nothing to do with the melt and quenching temperature. When decreasing either the melt or the quenching temperature the intensity of the first peak and pre-peak increase. On the X-ray intensity curves, the ratio of the pre-peak area (the integrated intensity of the diffraction curve) to the total area of the X-ray intensity curve can reflect the ratio

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of the structure corresponding to the pre-peak in the matrix. Fig.3 shows $S_{pre\text{-}peak}/S_{total}$ of amorphous $Al_{90}Fe_5Ce_5$ alloy quenched from different temperatures. The structure corresponding to the pre-peak increases with decreasing quenching temperature. We may linearly extrapolate the total structure factors of liquid $Al_{90}Fe_5Ce_5$ alloy

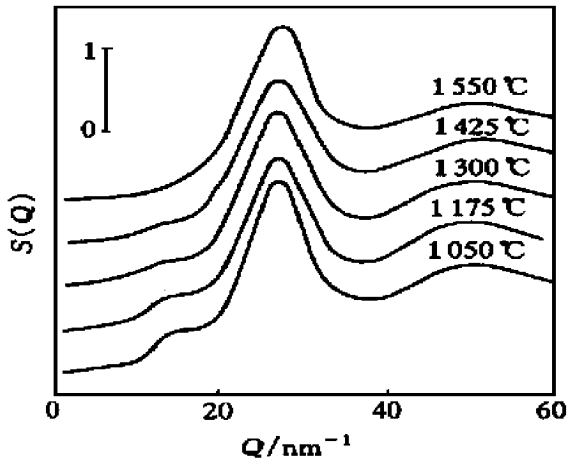

Fig.1 The pre-peak disappears at quenching temperature of 1 557 ℃.

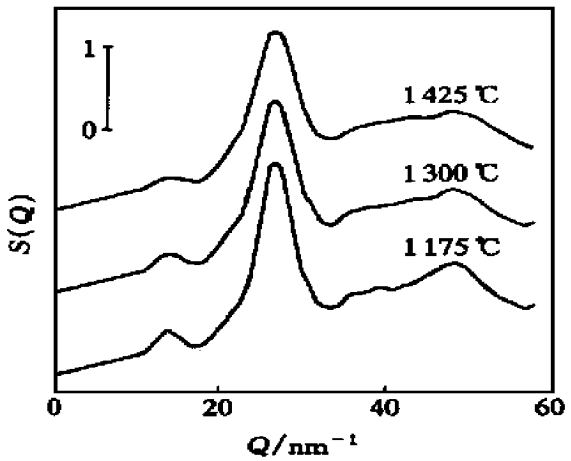

Fig.2 Total structure factors of amorphous $Al_{90}Fe_5Ce_5$ alloy quenched from different temperatures

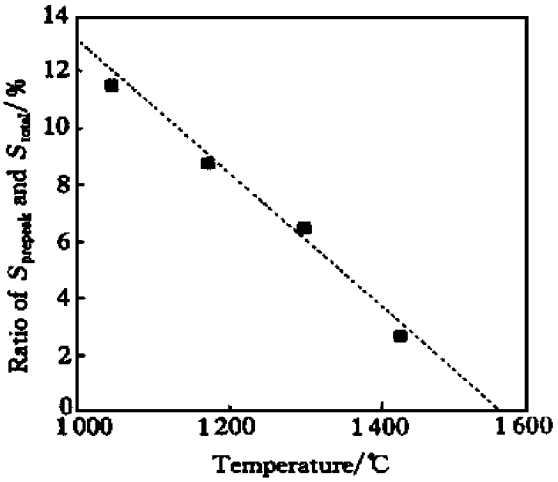

Fig.3 $S_{pre\text{-}peak}/S_{total}$ of amorphous $Al_{90}Fe_5Ce_5$ alloy quenched from different temperatures

for the disappearance of the pre-peak. The pre-peak disappears at quenching temperature of 1 557 ℃.

At lower quenching temperature of 1 050 ℃, only partial amorphous structure was obtained. Then the X-ray intensity curve of amorphous $Al_{90}Fe_5Ce_5$ alloy is given in Fig.4. The crystalline diffraction peaks are piled on top of the amorphous humpbacked peak, and the crystalline peaks are determined as fcc-Al diffraction peaks. Since the microcrystallite can cause peak broadening, according to Scherrer's law we then estimate the Al particle size to be about 40 nm.

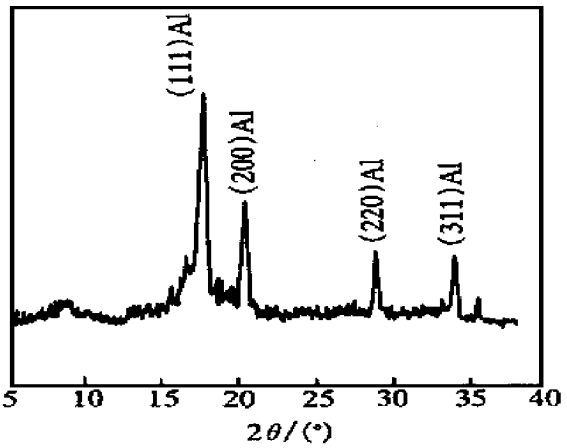

Fig.4 X-ray pattern of amorphous $Al_{90}Fe_5Ce_5$ alloy quenched from 1 050 ℃

According to the formula[10]: $R = 2\pi/Q_{pp}$, where Q_{pp} is the pre-peak position, we can estimate the structural unit size corresponding to the pre-peak R. The structural unit sizes corresponding to the pre-peaks of liquid and amorphous $Al_{90}Fe_5Ce_5$ alloys are shown in Fig.5, which are almost the same, and they imply that reaction happens between the liquid structure and the amorphous structure.

DSC continuous heating curves for amorphous $Al_{90}Fe_5Ce_5$ alloy quenched from different temperatures are given in Fig.6. At the quenching temperature of 1 175 ℃, an exothermic peak is seen at 302.6

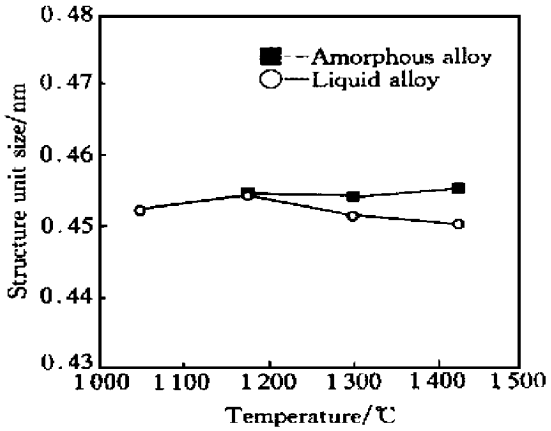

Fig.5 Structural unit sizes of liquid and amorphous $Al_{90}Fe_5Ce_5$ alloys

℃ with a crystallization activation energy of 247.7 mW; at 1 300 ℃, there are two exothermic peaks, the first peak is weaker and the second peak is found at 348.2 ℃ with a crystallization activation energy of 333.69 mW; at 1 425 ℃, there are also two exothermic peaks, the second is at 383.8 ℃ with a crystallization activation energy of 389.72 mW. From the results above, we can conclude that the elevation of quenching temperature weakens the micro-inhomogeneity in the amorphous alloy and increases the difficulty of crystallization. It is also shown that the micro-inhomogeneous structure in the melt increases with decreasing temperature. In order to further understand the crystallization process, X-ray measurements were carried out according to the DSC curves. Fig.7 shows the X-ray patterns at different temperatures of amorphous $Al_{90}Fe_5Ce_5$ alloy quenched from 1 300 ℃. At ambient temperature, the microstructure of $Al_{90}Fe_5Ce_5$ alloy is all amorphous and a pre-peak is found at the scattering angle of 9.5°; at 250 ℃, fcc-Al particles appear and the pre-peak still exists; at 400 ℃, the sample contains most Al phase

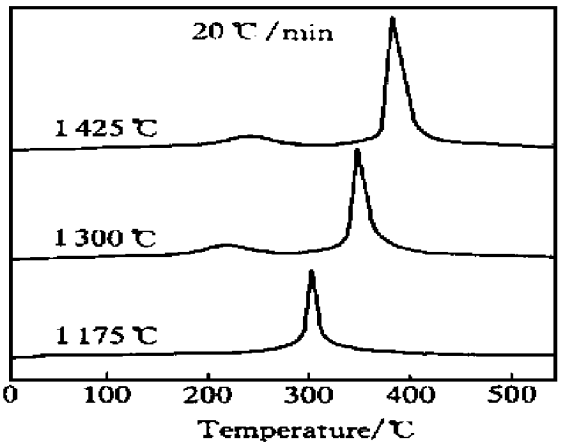

Fig.6 DSC curves of $Al_{90}Fe_5Ce_5$ alloy quenched from different temperatures

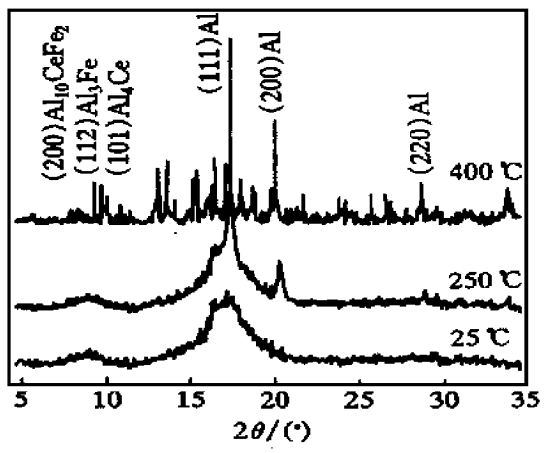

Fig.7 X-ray patterns of amorphous $Al_{90}Fe_5Ce_5$ alloy at different temperatures

and partial Al_4Ce, Al_3Fe, $Al_{10}CeFe_2$ compounds, the pre-peaks are Al_4Ce (101), Al_3Fe (112) and $Al_{10}CeFe_2$(200). Therefore, the presence of a pre-peak can be attributed to compound-forming behavior.

4 DISCUSSION

The smaller angles in reciprocal space contains the medium-range information, and the pre-peak expresses the strong correlation between unlike atoms[6]. Because of the stronger chemical bonds between unlike atoms, the cluster is formed and the MRO appears. Fig.7 shows that Al phase precipitates at lower temperature (250 ℃), but several compounds precipitate at higher temperature (400 ℃). Since Al amorphous matrix has metallic bonding between atoms, it can only form the dense random packing (DRP) structure. Less crystallization activation energy is needed for the amorphous alloy crystallizing turning from the DRP structure to the fcc structure, so Al phase crystallizes first. The existence of the pre-peak at 250 ℃ indicates that the structure corresponding to the pre-peak is much more stable than that of the Al matrix. At 400 ℃, the pre-peak is corresponding to Al_4Ce, Al_3Fe and $Al_{10}CeFe_2$ peaks. It is shown that the pre-peak corresponds to the Al-Fe-Ce cluster caused by strong Al-Fe and Al-Ce interactions. Strong Al-Fe and Al-Ce chemical bonds improve the crystallization activation energy and increase the difficulty of crystallization.

The quenching temperature can reflect the relation between the melt structure and the amorphous microstructure. The compound-like CSRO structure formed in the melt is stable, and this structure corresponding to the pre-peak exists at 1 425 ℃. The structural unit sizes of $Al_{90}Fe_5Ce_5$ liquid and amorphous alloys remain constant, which implies that the amorphous alloy inherits the CSRO structure from the liquid alloy. The pre-peak area and the ratio of the CSRO structure in the matrix increase with the reduction of quenching temperature, thus the micro-inhomogeneity of the melt becomes stronger with decreasing temperature. The X-ray diffraction of liquid $Al_{90}Fe_5Ce_5$ alloy at 1 550 ℃ agrees with the extrapolated quenching temperature of 1 557 ℃ for the disappearance of the pre-peak, which indicates that the liquid Al-Fe-Ce alloy is a homogeneous single phase at equilibrium above 1 557 ℃.

The micro-inhomogeneity of the melt becomes strong and the amorphous alloy crystallizes easily with the reduction of quenching temperature. There is no obvious Al phase crystallizing exothermic peak for the amorphous specimen quenched from 1 175 ℃. The crystallization temperature and the crystallization activation energy can be reduced with decreasing quenching temperature, and this indicates that the amount

of the Al-Fe-Ce clusters in the melt increases with the reduction of temperature, and the energy for the amorphous alloy transforming into the compounds decreases.

At lower quenching temperature of 1 050 ℃, a novel structure — a fine dispersion of Al particles homogeneously distributed in the amorphous matrix, was obtained. From Fig.4, Al phase was partly crystallized, but the pre-peak corresponding to the Al-Fe-Ce clusters still existed, in other words, the structure corresponding to the pre-peak crystallized much later than Al phase did, so it can not reduce the capacity of glass formability. The Al-Fe-Ce clusters can not become the crystal nuclei of Al phase, however, they can prevent Al phase from crystallizing and obtaining long-range order. Above 1 557 ℃, the liquid alloy is a homogeneous single phase; below 1 557 ℃, weak fluctuation or small separation in composition occurs and the Al-Fe-Ce cluster appears in the melt. These clusters caused by strong chemical bonds has a certain covalent characteristic, which improves the difficulty of crystallization and prevents Al matrix from crystallizing. Therefore, the clusters corresponding to the pre-peak make the Al-Fe-Ce amorphous alloy with Al content of 90 % favorable to glass formability.

Frank[11] suggested that the densest packing icosahedral structure with small atoms as interstitial atoms, the coordination number of 12 could exist in liquid and amorphous states, but this structure would be transformed into fcc or hcp in the long-periodic structure. Recently, the results of the studies on liquid $Al_{80}Mn_{20}$ and $Al_{71}Pd_{19}Mn_{10}$ alloys[12,13] suggest the presence of local icosahedral order in these liquid states. Here, the pre-peak position of liquid and amorphous $Al_{90}Fe_5Ce_5$ alloys is close to one of the prominent diffraction peaks of quasicrystalline Al-Fe (110001) reflection[14]. In addition, $Al_{10}CeFe_2$ quasicrystalline icosahedral phase has been reported in rapidly cooled Al-Fe-Ce alloy[15], and the quasicrystalline phase often appears in Al-based alloys[16]. Therefore, it is possible to speculate that the structural units corresponding to the pre-peaks of $Al_{90}Fe_5Ce_5$ alloy may be icosahedral quasicrystalline structure. It can be considered that the pre-peak is a diffraction peak broadened by fairly fine (< 2.0 nm) icosahedral clusters.

5 CONCLUSIONS

1) The structural unit sizes of $Al_{90}Fe_5Ce_5$ liquid and amorphous alloys remain constant, which implies that the amorphous alloy inherits the CSRO structure from the liquid alloy. The micro-inhomogeneity does exist in the melt.

2) The pre-peak area and the ratio of the CSRO structure in the matrix increase with the reduction of quenching temperature, which shows that the micro-inhomogeneity of the melt becomes strong with decreasing temperature.

3) The crystallization temperature and the crystallization activation energy of the Al-Fe-Ce amorphous alloy can be reduced with decreasing quenching temperature.

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