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Crystallization kinetics of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass①

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[Abstract] The crystallization kinetics of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass has been studied by using DSC and XRD. The results show that two exothermal peaks are observed when the alloy is heated to 500 ℃, one peak results dominantly from the formation of Ti_2Ni (α phase transition), the other peak is mainly due to the formation of Zr_2Cu (β phase transition). At the beginning of the crystallization, the activation energy of the α phase is smaller, and it increases with increasing crystallized fraction (x_c). When x_c increases to 90%, the crystallization activation energy shows the largest value (220 kJ/mol). The crystallization activation energy of the β phase remains about 227 kJ/mol, as it's crystallized fraction is below 60%, and then it increases with increasing crystallized fraction, and shows the largest activation energy of 257 kJ/mol, as the x_c is 65%.

[Key words] bulk metallic glass; $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy; crystallization kinetics; activation energy
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1 INTRODUCTION

The metallic glasses have the structure of long-range random and short-range order. Compared with crystalline alloy, they have a lot of special properties, such as highstrength, high hardness, and good wear and corrosion resistances. Previously, the practical application of amorphous alloy is limited, because the preparation of amorphous alloy is very difficult, and the alloy is made as ribbons or powders. Recently, Inone[1] and Johnson[2] developed a series of multi-component bulk metallic glasses. They have produced the metallic glass whose diameter and mass reaches 10 cm and 20 kg. Particularly, Zr-Ti-Cu-Ni-Be is an alloy system, which has good amorphous forming capability. This new type multi-component bulk metallic glass shows a lot of excellent properties, including high strength, high hardness, corrosion resistance, as well as soft magnetic behavior[3~5]. After crystallizing of bulk metallic glass, the obtained product is nanocrystalline material, which has excellent mechanical soft magnetic and high catalysis property[6]. Crystallization kinetics of bulk amorphous alloys is very important as the structure of nanocrystalline alloy is closely related to crystallizing process[7,8]. In this paper we study the crystallization kinetics of $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk amorphous alloy.

2 EXPERIMENTAL

$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy was prepared by melting a mixture of elements in a titanium-getter arc furnace, then remelted in a vacuum-sealed quartz tube and quenched in water to get an amorphous rod with a diameter of 8 mm. The amorphous nature of the rod was confirmed by X-ray diffraction (XRD). The crystallization process of the amorphous alloys was investigated by DSC and XRD. The DSC measurements were carried out by Perkin-Elmer analyzer at different heating rates from 10 to 20 ℃/min. The XRD measurements were conducted on the D/max-ⅣB, diffractometer with Cu K_α radiation.

3 RESULTS

Fig. 1 shows the DSC curve of crystallization process of the amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy at a heating rate of 10 ℃/min. Fig. 2 shows the XRD patterns of the amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy after DSC measurements. Two exothermal peaks can be seen in the DSC curve, the parame-

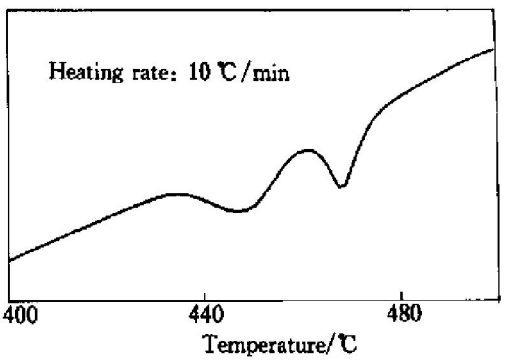

Fig. 1 DSC curve of amorphous at heating rate of 10 ℃/min

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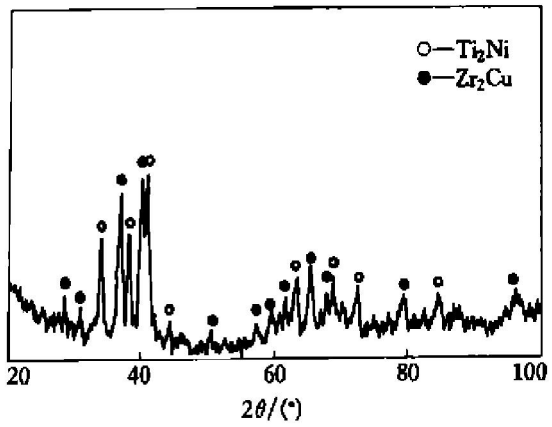

Fig. 2 XRD patterns of amorphous after DSC measurements

ters of t_x (crystallization start temperature) and t_p (temperature at peak crystallization) are listed in Table 1. Correspond to the formation of α phase (major phase is Ti_2Ni) and β phase (major phase is Zr_2Cu) by the analyses of XRD.

Table 1 t_x and t_p at different heating rates

F/(℃·min^{-1})	t_{x1}/℃	t_{x2}/℃	t_{p1}/℃	t_{p2}/℃
10	435	462	448	468
15	442	468	455	475
20	450	474	462	481

The t_{x1}, t_{x2}, t_{p1}, t_{p2}, for the alloy at heating rate of 10 ℃/min are 435, 462, 448 and 468 ℃, respectively, and increased with increasing heating rate (F).

Using the experimental data in Table 1, the apparent crystallization activation energy at the start and peak crystallization E_c can be calculated by Kissinger plots:

$$\ln(F/T^2) = E_c/RT + \text{constant} \quad (1)$$

The E_{cx} and E_{cp}, can be deduced from the slope of $\ln(F/T^2)$ vs $1/T$, where T stands for the t_x or t_p. The E_{cx} and E_{cp} of the Ti_2Ni phase are 178, and 213 kJ/mol, respectively. Thus, E_{cx} and E_{cp} of the Zr_2Cu phase are 233 and 240 kJ/mol, respectively. The above experimental results indicate that the difference between E_{cx} and E_{cp} of Ti_2Ni phase is lager than that of Zr_2Cu phase. Therefore, the growth of nuclei with Ti_2Ni phase is more difficult than Zr_2Cu, and the grains will be fine.

Using the DSC experimental data, the plots between crystallization fraction (x) and temperature (t) can be drawn and shown in Fig. 4. The activation energy of crystallization of the Ti_2Ni and Zr_2Cu at a certain crystallized fraction, E_x can be calculated by the Doyle method[10]:

$$\lg F = \lg A E_x [RF(x)]^{-1} - 2.315 - 0.4567 E_x (RT)^{-1} \quad (2)$$

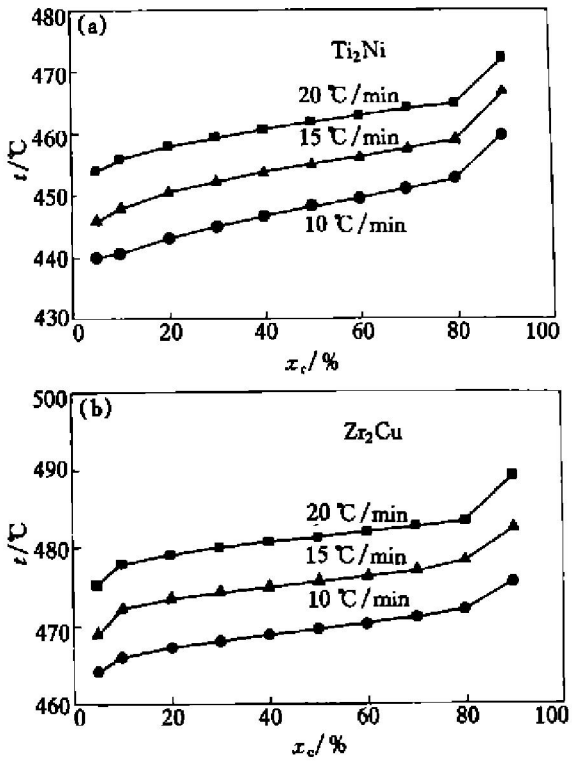

Fig. 3 Dependence of crystallized volume fraction (x_c) on temperature (t) for different heating rates

where F is the heating rate, R is the gas constant, T is the temperature, x is the crystallized fraction, A is the frequency factor, and $F(x)$ is the function which only relates to the crystallized fraction, x.

The curves of crystallized fraction of crystal (x) and temperature (t) at different heating rates can be determined by the DSC data, as shown in Fig. 2. The crystallized fraction $x = S_i/S$, where S_i is the area covered by the DSC curve between crystallization starting temperature to t, S is total area of exothermal peaks. Given a certain crystallized fraction x for a crystal, one can obtain different temperatures t which correspond to different heating rates F for the crystal, as shown in Fig. 4. According to Eqn. (2), the activation energy of crystallization at a certain crystallized fraction x for the crystal, E_x, is obtained by the slope of the plot of $\lg F$ vs $1/T$.

Fig. 5 shows the dependence of the activation energy of crystallization of the Ti_2Ni phase and Zr_2Cu in amorphous $Zr_{41}Ni14Cu_{12.5}Ni_{10}Be_{22.5}$ alloy on their crystallized fraction. At the beginning of crystallization, the activation energy of crystallization of the Ti_2Ni phase is about 159 kJ/mol, and it increases with increasing crystallized volume fraction (x_c), When the volume fraction of Ti_2Ni phase is 90%, its activation energy of crystallization arrived at the largest. As the crystallized fraction of the Zr_2Cu is below 60%, the activation energy of crystallization has little change, it is about 227 kJ/mol, and then it increases with increasing the crystallized fraction.

When the volume fraction of Zr_2Cu phase is 65%, its activation energy of crystallization is the largest, it is 257 kJ/mol.

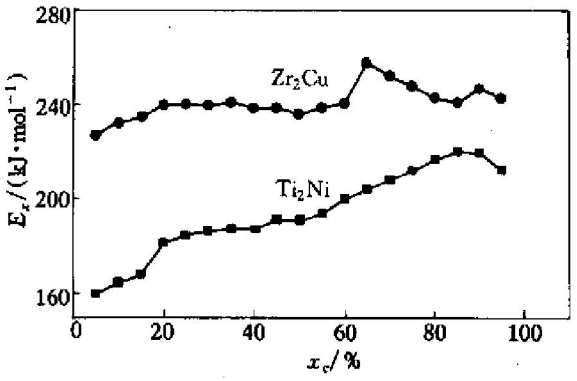

Fig. 4 Dependence of apparent crystallization activation energy (E_x) on crystallized volume fraction (x_c) of amorphous

Usually, the crystallization process in an amorphous alloy consists of nucleation and growth. During the beginning stage of crystallization, the crystallization process of the amorphous alloy strongly depends on the nucleation of the crystal. Naturally, a smaller activation energy of crystallization at the beginning stage of crystallization promotes the nucleation of the crystal, and a following increase in the activation energy of crystallization is helpful for impeding its growth during the crystallization process of the amorphous alloy. Such a crystallization behavior is required for the crystal to form a microstructure with a fine grain size. This relationship between the crystallization behavior and the formation of a microstructure with an ultrafine fine grain size in an amorphous alloy has revealed by our recent work[10]. The activation energy of crystallization of the Ti_2Ni in amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy is smaller at the beginning stage of crystallization, it is helpful for nucleation. A large amount of Zr, Cu, Be are out of Ti_2Ni phase during the crystallization process, and the amorphous region around Ti_2Ni phase becomes Zr, Cu and Be-rich. This not only retards the growth of the Ti_2Ni phase, and leads to the increase of the activation energy of crystallization but also is very helpful to the formation of the Zr_2Cu phase. At the beginning stage of crystallization, the activation energy of crystallization of Zr_2Cu phase in amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy has a little change. This is attributed to the heterogeneous nucleation of Zr_2Cu on the existing Ti_2Ni. Due to the appearance of inter boundaries and the interaction of the diffusion of atoms, the activation energy of crystallization of the Zr_2Cu phase increases rapidly. When the temperature continuously goes up, the structural relaxation takes place, and the hotresistance decreases, and hence the crystallization activation energy decreases.

4 CONCLUSIONS

1) The crystalline phase composed of Ti_2Ni and the crystalline phase composes of Zr_2Cu precipitated when amorphous $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ was heated at a rate of 10 ℃/min to 435 ℃ and 461 ℃, respectively.

2) At the beginning of the crystallization, the activation energy of Ti_2Ni phase is about 159 kJ/mol which increases with increasing crystallized volume fraction (X_c). When the volume fraction of the phase is 90%, its activation energy of crystallization get to the largest (220 kJ/mol). When the volume fraction of the Zr_2Cu phase is below 60%, the crystallization activation energy of the phase remains about 227 kJ/mol, and then increases with increasing crystallized volume fraction. When the volume fraction of Zr_2Cu phase is 65%, the crystallization activation energy is the largest (257 kJ/mol).

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