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# Effect of preannealing on crystallization process of amorphous $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ alloy ①

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[Abstract] In the view of crystallization activation energy of amorphous alloy, the mechanism of coarse grain in annealed $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ amorphous alloy was analyzed. It reveals the effect of preannealing on the process crystallization. The results show that preannealing can be used to change the crystallization behavior of the α-Fe phase in the $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ amorphous alloy, which is helpful for forming α-Fe phase grains; and it is not large for $Sm_2Fe_{17}C_x$ phase.

[Key words] $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ amorphous alloy; preannealing; crystallization
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## 1 INTRODUCTION

Nanocomposite magnets consisting of two-phase distribution of hard- and soft- magnetic grains have attracted considerable interest since they could, by exchange coupling, potentially provide a maximum energy product, $(BH)_{max}$, in excess of 100 MGOe[1], which will become a kind of the new magnetic material. Unfortunately, as a result, the energy product of practical nanocmposite magnets, 10~ 20 MGOe, obtained was significantly lower than the theoretical value 100 MGOe. The primary reason is that the grain size (20~ 100 nm) was much larger than the required theoretical calculation (< 10 nm)[1~6]. Researches[7, 8] show that the preanealing can optimize the microstructure of the amorphous alloy, and refine the grain. But little progress has been made on this aspect due to lacking basic understanding. In addition, the reports about the influence of preannealing on the nanocomposite magnets were very lacking.

In the present work, the crystallization kinetics of $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ amorphous alloy are investigated. Crystallization kinetics of the $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ amorphous alloy will give us an insight into the mechanism of nucleation and growth of a crystalline phase and the influence of preannealing on the amorphous alloy, optimize their microstructure. This is helpful for us to provide a guidance for improving the maximum energy product in the future.

## 2 EXPERIMENTAL

The $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ amorphous alloys were prepared by argon arc melting the pure constituent elements. These ribbons were 20 μm thick and 2~ 3 mm wide. The amorphous nature of the ribbons was confirmed by X-ray diffraction (XRD), as shown in Fig. 1. Some samples were preannealed at 400 ℃ for 10 min after sealing in a quartz capsule under high purity argon. The structure evolutions and crystallization kinetics of the as- quenched and

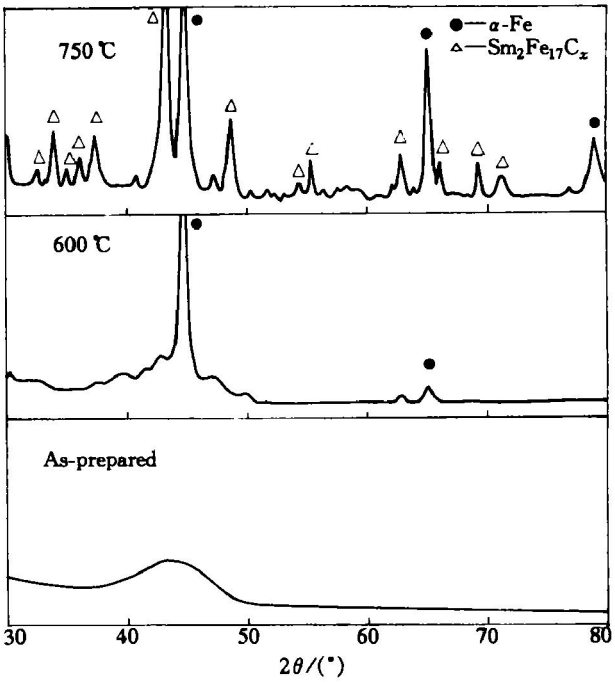


**Fig. 1** X-ray diffraction patterns of as-quenched and annealed amorphous $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ alloy

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the preannealing amorphous ribbons were investigated by a Perkin-Elmer seven differential thermal analysis (DTA) system, using a heating rate of 10, 15, 20 ℃/min. The as-quenched and the preannealing samples were annealed simultaneously at 750 ℃ for 10 min after sealing in a quartz capsule under high purity argon. The XRD analyses were conducted using D/Max-rB diffractometer equipped with a graphite monochromator, and Cu $K_\alpha$ radiation was used. The grain size after the annealed alloys was calculated by the Scherrer formula[9].

## 3 RESULTS AND DISCUSSION

Fig. 2 shows the DTA curves of the as-quenched and the preannealing $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ amorphous alloy at 10 ℃/min heating rates. Two exothermal peaks are obviously observed from Fig. 2. These exothermal peaks are, respectively, determined to correspond to the formation of α-Fe phase and $Sm_2Fe_{17}C_x$ by the analyses of XRD. This indicates that the preannealing does not change the categories of the crystallization phases. But it reduces the intensity values of the X-ray diffraction for the two phases.

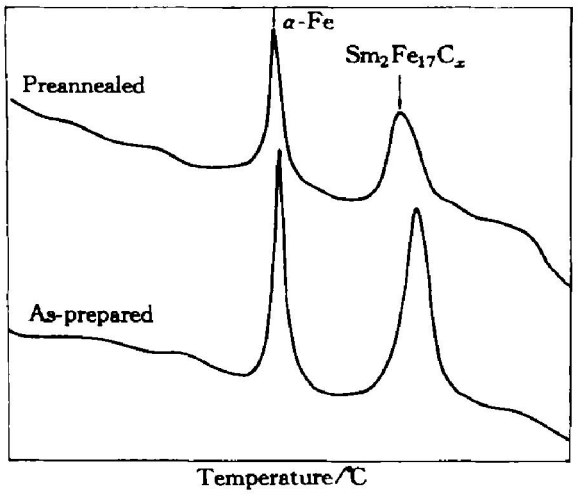


**Fig. 2** DTA curves at heating rate of 10 ℃/min

Given a certain crystallized fraction $x$ for a crystal[10], one can obtain different temperatures. Fig. 3 shows the dependence of crystallized fraction of crystal of the α-Fe phase and $Sm_2Fe_{17}C_x$ on their temperature in two types of the amorphous alloys. According to the Doyle method[11], their activation energies of crystallization at a certain crystallized fraction $x$ for the crystal, $E_c(x)$, are obtained, as shown in Fig. 4.

For the as-prepared amorphous alloy, at the beginning stage of crystallization, the activation energy of crystallization of α-Fe phase is about 612.23 kJ/mol, 834.2 kJ/mol for $Sm_2Fe_{17}C_x$, and then decreases with increasing the crystallized fraction. But for the preannealing amorphous alloy, the activation energies of crystallization of the α-Fe phase and the $Sm_2Fe_{17}C_x$ are 480.12 kJ/mol and 803.26 kJ/mol, respectively. The activation energy of crystallization of the α-Fe phase is rising as the crystallized fraction is below 60%. As the crystallized fraction is 60%, the activation energy of the α-Fe phase achieves a maximum value, 587.05 kJ/mol. The activation energies of the $Sm_2Fe_{17}C_x$ decreases sharply with increasing the crystallized fraction. The lessening trend of the activation energies of $Sm_2Fe_{17}C_x$ in preannealing amorphous alloy is similar to that of as-quenched amorphous alloy.

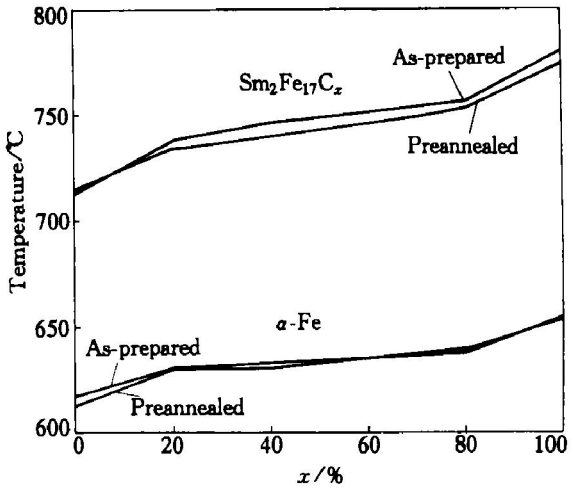


**Fig. 3** Dependence of crystallized fraction of crystalline phase on temperature, at heating rate of 10 ℃/min

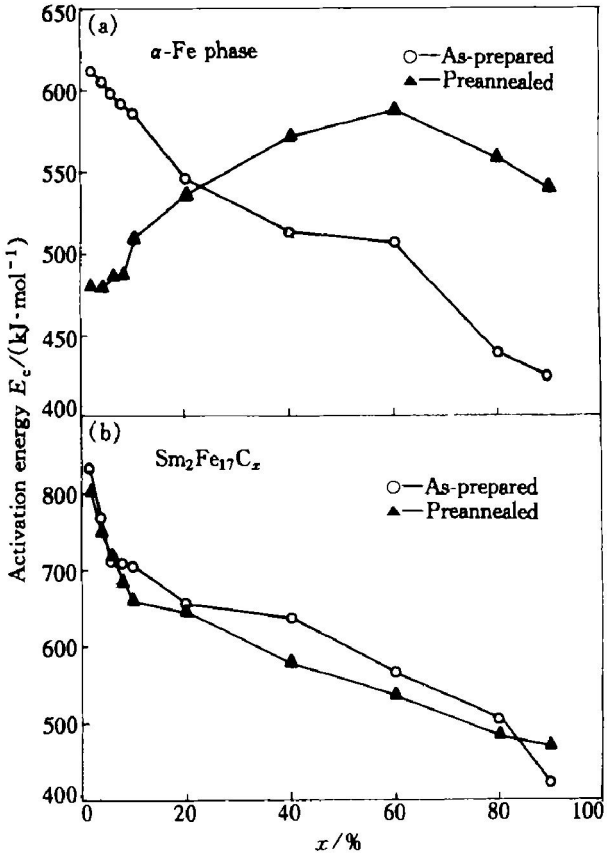


**Fig. 4** Dependence of activation energy of α-Fe phase and $Sm_2Fe_{17}C_x$ in amorphous alloy on their crystallized fraction

Fig. 5 shows X-ray diffraction patterns of the as-quenched and preannealing alloys after crystallization annealing at 750 ℃ for 10 min. The grain size was calculated and listed in Table 1. The calculation results indicate that the preannealing has refined the grain size of α-Fe phase. But it hardly shows an obvious change for the $Sm_2Fe_{17}C_x$ in the preannealing amorphous alloy.

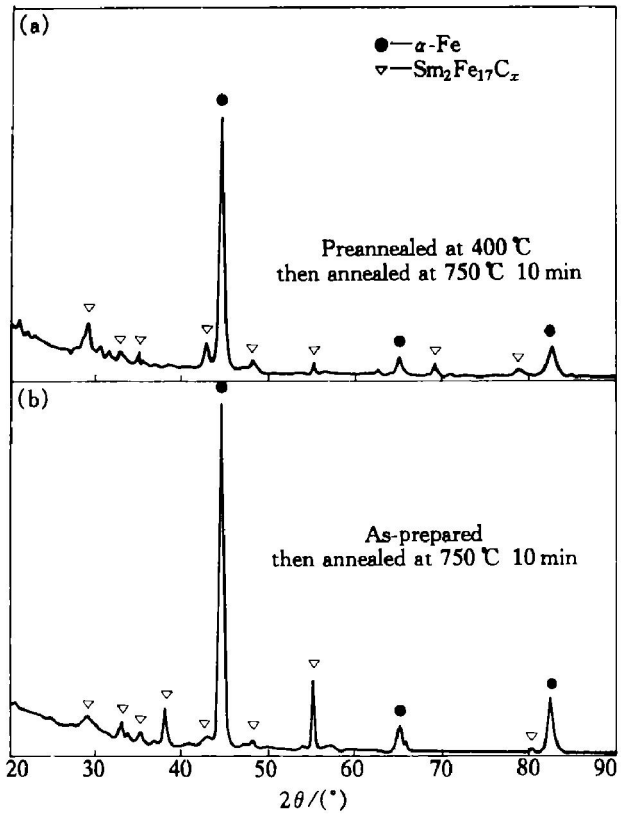


**Fig. 5** X-ray diffraction patterns for amorphous alloys of as-prepared and preannealing

**Table 1** Grain sizes of crystalline phases of as-prepared and preannealing amorphous alloys(nm)

| Phase | As-prepared | Preannealing |
|---|---|---|
| α-Fe | 30.30 | 18.95 |
| $Sm_2Fe_{17}C_x$ | 12.39 | 12.60 |

Researches presented that the crystallization activation energies of α-Fe phase and $Sm_2Fe_{17}C_x$ in the $Sm_5Fe_{80}$ $Cu_1Si_5B_3C_{2.5}$ $Zr_{3.5}$ amorphous alloy are strongly related to the nucleation and growth of the crystallization process. Usually, the crystallization process of a crystal in an amorphous alloy consists of nucleation and growth. During the beginning stage of crystallization, the crystallization process of the amorphous alloy is strongly dependent on the nucleation of the crystal. Naturally, a larger activation energy of crystallization at beginning stage of crystallization impedes its nucleation, and a following decrease of the activation energy of crystallization will reduce the resistance in the process of the growth of the crystal, which results in the product of a coarse grain size.

Fig. 4 shows the dependence of the activation energy of crystallization of the α-Fe phase and the $Sm_2Fe_{17}C_x$ for the as-quenched and the preannealing amorphous alloys on their crystallized fraction. Fig. 4 presents also at beginning stage of crystallization, the activation energy of crystallization of α-Fe phase of the preannealing amorphous alloy is much lower than that of the as-quenched, which is helpful to the formation of the nucleation for the α-Fe phase with a fine grain size. On the other hand, since there is an increase in the activation energy of crystallization of the α-Fe phase during its crystallization process, the growth of the α-Fe phase is more difficult once it forms in the alloy because more energy is required to promote its growth. Hence, the α-Fe phase with a fine grain size can be obtained by this method. But, the activation energy of crystallization of the $Sm_2Fe_{17}C_x$ shows little change in Fig. 4 by the preannealing, which almost have no effect on the grain size of the $Sm_2Fe_{17}C_x$.

Obviously, the preannealing has changed the crystallization behavior of the α-Fe phase in the amorphous $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ alloy, and it is in favor of the formation of α-Fe phase with a fine grain size. This result is attributed to the changing in microstructure of the amorphous alloy. Because the preannealing can increase the order degree in the amorphous alloy, and produce a large number of clusters[7, 8, 12]. These clusters are helpful to inducing the nucleation of the α-Fe phase, which result in decreasing the crystallization temperature and the activation energy at beginning stage of crystallization. On the other hand, a great number of nucleation of the α-Fe phase enhance the concentration of Sm, Si, C elements in the remaining amorphous region, improving the stability of the amorphous alloy strongly, which will impede the growth of the α-Fe phase and increase the activation energy of crystallization. In addition, structure relaxation appears in the preannealing amorphous alloy, lessening the movement ability of the elements[7], restraining the growth of the α-Fe phase. The crystallization process of the $Sm_2Fe_{17}C_x$ is different from the α-Fe phase, which is attributed to the fact that the formation and growth of the $Sm_2Fe_{17}C_x$ are dependent not only on the diffusion of atom Fe but also on the diffusion of atoms, such as Sm, Si and C. Moreover, a proper ratio among these atoms is also required for the formation and growth of the $Sm_2Fe_{17}C_x$. This can essentially result in little change for the grain size of the $Sm_2Fe_{17}C_x$. The detailed results will be reported in our following article.

In a word, the preannealing can reduce the distance of the grains between the α-Fe phase and $Sm_2Fe_{17}C_x$, which is favor for improving the exchange coupling and providing further the maximum energy product.

## 4 CONCLUSIONS

The change of the activation energy of crystallization of the preannealing amorphous $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ alloy has an effect on the grain sizes of the crystals. It is attributed to the preannealing which has changed the crystallization behavior of the α-Fe phase in the amorphous $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ alloy, and it results in an activation process with an easy nucleation and a difficult growth for the α-Fe phase. It will be helpful to the formation of a fine grain size for the α-Fe phase. But there is little change for grain size for the $Sm_2Fe_{17}C_x$. The preannnealing method has reduced the distance of the grains between the α-Fe phase and $Sm_2Fe_{17}C_x$ in the amorphous $Sm_5Fe_{80}Cu_1Si_5B_3C_{2.5}Zr_{3.5}$ alloy. The energy product of the magnets can be further enhanced by the preannealing method.

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