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STUDIES OF NANOCRYSTALLINE PHASE AND RESIDUAL AMORPHOUS PHASE OF FeCuNbSiB ALLOY*

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The σ-T and $\mathrm{d}\sigma/\mathrm{d}T$-$T$ curves of the FeCuNbSiB amorphous alloy, which are the relationship between "apparent weight loss"and temperature, are investigated by magnetic thermogravimetry analysis (MTGA) technique. It is found that the crystallization process of the samples can be divided into five stages. The studies of samples annealed in the temperature range of 480–610 ℃ for 1 h show that when the annealing temperature (T_a) is lower than 540 ℃, the quantity of nanocrystalline α-Fe(Si) phase increases evidently with T_a, and the Curie temperature (T_C) of residual amorphous phase also increases linearly with T_a, i.e., $T_\mathrm{C}=0.52T_\mathrm{a}+91.7$ ℃, with correlation coefficient $\gamma=0.98$. The variation of volume fraction of α-Fe(Si) nanocrystalline phase or residual amorphous phase with T_a is measured.

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I. INTRODUCTION

The nanocrystalline FeCuNbSiB alloy was developed in 1988 by Yoshizawa and his coworkers,[1] it exhibits excellent soft magnetic properties. Since its development, scientific workers have investigated the microstructure and crystallization process of amorphous alloys. In this paper, we examine the changes of nanocrystalline phase and residual amorphous phase during crystallization process of FeCuNbSiB amorphous alloys. The variation of "apparent weight loss" (i.e., saturation magnetization per unit mass) with temperature (σ-T curve) and variation of "apparent weight loss rate" with temperature ($\mathrm{d}\sigma/\mathrm{d}T$-$T$ curve) were investigated by magnetic thermogravimetry analysis (MTGA) and magnetic derivative thermogravimetry (MDTG) techniques.

II. EXPERIMENTAL

Ribbons of the FeCuNbSiB alloy were prepared by a conventional single-roller melt-spinning method. The ribbon was about 30 μm in thickness, about 10 mm in width, and was identified to be amorphous by X-ray diffraction (XRD). Differential scanning calorimetry (DSC), XRD and transmission electron microscopy (TEM) techniques were used to examine the crystallization behavior of the amorphous ribbons, samples of which were annealed at 480, 500, 520, 530, 540, 565, 610 ℃ for 1 h in Ar atmosphere. Furthermore, both the σ-T and $\mathrm{d}\sigma/\mathrm{d}T$-$T$ curves of the as-quenched and annealed samples were measured by MTGA and MDTG techniques. The weight of the samples measured was about 1mg. The principle and technique of MTGA measurement has been described elsewhere.[4]

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Ⅲ. RESULTS AND DISCUSSION

A. Study of DSC curve, XRD and TEM

The DSC curve of the as-quenched sample of FeCuNbSiB amorphous alloy at a heating rate of 10 ℃/min is shown in Fig.1. It shows two exothermic peaks, indicating the two-step crystallization process before the final stable phase is attained. The first exothermic peak ("*abc*" peak) occurs between 512 and 599 ℃, and the peak temperature is 534.3 ℃. The crystallization enthalpy associated is 46.8 J/g, which corresponds to the transformation process from amorphous matrix into α-Fe(Si) nanocrystalline phase. The second peak ("*def*" peak) occurs between 661 and 755 ℃, and the peak temperature is 697.5 ℃. The crystallization enthalpy associated is 35.5 J/g,

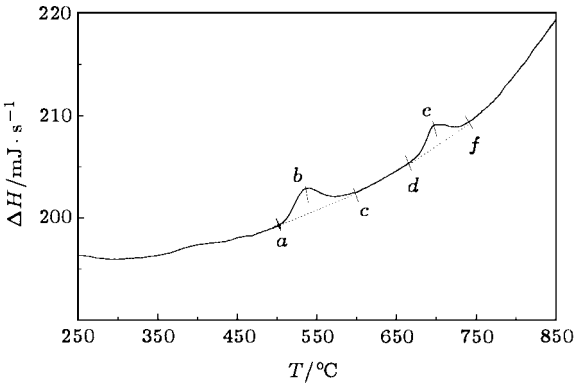

Fig.1. DSC curve of the as-quenched sample of FeCuNbSiB amorphous alloy.

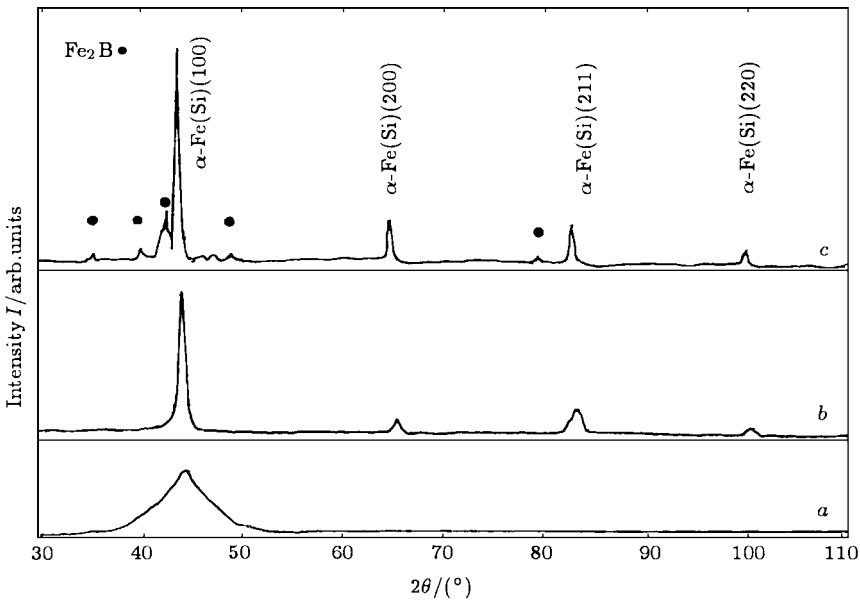

Fig.2. XRD patterns of the as-quenched alloy and the alloy annealed at 540 and 700 ℃ for 1 h.

which shows that α-Fe(Si) nanocrystalline phase is transformed into the final stable crystalline phase. These results are confirmed by XRD and TEM measurements. Figure 2 shows the XRD patterns of the as-quenched alloy and the alloy annealed at 540 and 700 ℃. Curve *a* in Fig.2 is a typical amorphous pattern with a broad peak. Curve *b* shows

the nanocrystalline bcc α-Fe(Si) solid solution phase produced primarily in the amorphous matrix for samples annealed at 540 °C.[2] The average grain size calculated by Scherrer method[3] is about 15 nm. The broad peaks imply that crystalline size is small. The photomicrograph of TEM is shown in Fig.3, in which the calculated average grain size is about 15 nm, too. When the annealing temperature increases to 700 °C, the Fe_2B compound is formed in addition to the bcc α-Fe(Si) phase (see curve *c* in Fig.2). The significant narrower peaks as compared with curve *b* indicate that the grain size is evidently increased.

Fig.3. TEM photomicrograph of the alloy annealed at 540 °C for 1 h.

B. The σ-T and dσ/dT-T curves of the as-quenched sample

Both the σ-T and dσ/dT-T curves measured by MTGA and MDTG techniques for FeCuNbSiB amorphous alloy at a heating rate of 10 °C/min are shown in Fig.4. This technique

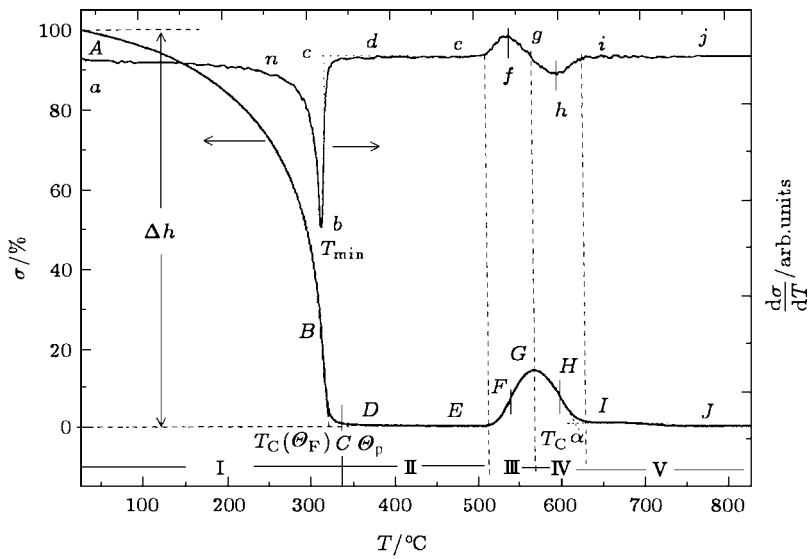

Fig.4. The σ-T and dσ/dT-T curves measured by MTGA and MDTG technique for FeCuNbSiB amorphous alloy.

for the study of crystallization process of amorphous alloy is more distinct than the DSC technique. The curves of Fig.4 can be divided into five stages:

(1) The first stage (ABC) ranges from room temperature to 337 ℃. Around room temperature, the as-quenched sample is in ferromagnetic amorphous state, and σ decreases slightly with increasing temperature. However, with increasing temperature, the quantity of anti-parallel spin electron increases, and the decrease of σ becomes more evident. Above 300 ℃, there are three characteristic temperature points within a temperature range of 30 ℃: $T_{\min}$, T_C (or Θ_F), and Θ_p.

Temperature $T_{\min}$=310.2 ℃, which is a minimum (sharp valley) of $d\sigma/dT$-T curve. It corresponds to T_F, which is the thermal activated temperature of Fermi energy ($\varepsilon_F=kT_F$) for Fermi-Dirac statistics of free electron gas in metal. The transition rate of the samples from ferromagnetic amorphous phase into paramagnetic one is the fastest at T_F.[4]

Temperature T_C=322 ℃ is the ferromagnetic Curie temperature. The characteristic point T_C is defined as the intersection of the extrapolated line of curve AB and baseline EDC in Fig.4. It reflects the temperature at which the spontaneous magnetization disappears. Sometimes T_C can also be represented by Θ_F.

Temperature Θ_p=337 ℃ represents the Curie temperature of paramagnetism, it is the extrapolated point on the curve of the inverse of the paramagnetic magnetic susceptibility with T, or it is a "tail" appearing on the σ-T curve, (Fig.4, point C). It reflects that there should be a course for the magnetic moment to disappear (temperature range from T_C to Θ_p). When the temperature is higher than Θ_p, the magnetic moment shows totally random statistical distribution.

(2) The second stage (CDE) ranges from 337 to 512 ℃, in which exists the paramagnetic amorphous phase.[5]

(3) The third stage (EFG) ranges from 512 to 565 ℃. The bcc α-Fe(Si) ferromagnetic nanocrystalline phase is formed from the paramagnetic amorphous phase. This stage corresponds to the initial stage of the first exothermal peak of DSC curve. When the quantity of α-Fe(Si) ferromagnetic nanocrystalline phase increases with temperature, the σ-T curve shows an evident process of "apparent weight gaining". When the temperature is close to 535 ℃ (Fig.4, point F), the transition rate of α-Fe(Si) ferromagnetic nanocrystalline phase is the fastest, its peak temperature corresponds to the peak temperature (b) of abc exothermal peak of the DSC curve in Fig.1.

(4) The fourth stage (GHI), from 565 to 632 ℃, indicates that the samples are transformed from ferromagnetic α-Fe(Si) phase into paramagnetic one. The σ-T curve still shows an evident process of "apparent weight loss". The $d\sigma/dT$-T curve also shows a sharp minimum (valley, ghi) at 596 ℃. This point corresponds to the finial temperature (point c) of the abc exothermal peak of DSC curve. The Curie temperature T_C^{α} of α-Fe(Si) phase is about 612 ℃, at which the samples transform from ferromagnetic α-Fe(Si) phase into paramagnetic α-Fe(Si) and form Fe_2B phase (see Fig.4, about point I).[5]

(5) The fifth stage (IJ), above 632 ℃, describes the process in which the samples are transformed from paramagnetic nanocrystalline phase into the final stable larger grains of α-Fe(Si) and Fe_2B phases. Since the weight and the saturated magnetic moment of the annealed samples keep unchanged, both σ and $d\sigma/dT$ curves hardly change with temperature. But the change of structure can be analyzed by DSC and XRD.

C. The σ-T curves of isothermal-annealed samples

The σ-T curves of samples annealed in the temperature range of 480–610 ℃ for 1 h is shown in Fig.5. It shows that when T_a is lower than T_F (535 ℃) of Fig.4, the shape of σ-T curve is similar to that of the as-quenched sample (see Fig.5(a)). However, the Curie temperature (T_C) of residual amorphous phase increases with T_a, and the length (L_t), which expresses the quantity of the residual amorphous phase, decreases with increasing T_a. The quantity of L_t is defined as the vertical distance between the transition point T_C and the horizontal line (σ=100%). Figure 5(b) shows the σ-T curves when T_a is higher than T_F. It is difficult to identify the different stages of the σ-T curves due to smaller L_t, and the change of T_C deviates from its linearity. This indicates that all residual amorphous phases have transformed gradually into α-Fe(Si) phase. Thus the T_C obtained for different annealing temperatures is about the same, and is close to the temperature of point I of σ-T curve in Fig.4, but is slightly higher than the temperature of point d of DSC curve in Fig.1.

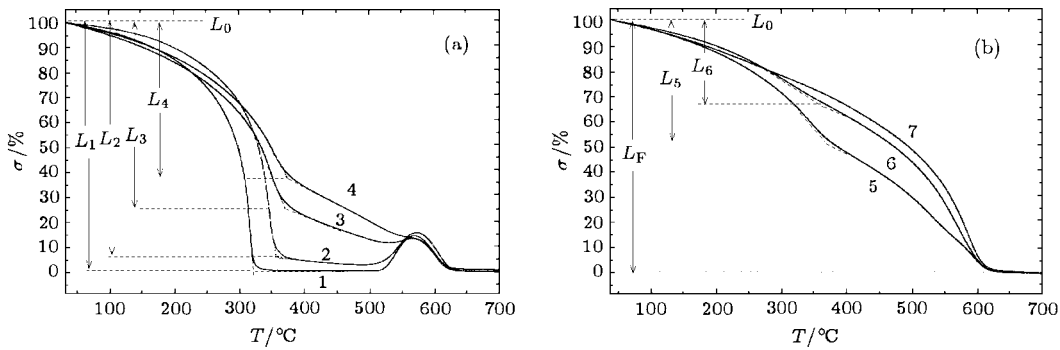

Fig.5. The σ-T curves of samples annealed in the temperature range of 480-610 ℃ for 1 h. (a) 1—as-quenched state, 2—500 ℃, 3—520 ℃, 4—530 ℃ ($T_a < T_F$, i.e., 535 ℃); (b) 5—540 ℃, 6—565 ℃, 7—610 ℃ ($T_a > T_F$).

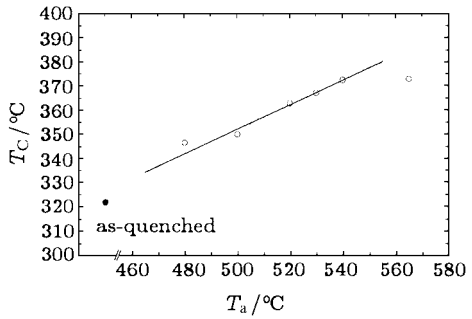

Fig.6. Variation of T_C for residual amorphous phase with T_a.

Figure 6 shows that the variation of T_C in residual amorphous phase with T_a, where T_C increases linearly with T_a, i.e., T_C=0.52T_a+91.7 ℃, with correlation coefficient γ=0.98, in the temperature range of 480–540 ℃. According to the results of the σ-T curve (see EFG region) in Fig.4, the higher the T_a is, the more the α-Fe(Si) phase in the residual amorphous phase is formed. Therefore, Fe atoms in the residual amorphous phase are decreased, while Nb, B

atoms increase, the Fe:B in the residual amorphous phase decreases. This is in agreement with the results reported by Hasegawa[6] and Hernando.[7] They found that a decrease of the Fe:B ratio induced an increase of Curie temperature in $Fe_{100-x}B_x$ and $Fe_{96-x}B_xNb_3Cu$ nanocrystalline alloy. In addition, the exchange interaction on the interface between Fe atoms of amorphous phase and ordered Fe atoms of ferromagnetic nanocrystalline phase is produced. Iron exchange-field can penetrate into residual amorphous phase, resulting in the increase of Curie temperature of residual amorphous phase in FeCuNbSiB nanocrystalline alloy. However, when T_a is higher than 540 ℃, since the quantity of the residual amorphous phase decreases evidently, the exchange interaction become weak, thus the variation of T_C deviates from linearity.

D. The dσ/dT-T curves of isothermal-annealed samples

The dσ/dT-T curves of samples annealed at different temperatures are shown in Fig. 7. The first minimum (B' valley) of dσ/dT-T curves (which expresses that the samples are transformed from ferromagnetic amorphous phase into paramagnetic one) is broadened with T_a due to the action of magnetic exchange-field of Fe atoms. The second minimum (H' valley) is also broadened and the depth (h_i) of valley H' increases with T_a. This shows that when T_a increases, the quantity of α-Fe(Si) phase increases; conversely, the quantity of residual amorphous phase decreases. For the sample annealed at 540 ℃, the two sides of the valley appears asymmetric. When the samples are annealed at higher temperatures, on the dσ/dT-T curve the B' valley disappears and only the H' valley remains.

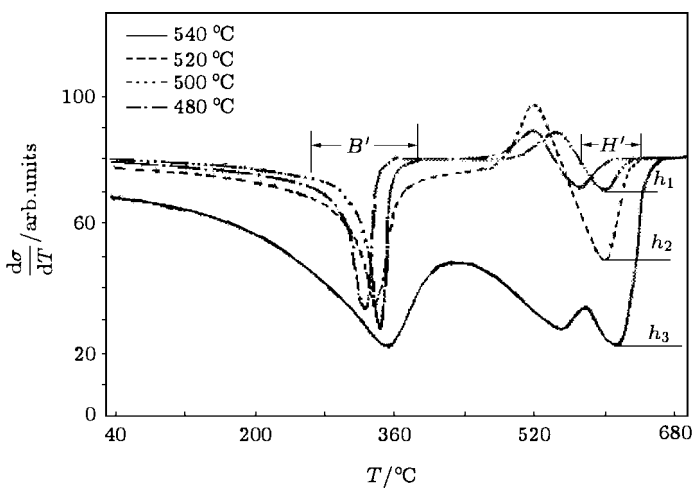

Fig. 7. The dσ/dT-T curves of FeCuNbSiB amorphous alloy annealed at different temperatures for 1 h.

E. The relationship between volume fraction of transformation and T_a

We can further analyze the relationship between the volume fraction of transformation

and T_a from the σ-T curves in Fig.5. According to the following formula:[8]

$$\sigma = \sum_{i=1}^{2} V_i \sigma_i \ , \quad \sigma = V_1\sigma_1 + V_2\sigma_2 \ , \tag{1}$$

where V_1, V_2 are the volume fractions of residual amorphous phase and nanocrystalline phase, respectively; σ_1, σ_2 are their corresponding saturation magnetization per unit mass. In addition, the volume fraction of residual amorphous phase (V_1) can be calculated according to formula (2).[9]

$$V_1 = (L_0 - L_t)/(L_2 - L_F) \times 100\% \ , \tag{2}$$

where L_0, L_F are the depths of the initial state and the final state, (in Fig.5, L_0=100%), L_t is the vertical distance between the T_C point of sample annealed at different temperature and the horizontal line (see Fig.5) and $V_2 = 1 - V_1$. Thus, the variation of volume fraction of α-Fe(Si) nanocrystalline phase or residual amorphous phase with T_a measured by MTGA technique is shown in Fig.8. It shows that, at the point T_a=540 ℃, the volume percentage of the α-Fe(Si) phase is 50%. This result agrees with that reported by Hono *et al.*[10]

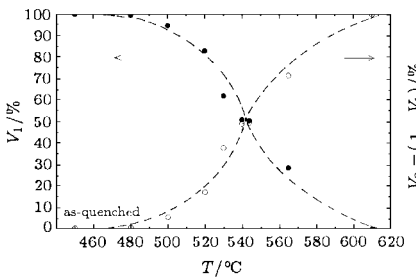

Fig.8. Variation of volume fraction of α-Fe(Si) nanocrystalline phase or residual amorphous phase with T_a measured by MTGA technique.

IV. CONCLUSIONS

A. The σ-T and dσ/dT-T curves of the FeCuNbSiB amorphous alloy are investigated by MTGA and MTDG techniques. It is found that the crystallization process of the samples can be divided into five stages: (a) ferromagnetic amorphous phase; (b) paramagnetic amorphous phase; (c) ferromagnetic nanocrystalline α-Fe(Si) phase; (d) paramagnetic nanocrystalline α-Fe(Si) phase; and (f) stable crystalline phase. These processes are more distinct than those by the DSC technique.

B. The studies of samples annealed in the temperature range of 480–610 ℃ for 1 h show that when the annealing temperature (T_a) is lower than 540 ℃, the quantity of nanocrystalline α-Fe(Si) phase increases evidently with T_a, and the Curie temperature (T_C) of residual amorphous phase also increases linearly with T_a, i.e., T_C=0.52T_a+91.7 ℃, with correlation coefficient γ=0.98.

C. The variation of volume fraction of α-Fe(Si) nanocrystalline phase with T_a can be measured by MTGA technique.

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