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STUDIES OF NANOCRYSTALLINE PHASE AND RESIDUAL AMORPHOUS PHASE OF FeCuNbSiB ALLOY USING TG(M) TECHNIQUE

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Abstract

The σ–T and dσ/dT–T curves of the FeCuNbSiB amorphous alloy, which are the relationship between the total saturated magnetic moment per unit mass σ and temperature, are investigated by magnetic thermogravimetry analysis (TG(M)) technique. It is found that the crystallization process of the samples can be divided into five stages. The studies of samples annealed in temperature range of 480–610°C for 1h show that when the annealing temperature (T_a) is less than 540°C, 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°C, with correlation coefficient γ=0.98. The variation of volume fraction of α-Fe(Si) nanocrystalline phase or residual amorphous phase with T_a is measured by TG(M) technique.

Keywords: Curie temperature, nanocrystalline, TG, TG(M) and DTG(M)

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 of these amorphous alloys. The differential scanning calorimetry (DSC), or differential thermal analyzer (DTA), X-ray diffraction (XRD), transmission electron microscopy (TEM), positron annihilation technique (PAT), and Mossbauer effect, magnetic measurement techniques and so on, were used to study the microstructure and crystallization behaviour of the amorphous alloys [1–10]. As a rule, the onset of the formation of the FeSi phase (T_{x1}) and Fe boride phase (T_{x2}) of this alloys was determined by DSC (or DTA) measurements, and the enthalpy change of crystallization (or phase transition) ΔH, was determined by means of DSC. However, magnetic thermogravimetry analysis (TG(M)) and DTG(M)) techniques are simple and very useful experimental methods for studying the phase transition behaviour of magnetic materials [2, 3, 8]. In this paper, we study the changes of nanocrystalline phase and residual amorphous phase during crystallization process of FeCuNbSiB amorphous

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alloys. The variation of σ (i.e. saturation magnetization per unit mass) with temperature (σ–*T* curve) and 'rate of σ variation' with temperature (dσ/d*T*–*T* curve) were investigated by magnetic thermogravimetry analysis (TG(M)) and magnetic derivative thermogravimetry (DTG(M)) techniques (i.e. thermomagnetometry) [11, 12].

Experimental

The initial alloy ingots were prepared in an arc furnace by melting appropriate quantities of elements: Fe, Cu, Nb, Si, and B, the purity of each element of which is higher than 99.9%, and 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). The differential scanning calorimetry (DSC) technique was used to examine the crystallization behaviour of the amorphous ribbons. Samples of amorphous ribbons were annealed at 480, 500, 520, 530, 540, 565, 610°C for 1 h in Ar atmosphere respectively. Furthermore, both the σ–*T* and dσ/d*T*–*T* curves of the as-quenched and annealed samples were measured by TG(M) and DTG(M) techniques. Mass of measured samples was about 1 mg. The principle and technique of TG(M) measurement is described elsewhere [12].

Results and discussion

DSC curve

The DSC curve of as-quenched sample of FeCuNbSiB amorphous alloy at a heating rate of 10°C min^{-1} is shown in Fig. 1. It shows two exothermic peaks that mean that the two-step crystallization processes before final stable phase is attained. The first exothermic peak ('abc' peak) is from 512 to 599°C, and the peak temperature is 534°C. The crystallization enthalpy associated to it is 46.8 J g^{-1}, which corresponds to a transformation process from amorphous matrix state into α-Fe(Si) nanocrystalline phase. The second peak ('def ' peak) is from 661 to 755°C, and the peak temperature is 697.5°C. The crystallization enthalpy associated to it is 35.5 J g^{-1},

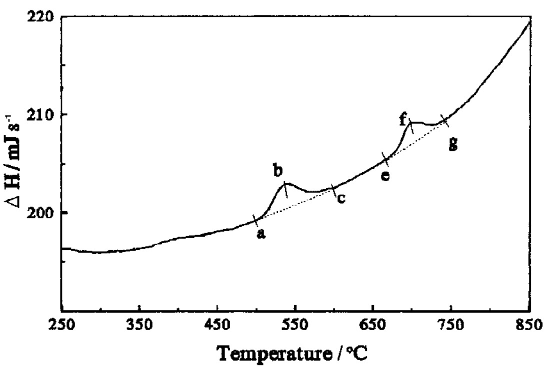

Fig. 1 DSC curve of the as-quenched sample of FeCuNbSiB amorphous alloy

which shows that α-Fe(Si) nanocrystalline phase is transformed into the final stable crystalline phase. These results were confirmed by X-ray diffraction measurement [13].

σ–T and dσ/dT–T curves of the as-quenched sample

Both the σ–*T* and dσ/d*T*–*T* curves measured by TG(M) and DTG(M) techniques for FeCuNbSiB amorphous alloy at a heating rate of 10°C min^{-1} are shown in Fig. 2.

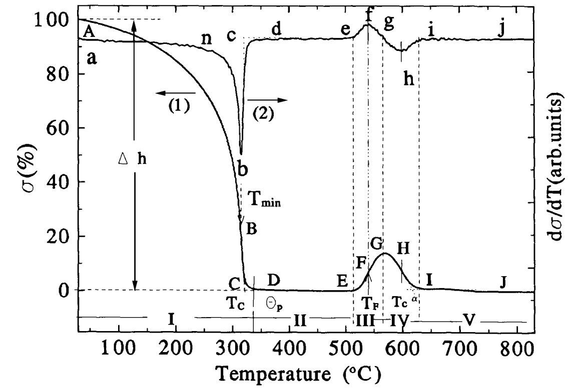

Fig. 2 σ–*T* and dσ/d*T*–*T* curves measured by TG(M) and DTG(M) techniques for FeCuNbSiB amorphous alloy (T_F is the temperature corresponding to that of the dσ/d*T*–*T* curve at which the efg region reaches its peak (point f). T_F=535°C, for FeCuNbSiB alloy)

This technique for the study of crystallization process of amorphous alloy is more distinct than DSC technique. The curves of Fig. 2 can be divided into five stages:

1. The first stage (ABC) is from room temperature to 337°C. Around room temperature, the as-quenched sample is in ferromagnetic amorphous state, and σ decreases slightly with increasing temperature. The dσ/d*T*–*T* curves seem to be a horizontal line. However, with increasing temperature, the quantity of anti-parallel spin electron increases, and the decrease of σ becomes more evident. Above 300°C, there are three characteristic temperature points within a temperature range of 30°C: T_{min}, T_C, and Θ_p.

Temperature T_{min}=310°C,which is a minimum (sharp valley) of dσ/d*T*–*T* curve. It corresponds to T_m which is the thermal activated temperature of Fermi energy ($\varepsilon_m=kT_m$) for Fermi-Dirac statistics of free electron gas in metal (i.e. the theory of the Pauli paramagnetism) [12, 14]. The transition rate of the samples from ferromagnetic amorphous phase into paramagnetic one is the fastest at the temperature [12].

Temperature T_C=322°C 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. 2. It reflects that the spontaneous magnetization disappears.

Temperature Θ_p=337°C, 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. 2, 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°C, in which exists paramagnetic amorphous phase [6].

3. The third stage (EFG) ranges from 512 to 565°C. The bcc α-Fe(Si) ferromagnetic nanocrystalline phase is formed from the paramagnetic amorphous phase. This stage corresponds to the initial stage of 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 mass gaining'. When temperature is close to T_F which is defined as the temperature corresponding to that of the dσ/dT–T curve at which the efg region of reaches its peak point f (T_F =535°C, for FeCuNbSiB alloy), 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) is from 565 to 632°C. It indicates that the samples are transformed from ferromagnetic α-Fe(Si) phase into paramagnetic one. The σ–T curve meanwhile shows an evident process of 'apparent mass loss'. On the dσ/dT–T curve also appears a sharp minimum (valley, ghi), at 596°C, which corresponds to final temperature (point c) of abc exothermal peak in DSC curve.The Curie temperature T_C^a of α-Fe(Si) phase is about 612°C, at which the samples transform from ferromagnetic α-Fe(Si) phase into paramagnetic α-Fe(Si), and formed Fe_2B phase (Fig. 2, point I) [6].

5. The fifth stage (IJ), above 632°C. It describes the process in which the samples are transformed from paramagnetic α-Fe(Si) nanocrystalline phase into final stable larger grain α-Fe(Si) and Fe_2B phases. Since mass and saturated magnetic moment of annealed samples maintain unchanged, both σ and dσ/dT hardly change with temperature. But DSC and XRD can analyze the change of structure.

σ–T curves of isothermal annealed samples

The σ–T curves of samples annealed in temperature range of 480 to 610°C for 1 h is shown in Fig. 3. It shows that when the annealed temperature T_a is lower than T_F of Fig. 2, the shape of σ–T curve is similar to that of the as-quenched sample (Fig. 3a). 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 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 3b shows the σ–T curves when T_a is higher than T_F. It is difficult to identify different stages of 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 T_C at different annealed temperatures is about the same, and is close to point I of σ–T curve in Fig. 2, but is slightly higher than the temperature of point 'd' of DSC curve in Fig. 1.

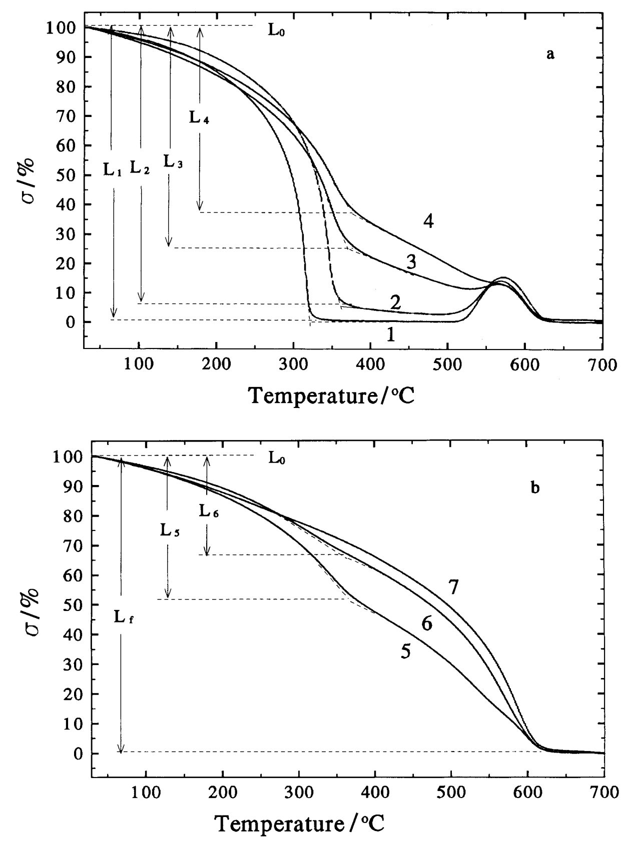

Fig. 3 The σ–T curves of samples annealed in temperature range of 480–610°C for 1 h; (T_a is the annealed temperature); a: 1 – as-quenched state, 2 – 500°C, 3 – 520°C, 4 – 530°C (T_a<T_F, i.e. 535°C); b: 5 – 540°C, 6 – 565°C, 7 – 610°C (T_a>T_F)

Figure 4 shows the variation of T_c in residual amorphous phase with T_a, where T_C increases linearly with T_a, i.e. T_C=0.52 T_a+91.7°C, with correlation coefficient γ=0.98, in the temperature range of 480–540°C. According to the results of the σ–T curve (EFG region) in Fig. 2, 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, thus the Fe:B in the residual amorphous phase decreases. This is in agreement with the results reported by Hasegawa [15] and Hernando [16]. They found that a decrease of the Fe:B ratio induced an increase of Curie temperature in $Fe_{100-x}B_x$ amorphous alloy 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 in FeCuNbSiB nanocrystalline alloy. However, when T_a is higher than 540°C, since the quantity of the residual

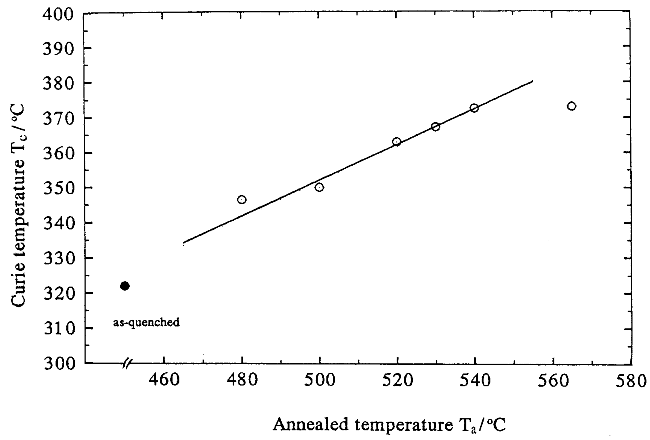

Fig. 4 Variation of T_C for residual amorphous phase with T_a

amorphous phase decreases evidently, the exchange interaction becomes weak, thus the variation of T_C deviates from linearity.

dσ/dT–T curves of isothermal annealed samples

The dσ/d*T*–*T* curves of samples annealed at different temperatures are shown in Fig. 5. The first minimum (*B*' valley) of dσ/d*T*–*T* curves (which expresses that the samples 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. It 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°C, the two sides of valley appears non-symmetry. When the samples were annealed at higher temperature, the *B*' valley of the dσ/d*T*–*T* curve disappears and only the *H*' valley remains.

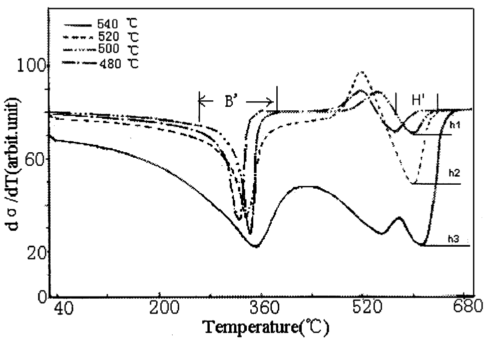

Fig. 5 The dσ/d*T*–*T* curves of FeCuNbSiB amorphous alloy annealed at different temperatures for 1 h

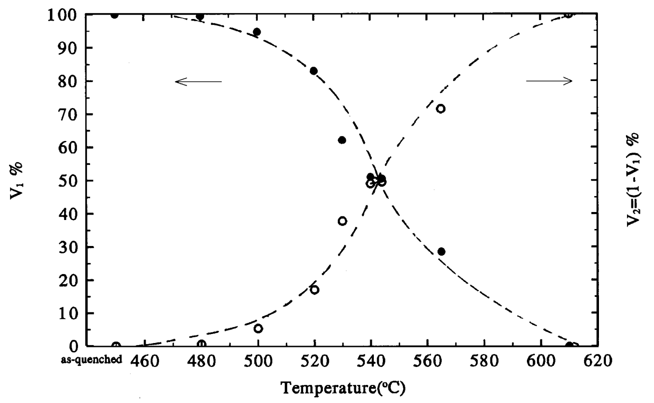

Fig. 6 Variation of volume fraction of α-Fe(Si) nanocrystalline phase or residual amorphous phase with T_a measured by DTG(M) technique

Relationship between volume fraction of transformation and T_a

We can further analyze the relationship between volume fraction of transformation and T_a of the σ–T curve. According to the following formula (1) [17]

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

where V_1, V_2 are the volume fraction 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) [18]

$$V_1 = \frac{L_o - L_t}{L_o - L_F}100\% \tag{2}$$

where L_o, L_F are depth of initial state and final state, (in Fig. 3, L_o=100%), L_t is the vertical distance between the T_C point of sample of different annealed temperature and the horizontal line (Fig. 2). V_2=1–V_1. Thus, variation of volume fraction of α-Fe(Si) nanocrystalline phase or residual amorphous phase with T_a measured by TG(M) technique is shown in Fig. 6. It shows that, at the point T_a=540°C, the volume percentage of the α-Fe(Si) phase is 50%, this result corresponds to the result reported by Hono *et al.* [19].

Conclusions

1. DSC measurement shows two exothermic peaks mean that the two-step crystallization processes before final stable phase is attained.

2. The σ–T and dσ/dT–T curves of the FeCuNbSiB amorphous alloy are investigated by TG(M) technique. 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. Those processes are more distinct than DSC technique.

3. The studies of samples annealed at temperature range of 480–610°C for 1 h show that when the annealing temperature (T_a) is less than 540°C, 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, in the temperature range of 480 to 540°C i.e. T_C=0.52T_a+91.7°C, with correlation coefficient γ=0.98.

4. The variation of volume fraction of α-Fe(Si) nanocrystalline phase with T_a is measured by TG(M) technique.

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