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Crystallization kinetics and soft magnetic properties of Fe$_{71}$Si$_{16}$B$_{9}$Cu$_{1}$Nb$_{3}$ amorphous alloys

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Abstract

Fe$_{71}$Si$_{16}$B$_{9}$Cu$_{1}$Nb$_{3}$ amorphous alloy ribbons were prepared with a single roll polar method. X-ray diffraction analysis of the surface samples was completely amorphous. The thermal stability parameters $T_x$, $T_m$, and $T_{end}$ of amorphous ribbons were measured with a synchronous thermal analyzer under high purity argon gas and analyzed for their crystallization behavior. The heating rate was 10 K min$^{-1}$, 15 K min$^{-1}$, 20 K min$^{-1}$, and 30 K min$^{-1}$. The $T_x$ and $T_m$ of the Fe$_{71}$Si$_{16}$B$_{9}$Cu$_{1}$Nb$_{3}$ amorphous alloy increased with an increase in the heating rate, indicating that the crystallization behavior has a kinetic effect. The crystallization activation energy of the amorphous alloy was calculated using the Kissinger and Ozawa equations, respectively. The calculation results of the two methods were consistent. The sample was annealed (761 K, 786 K, 801 K, and 858 K, holding for 300 s) under the protection of high purity argon. The phase transition and microstructure transformation of the amorphous alloy during isothermal crystallization were analyzed by x-ray diffraction. When the alloy was annealed at 801 K, a single $\alpha$-Fe($Si$) solid solution precipitated on the amorphous matrix. Magnetic properties were measured using a vibrating sample magnetometer and observed by transmission electron microscopy. When the alloy was annealed at 786 K and 801 K, the saturation magnetic induction reached 1.22~1.27 T, coercivity was as low as 5.3~7.2 A m$^{-1}$, and the average grain size was about 10~20 nm.

1. Introduction

In 1967, Duwez and Lin of the California Institute of Technology first prepared ferromagnetic Fe–C–P amorphous alloy ribbons, prompting widespread interest and research [1–5]. In 1988, Yoshizawa et al [6] developed the FeSiBCuNb series of iron-based nanocrystalline soft magnetic alloys. These alloys are inexpensive, quickly prepared, and stable, with excellent soft magnetic properties. Subsequently, they have been widely used under the brand name ‘FINEMET’. FINEMET alloys offer low loss, high magnetic permeability, and high saturation magnetic induction [7–9]. They can reach above 1.2 T, higher than permalloys and co-based amorphous alloys, and, like these alloys, their expansion factor approaches zero [10–12]. They have been widely used for the commercial production of motor stators and rotor materials, high-frequency switching power supplies, and common-mode inductors. However, during the production process of amorphous ribbon, there are problems related to thermodynamic performance, unstable magnetic properties, and a large error range. Since the magnetic properties of amorphous nanocrystalline materials are extremely sensitive to the annealing temperature, many studies have been conducted on the magnetic mechanism from the annealing process [13–15]. Wang et al [16–20] studied the effects of the annealing rate, annealing temperature, holding time, and annealing atmosphere on the magnetic properties from the perspective of the annealing process. Han et al [21–23] studied the effects of the magnetic metal content and alloying elements on the magnetic properties from the perspective of composition. To our knowledge, however, there are no studies on the magnetic mechanism from the perspective of the crystallization process. To address this, we used an Fe$_{71}$Si$_{16}$B$_{9}$Cu$_{1}$Nb$_{3}$ amorphous alloy to study the influence of its crystallization process on the soft magnetic properties. Our study provides a
theoretical basis for the production process of amorphous nanocrystalline ribbons, and has practical implications for the production of amorphous nanocrystals.

2. Experimental

A master alloy of Fe$_{71}$Si$_{16}$B$_9$Cu$_1$Nb$_3$ was prepared in an electromagnetic induction melting furnace. To ensure the individual atomic percentages of the materials, the smelting was repeated four times, where the high purity metal elements were Fe (99.95 mass%), Si (99.5 mass%), B (99.9 mass%), Cu (99.9 mass%), and Nb (99.95 mass%). The metal raw material was configured in accordance with the atomic percentage of the Fe$_{71}$Si$_{16}$B$_9$Cu$_1$Nb$_3$ alloy. The experimental ribbon sample was prepared with a single roll quenching method. The surface speed of the copper roll was 40 ms$^{-1}$, and the obtained amorphous ribbon sample was about 20 μm thick and 1 mm wide. We used the chemical method (ICP) to determine the atomic percentage of the prepared sample, and confirmed that the atomic percentage of each element of the prepared sample was consistent with the target component. The amorphous phase was then confirmed and the precipitated phase was analyzed with a PANalytical x-ray diffractometer (XRD). Finally, a French Setsys-type synchronous thermal analyzer (DSC) was used to confirm the characteristic temperature and develop the annealing temperature mechanism. Finally, the magnetic properties of the samples were measured with a US Lake Shore Model 7404 Vibrating Sample Magnetometer (VSM) and the microstructure of the ribbon samples was characterized by FEI Tecnai G$^2$F20 transmission electron microscopy (TEM).

3. Results and discussion

3.1. Thermal stability of Fe$_{71}$Si$_{16}$B$_9$Cu$_1$Nb$_3$ amorphous ribbon

The XRD diffraction pattern of the Fe$_{71}$Si$_{16}$B$_9$Cu$_1$Nb$_3$ amorphous ribbon fabricated with the single roll quenching method is shown in figure 1. As shown in the figure, a wide diffuse scattering peak appeared at about 44°, without the appearance of any sharp diffraction peak corresponding to the crystal, indicating that the prepared thin strip sample was completely amorphous.

The thermodynamic properties of the Fe$_{71}$Si$_{16}$B$_9$Cu$_1$Nb$_3$ amorphous thin strip were measured with the synchronous heat analyzer DSC. The warming rates were set at 10, 15, 20, and 30 K min$^{-1}$, respectively. The resulting DSC curve is shown in figure 2. With an increase to the heating rate, the initial crystallization temperature $T_x$ and the crystallization peak temperature $T_p$ moved toward a higher temperature. This showed that the crystallization behavior of the Fe$_{71}$Si$_{16}$B$_9$Cu$_1$Nb$_3$ amorphous thin strip was closely related to the warming rate. That is, the crystallization process of the Fe$_{71}$Si$_{16}$B$_9$Cu$_1$Nb$_3$ amorphous alloy had a significant kinetic effect. The thermodynamic parameters are shown in table 1.

In general, $T_x$ and $T_p$ at a certain heating rate can be used as indicators of the formation ability and thermal stability of an amorphous alloy. The crystallization activation energy $E$ better reflects the energy barrier that the amorphous alloy needs to overcome. The activation energy magnitude is described by the Kissinger [24] equation and the Ozawa [25] equation, respectively:

$$E = -\frac{R \ln(α)}{T_x}$$

$$E = \frac{1}{T_p} \ln\left(\frac{\beta}{T_p} \frac{\partial T_p}{\partial \ln\beta}\right)$$
\[ \ln \left( \frac{T^2}{\beta} \right) = \frac{E}{RT} + C \]  

(2-1)

\[ \ln \beta = - \frac{E}{RT} + C \]  

(2-2)

where \( T \) is the characteristic temperature (K), \( \beta \) is the heating rate (K min \(^{-1}\)), \( E \) is the crystallization activation energy, \( R \) is the ideal gas constant, and \( C \) is a constant. According to the characteristic temperature of the Kissinger equation and the different heating rates shown in Table 1, the least squares method was used to fit the data and obtain the \( 1/T \cdot \ln(T^2/\beta) \) straight line (Figure 3). The crystallization activation energy was obtained from the slope of the fitted straight line. The first crystallization activation energy was \( E_{x1} = 389 \text{ KJ mol}^{-1} \) and the first activation energy was \( E_{p1} = 349 \text{ KJ mol}^{-1} \). The second crystallization activation energy was \( E_{x2} = 493 \text{ KJ mol}^{-1} \) and the second activation energy was \( E_{p2} = 507 \text{ KJ mol}^{-1} \). Similarly, the \( \ln \beta \) and \( 1/T \) lines were obtained according to the Ozawa equation (Figure 4). The slope of the line was found at \( E_{x1} = 400 \text{ KJ mol}^{-1} \), \( E_{p1} = 361 \text{ KJ mol}^{-1} \), \( E_{x2} = 411 \text{ KJ mol}^{-1} \), and \( E_{p2} = 507 \text{ KJ mol}^{-1} \).

Two distinct crystallization peaks appeared on each DSC curve as shown in Figure 2, indicating that the Fe\(_{71}\)Si\(_{16}\)B\(_{9}\)Cu\(_{1}\)Nb\(_{3}\) amorphous alloy underwent a multi-stage crystallization process, and that the crystallization phase was not precipitated at the same time. Thus, the crystallization process was closely related to the crystallization temperature. The higher the initial crystallization temperature, the more difficult the nucleation during crystallization. Moreover, the higher the crystallization peak temperature, the more difficult it is for the crystal to grow during crystallization [26]. Table 2 lists the values of the activation energy calculated for the Fe\(_{71}\)Si\(_{16}\)B\(_{9}\)Cu\(_{1}\)Nb\(_{3}\) amorphous ribbon using the Kissinger and Ozawa equations. It can be seen that the results calculated by the Kissinger equation and the Ozawa equation were close and consistent. \( E_{x2} \) was much higher than \( E_{x1} \), indicating that the nucleation process of the second-stage crystallization was more difficult than the nucleation process of the first-stage crystallization. Furthermore, \( E_{x1} \) was higher than \( E_{p1} \), indicating that the crystal nucleation process was longer than the crystal during the first-stage crystallization. The large process was more difficult; \( E_{p2} \) was higher than \( E_{x2} \), indicating that the crystal growth process was more difficult than the nucleation process in the second-stage crystallization process.
3.2. Effect of crystallization process on soft magnetic properties

To investigate the influence of the crystallization process on the soft magnetic properties, the saturation magnetic induction $B_s$, the coercive force $H_c$ of the original strip, and the annealing samples at different temperatures were measured by VSM (as shown in table 3 and figure 5). It can be seen that when the annealing temperature increased from $T_{x1}$-30 K (761 K) to $T_{end} + 5$ K (858 K), the magnetic properties of the amorphous ribbon increased with an increase in the annealing temperature, and the saturation magnetic induction $B_s$ increased from 1.19 T to 1.35 T. Since 761 K, 786 K, and 801 K are in the supercooled liquid phase of the amorphous ribbon to the initial stage of the crystallization process, nucleation is difficult at this stage. As such, the annealing process does not have much influence on the crystallization process; it mainly serves to remove residual stress [27]. The coercive forces of the amorphous ribbon after annealing at 761 K, 786 K, and 801 K for 300 s were reduced compared to that of the original amorphous ribbon. When annealing at 858 K, $H_c$ increased

| Equation | $E_{x1}$ | $E_{p1}$ | $E_{x2}$ | $E_{p2}$ |
|----------|----------|----------|----------|----------|
| Kissinger | 389      | 349      | 397      | 493      |
| Ozawa    | 400      | 361      | 411      | 507      |

3.2. Effect of crystallization process on soft magnetic properties

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significantly. This was because 858 K was the temperature after the completion of the first crystallization process. Therefore, it had a greater impact on $H_c$. Amorphous ribbons annealed at $T_{x1} + 10$ K (801 K) for 300 s were used to determine the XRD precipitation phase (figure 6). It can be seen that $\alpha$-Fe(Si) occurred around 45°, 66°, and 83°. The crystallization peaks corresponded to the (0 1 1), (0 0 2), and (1 1 2) crystal planes, respectively. Since 801 K was in the first-stage crystallization process, it was determined that a single $\alpha$-Fe(Si) precipitated during crystallization.

Figure 7 shows a TEM bright field image and the selected area electron diffraction (SAED) pattern of Fe$_{71}$Si$_{16}$B$_9$Cu$_1$Nb$_3$ amorphous nanocrystalline ribbon after annealing at 761 K (a), 786 K (b), and 801 K (c) for 300 s. The image shows that crystal grains of about 5 nm, 10 nm, and 20 nm were uniformly deposited on the amorphous sample substrate, and a body-centered cubic (bcc) crystal phase was observed in the SAED.
spectrum. This indicated that, as the annealing temperature increased, the crystallization process accelerated and the grain size gradually grew. Annealing treatment near the first-stage crystallization temperature obtained amorphous nanocrystalline ribbons with better soft magnetic properties. When the Fe$\text{71Si}_{16}\text{B}_{9}\text{Cu}_{1}\text{Nb}_{3}$ amorphous alloy was anisotropically annealed at 786 K and 801 K for 300 s, α-Fe(Si) grains with an average grain size of about 10–20 nm precipitated on the amorphous ribbon samples, and the saturation magnetic induction reached 1.22–1.27 T with coercivity as low as 5.3–7.2 A m$^{-1}$.

4. Conclusions

(1) The $T_x$ and $T_p$ of the Fe$\text{71Si}_{16}\text{B}_{9}\text{Cu}_{1}\text{Nb}_{3}$ amorphous alloy all moved in the direction of a higher temperature with an increase to the heating rate, indicating obvious kinetic effects.

(2) The crystallization activation energy of the Fe$\text{71Si}_{16}\text{B}_{9}\text{Cu}_{1}\text{Nb}_{3}$ amorphous alloy was higher than the activation energy, indicating that the nucleation of the Fe$\text{71Si}_{16}\text{B}_{9}\text{Cu}_{1}\text{Nb}_{3}$ amorphous alloy was more difficult than the growth.

(3) When the Fe$\text{71Si}_{16}\text{B}_{9}\text{Cu}_{1}\text{Nb}_{3}$ amorphous alloy was anisotropically annealed at 786 K and 801 K for 300 s, α-Fe(Si) grains with an average grain size of about 10–20 nm precipitated on the amorphous ribbon samples, and the saturation magnetic induction reached 1.22–1.27 T with coercivity as low as 5.3–7.2 A m$^{-1}$.

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