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Crystallization progress and soft magnetic properties of Finemet alloy with Ge addition

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ABSTRACT

The influence of the partial substitution of Si by Ge (6 at.%) on the structure, crystallization kinetics and magnetic properties of Finemet-type alloys were studied by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimeter (DSC) and room-temperature hysteresis loops measurements. Amorphous ribbons were heat treated at different temperatures for 1 *h* in a vacuum furnace to induce nanocrystallization. It was found that a homogeneous structure of α-Fe_3Si structure nanocrystals with a grain size less than 15 nm embedded in an amorphous matrix was obtained within the temperature range of 510–590 °C. The crystallization activation energies calculated using Kissinger model were 331 and 356 kJ/mol for the first and the second crystallizations, respectively. The saturation magnetization of the as-quenched amorphous ribbon is 138 Am^2/kg and decreases gradually with the increase of annealing temperatures from 125 Am^2/kg for 510 °C to 115 Am^2/kg for 590 °C.

Fe-based nanocrystalline alloy, with the typical composition of $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$, was first found by Yoshizawa in 1988, by adding some Cu and M (M = Nb, Mo, W, Ta, etc) into the amorphous alloy of Fe–Si–B [1]. The $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ alloy, which is called Finemet alloy, displays excellent soft magnetic properties with high initial relative permeability (~10^5 at 1 kHz), relatively high saturation magnetization (1.2 T), very low coercive field ($H_C < 1$ A/m) and near zero saturation magnetostriction (~10^{-6}) [2,3]. The excellent soft magnetic properties are attributed to the ultrafine structure composed of α-Fe (Si) nanocrystallites embedded in remaining amorphous matrix. In such a structure, the effective magnetostriction constant of the whole materials is reduced about one order of magnitude because of the compensation effect between the negative magnetostriction of α-Fe (Si) phase ($\lambda_S = -6 \times 10^{-6}$) and the positive value of the amorphous one ($\lambda_S = 22 \times 10^{-6}$) [4,5]. Furthermore, since the size of nanocrystallites (~10–15 nm) is smaller than the ferromagnetic exchange interaction length (about 35 nm for FeSiBCuNb amorphous/nanocomposite system), ferromagnetic exchange coupling between the nanocrystalline α-Fe (Si) grains through amorphous matrix results in an averaging out of the magnetocrystalline anisotropy (as explained by the random anisotropy model) [6].

The influence of the addition of Ge to Finemet-type alloy was thoroughly studied in the past years [7–15]. Some interesting results can be drawn from these works. The M_S of the alloy remained independent of the Ge content. The Curie temperature of the amorphous increased with the addition of Ge for all the studied alloys reaching a maximum value of 664 K for the $Fe_{73.5}Ge_{15.5}B_7Nb_3Cu_1$ alloy. The replacement of Si or B for Ge reduced the amount of amorphous matrix when heat treated at the same temperature. The partial substitution of Ge for B reduces the onset temperature of crystallization phase and increase the temperature of boride precipitation in a continuous heating process. However, there is little report about the effect of Ge substitution for Si on the crystallization kinetics of the Finemet-type amorphous alloy. In this paper, the crystallization kinetics of amorphous $Fe_{73.5}Si_{7.5}Ge_6B_9Cu_1Nb_3$ alloy is analyzed by using the Kissinger method. Crystallization of amorphous alloy is studied by XRD and TEM techniques. Meanwhile, the influence of heat treatment on the magnetic properties is investigated.

The master alloy ingot of amorphous $Fe_{73.5}Si_{7.5}Ge_6B_9Cu_1Nb_3$ was prepared by arc melting purity metals under argon atmosphere. Amorphous ribbons, about 3 mm wide and 25 μm thick, were obtained from the ingot by melt spinning technique in air. The amorphous ribbons were isothermally annealed at different

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temperatures for 1 h in vacuum for nanocrystallization. The microstructure and mean grain size of the as-spun and the annealed samples were analyzed by the technique of XRD (PHILIPS Xpertpro diffractometer with Cu-K_α radiation) and TEM (JEM2100F). DSC was performed using Thermal Analysis System NETZSCH STA 449C under argon flow at different heating rates to analyze the thermal stability and the crystallization kinetic of the alloy. The hysteresis loops of different samples were measured by a vibrating sample magnetometer (VSM: Lakeshore Model 7404) at room temperature and at a maximum applied field of 2.17 T.

Fig. 1 shows the room-temperature powder XRD patterns for the amorphous and the annealed samples at different temperatures. For the rapidly quenched ribbon (Fig. 1a), the diffraction pattern exhibits only one broad band centered at around $2\theta = 45°$ and no any appreciable diffraction peaks corresponding to crystalline phases are detected, indicating that the quenched ribbon is fully amorphous. The ribbon annealed at 470 °C remained amorphous but began to nanocrystallize at 510 °C (Fig. 1b and c). The patterns of the ribbons annealed at 510 °C, 550 °C and 590 °C remained almost unaffected with increasing temperatures except for the higher and narrower peaks, which indicates an increase of the phase volume fraction and a grain size growth, respectively. The lattice parameter of the nanocrystalline alloy annealed at 550 °C ($a = 5.73$ Å) is larger compared with the pure Finemet alloy ($a = 5.68$ Å [12],) due to the difference in atomic size between Ge and Si. From a previous work [16] it is known that in the $Fe_{71.5}Si_{9.5}Ge_6B_9Nb_3Cu_1$ alloy a nanocrystalline α-Fe (Si, Ge) phase is formed. According to the above results, the patterns of the ribbons annealed at 510 °C, 550 °C and 590 °C may be attributable to the α-Fe (Si, Ge) phase. A detailed study is in progress to determine this. From the XRD diffraction patterns the average grain size of nanocrystalline phase (D) can be determined with the Scherrer relationship [17]:

$$D = \frac{0.9\lambda}{\sigma \cos\theta} \tag{1}$$

where λ is the X-ray wavelength ($\lambda = 1.54056$ Å), 2θ is the angle of the dominant Bragg maximum and the σ (rad) is the full-width at half-maximum of the diffraction peak. The average grain sizes are 7.7 nm, 10.9 nm and 15.0 nm for samples annealed at 510 °C, 550 °C and 590 °C, respectively. The X-ray measurements were confirmed by TEM. Fig. 2 shows the bright field images with the corresponding diffraction patterns. No grain structures were observed in as-quenched ribbon and the ribbon annealed at 470 °C for 1 h due to the amorphous structure. When the annealing temperature is up

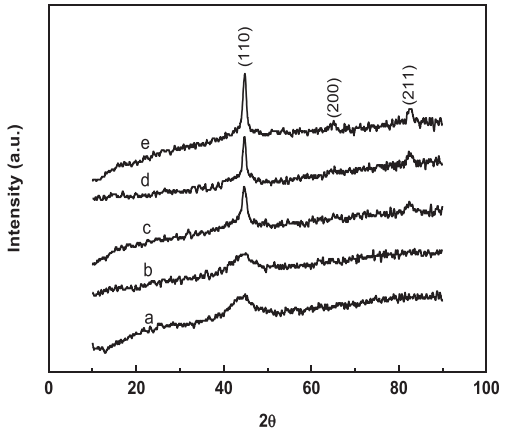

Fig. 1. The room-temperature powder XRD patterns of $Fe_{73.5}Si_{7.5}Ge_6B_9Cu_1Nb_3$: (a) as-quenched amorphous ribbon; (b,c,d,e) ribbons annealed at 470 °C, 510 °C, 550 °C and 590 °C for 1 h in a vacuum, respectively.

to 510 °C, α-Fe_3Si structure nanocrystallines would precipitate and distribute randomly in the amorphous matrix. When the annealing temperature reaches 590 °C, numerous nanocrystallines precipitate from the amorphous matrix with a grain size less than 15 nm. Comparing the three TEM images, it can be seen that increasing annealing temperature results in an increase of grain size and an increase of the number of nanocrystallines.

The typical DSC spectra obtained from as as-quenched ribbons during continuous heating at different heating rates from 5 to 20 °C/min are shown in Fig. 3. The DSC curves exhibit clearly two exothermal peaks, corresponding to the crystallization stages during heating progress. The first peak is due to the crystallization of crystalline α-Fe_3Si soft magnetic phase from amorphous matrix and the second peak is related to formation of the boride-type phases and recrystallization phenomena [18]. Thermal parameters such as two onset temperatures T_{x1}, T_{x2} and two peak temperatures T_{p1}, T_{p2} are determined from the DSC curves, whose values are listed in Table 1. As shown in Fig. 3, the thermal parameters T_{x1}, T_{x2}, T_{p1} and T_{p2} are affected by the heating rates. It is obvious that thermal parameters T_{x1}, T_{x2}, T_{p1} and T_{p2} shift to the higher temperatures with increasing heating rate, which means the nanocrystallization process has kinetic effects. It is found that the thermal parameters T_{x1}, T_{x2}, T_{p1} and T_{p2} are lower than that of pure Finemet alloy [19]. The precipitation temperature of the α-Fe_3Si soft magnetic phase decreases by Ge doping, which means that the substitution of Ge for Si facilitate the formation of α-Fe_3Si structure nanocrystalline phase. In addition, The formation of the boride phase, which promotes the grain growth are reported to have adverse effect on the initial magnetic permeability and give rise to the decline of soft magnetic properties due to the increase of the magnetocrystalline anisotropy [20]. Hence, the shift of the second crystallization peak towards lower temperatures would be disadvantageous. The range of the peak temperature, $\Delta T = T_{p2} - T_{p1}$, changes slightly, which is 139 °C for the pure Finemet alloy, 140 °C for the present sample under the conditions of the same heating rate [21]. It indicates that the substitution of Ge for Si has nearly no effect on the precipitation temperature range of α-Fe_3Si structure nanocrystalline phase.

It is important to know the activation energy of the crystallization process. The activation energy generally defined as the threshold value of energy above which the energy fluctuation is sufficient for the elementary reaction to occur, and it should have a characteristic constant value for each particular reaction. The activation energy can be obtained from the DSC results using Kissinger equation [22], which is widely used for the calculation of activation energy in Finemet-type alloys. The Kissinger equation is as follows:

$$\ln\frac{\beta}{T^2} = -\frac{E_a}{RT} + \text{const} \tag{2}$$

where β is the heating rate, R is the universal gas universal gas constant, E_a is the activation energy for the crystallization of the amorphous phase and T is a specific absolute temperature such as peak temperature T_{pi} ($i = 1, 2$). Fig. 4 shows the dependence of $\ln(\beta/T^2)$ on the inversed exothermal temperature, $1000/T_p$. The linear dependence of the $\ln(\beta/T^2)$ on the $1000/T_p$ confirms that the Kissinger model is reasonable for describing the crystallization in this study. As a result, the activation energies of E_{a1} and E_{a2} in this case can be easily determined by linear fitting the dependence in Fig. 4, and shown to be 331 and 356 kJ/mol, respectively. Here, the activation energies E_{a1} and E_{a2} indicate the participation of different phases in the first and second stages of continuous heating for the sample. G. Herzer showed that the activation energy (E_{a1}) for the crystallization of the pure Finemet alloy $Fe_{73.5}Si_{13.5}B_9Cu_1Nb_3$ was 413 kJ/mol [3,4]. Thus the activation energy for the crystallization of