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Study of the crystallization kinetics in amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy

A. CSEREI
Department of Nuclear Chemistry, Eötvös University, Budapest, Hungary
J. JIANG, F. AUBERTIN, U. GONSER
Werkstoffwissenschaften, Universität des Saarlandes, Saarbrücken, Germany

The kinetics of the crystallization of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy was studied using Mössbauer spectroscopy and X-ray diffractometry. During isothermal annealing of the samples, two phases were observed: a crystalline $D0_3$-FeSi alloy with fine grains and an amorphous phase enriched with niobium, boron and copper. It was found that the growth rate of the particles of the crystalline alloy was controlled by diffusion. For longer annealing time or at higher annealing temperature the growth process was found to be suppressed, probably by the niobium atoms. The activation energy obtained for the crystallization was about 143 kJ mol^{-1}.

1. Introduction

Amorphous magnetic alloys have been intensively studied over the last decade with the aim of application in electrical devices [1]; cobalt-based amorphous alloys, in particular, have been studied because of their excellent soft magnetic properties. Recently, Yoshizawa and co-workers [2, 3] reported that superior soft magnetic properties can be obtained for a crystalline alloy by crystallization of Fe–Si–B amorphous alloy containing, in addition, niobium and copper. This crystalline material is composed of fine grains of about 10 nm diameter. Considerable interest in the investigation of this material has arisen with respect to its crystallization behaviour and because of its excellent soft magnetic properties [4–8].

In our earlier work [7], the crystallization behaviour of the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy was studied by X-ray diffractometry and Mössbauer spectroscopy. On annealing the samples isochronally, two crystallization steps were observed. From 753–973 K two phases existed: the $D0_3$-FeSi alloy with ultrafine grains and a residual amorphous phase enriched with niobium, boron and copper. At 973 K, the amorphous part crystallized into $Fe_{23}B_6$ compound and presumably FeNbB alloy.

In the present work, the kinetics of the crystallization of amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy was studied using Mössbauer spectroscopy and X-ray diffractometry.

2. Experimental procedure

Amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ ribbons with a width of about 10 mm and a cross-section of about 23 μm were prepared by the melt-spinning technique. The ribbons were isothermally annealed in a vacuum of 1.3×10^{-3} Pa at 750, 793 and 800 K for different times (from 20 min to 24 h). Mössbauer spectra of the samples were recorded at room temperature by a constant acceleration type spectrometer. The source was ^{57}Co in a rhodium matrix. The isomer shift values are given relative to the centre of α-Fe at room temperature. X-ray diffraction measurements on as-prepared and annealed samples were carried out using CuK_α radiation.

3. Results and discussion

3.1. Phases

Fig. 1 shows X-ray diffraction patterns for the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloys in the as-prepared state and after annealing at 793 K for different times. The as-prepared sample reflects a typical amorphous state with a broad peak (Fig. 1a) at about 44.20°. After annealing the alloy for 30 min (Fig. 1b), in addition to the amorphous phase, a new phase exists with peaks (2θ) at 45.16°, 65.76° and 83.16°. The new phase is identified as a crystalline Fe–Si alloy with $D0_3$ structure [5, 7]. The grain size estimated from the line broadening of the peak at 45.16° ((2 2 0) peak of the $D0_3$-FeSi phase) is 8.7 nm. The lattice constant obtained is 0.5674 nm. With increasing annealing time (Fig. 1c–e) the amount of $D0_3$-FeSi phase and its grain size increase, while the amorphous part decreases. This change can be seen in Fig. 2 which shows the average crystal size as a function of the amorphous fraction.

Fig. 3 shows Mössbauer spectra for the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloys in the case of the as-prepared state and after annealing at 793 K for different times. In the as-prepared state the spectrum (Fig. 3a) was fitted by a sextet with broad lines that is typical of the amorphous state because of the occurrence of hyperfine field distribution. The mean

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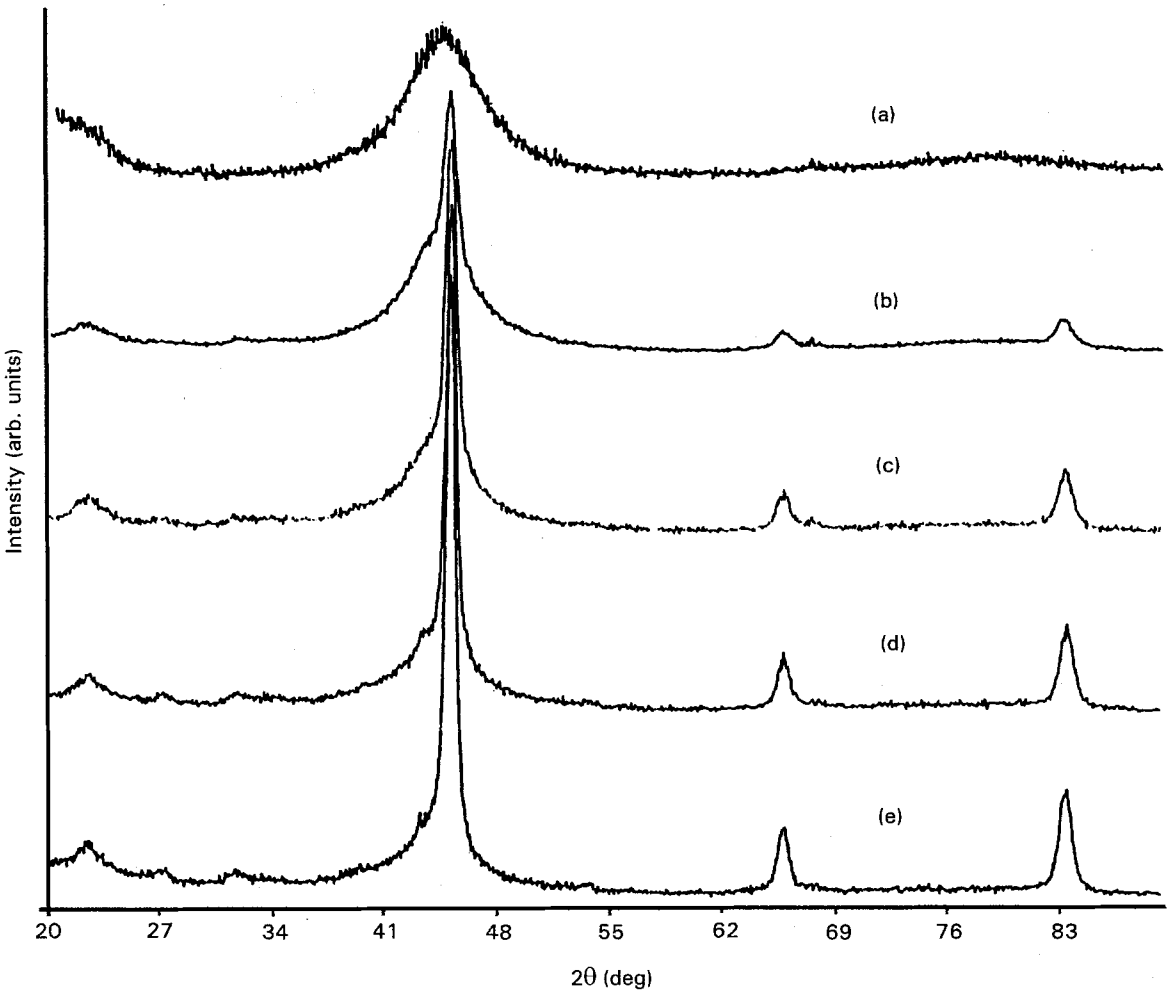

Figure 1 X-ray diffraction patterns for the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloys in (a) the as-prepared state and after annealing in a vacuum of 1.3×10^{-3} Pa at 793 K for (b) 0.5, (c) 1.0, (d) 5.0 and (e) 24.5 h.

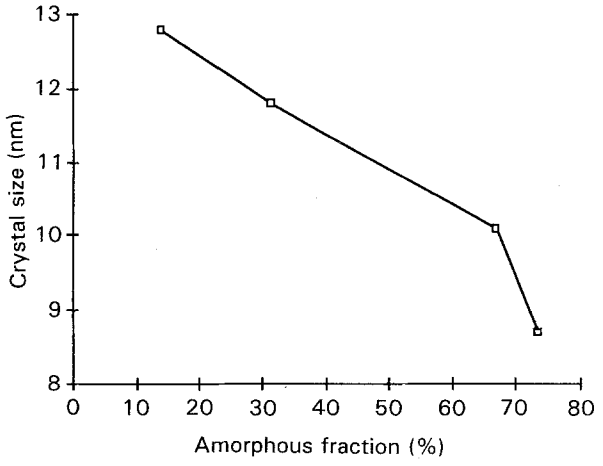

Figure 2 The crystal size as a function of the amorphous fraction.

hyperfine field at the iron atoms in the amorphous alloy is 208 kOe. After annealing the samples, the spectra (Fig. 3b–e) consist of five subspectra: a broadened sextet characterizing the amorphous state and four sharp sextets belonging to the crystalline $D0_3$-FeSi alloy. The sextets of $H = 315$, 286, 244, 194 kOe (1 Oe = $10^3/4\pi$ A/m) can be associated with iron atoms having 8, 6, 5, 4 Fe atoms as nearest neighbours, respectively [4, 9].

The Mössbauer parameters of the four subspectra are shown in Table I. On increasing the annealing time, the amount of the crystalline $D0_3$-FeSi alloy increases with a decrease of the amorphous part. Fig. 4 shows the mean hyperfine field of the amorphous phase as a function of the amount of amorphous component. The mean hyperfine field is found to decrease with a decrease of the amorphous fraction. This result can be explained by the weakening exchange interaction between the iron atoms in the amorphous phase during crystallization owing to enrichment of niobium, boron and copper atoms in the vicinity of the iron atoms. The larger amounts of niobium, boron and copper in the amorphous component supports the results reported elsewhere [6, 7, 10].

3.2. Crystallization kinetics

In a number of amorphous metallic alloys, the radii of primary crystals have been found to follow a parabolic relationship with the annealing time, indicating that growth is controlled by volume diffusion [11]. Fig. 5 shows the average radii of the crystalline particles estimated from the X-ray diffractograms as a function of the square root of the annealing time at 793 K. At the beginning of the crystallization, the mean radius of

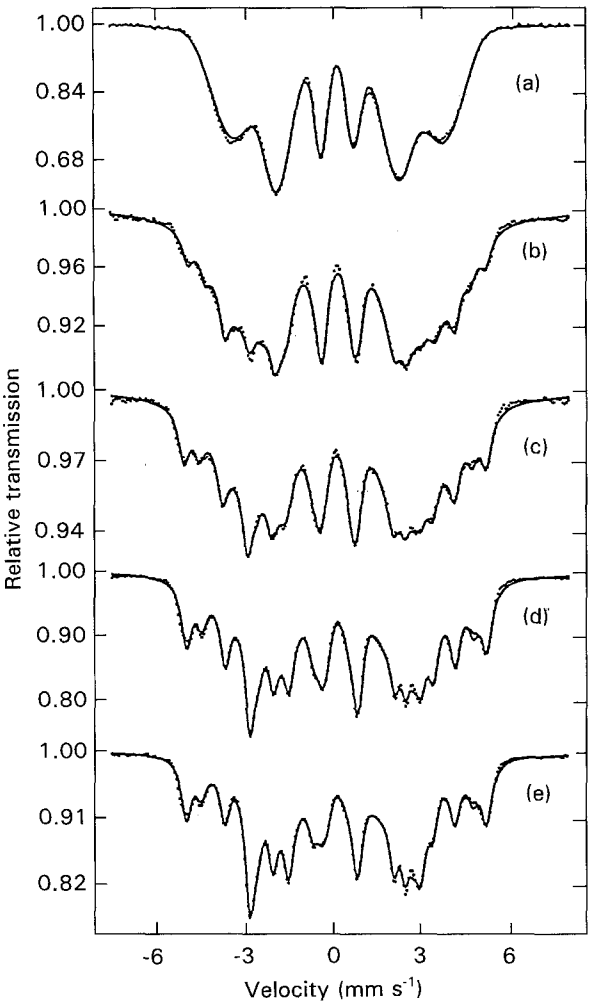

Figure 3 Room-temperature Mössbauer spectra for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloys in (a) the as-prepared state, and after annealing in a vacuum of 1.3×10^{-3} Pa at 793 K for (b) 0.5, (c) 1.0, (d) 5.0 and (e) 24.5 h.

TABLE I Mössbauer parameters of the subspectra for the crystalline $D0_3$-FeSi alloy obtained during isothermal annealing of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy

Subspectrum	H(kOe)	IS (mm s^{-1})
1	315(1)	0.05(1)
2	286(1)	0.08(1)
3	244(1)	0.17(1)
4	194(1)	0.25(1)

the crystals increases linearly with the square root of the annealing time, which shows that growth of the $D0_3$-FeSi alloy particles is controlled by diffusion. After about 40 min, the growth rate decreases considerably. The decrease of the growth rate was also observed by *in situ* transmission electron microscopy (TEM) measurements [12]. During the first few minutes, ultrafine grains are formed due to crystallization of the $D0_3$-FeSi alloy. The TEM results for longer annealing times reveal that the size of the grains does not change considerably. The decrease of growth rate can be caused by the surrounding niobium atoms because they seem to retard the diffusion of silicon and iron, thus they suppress the growth process.

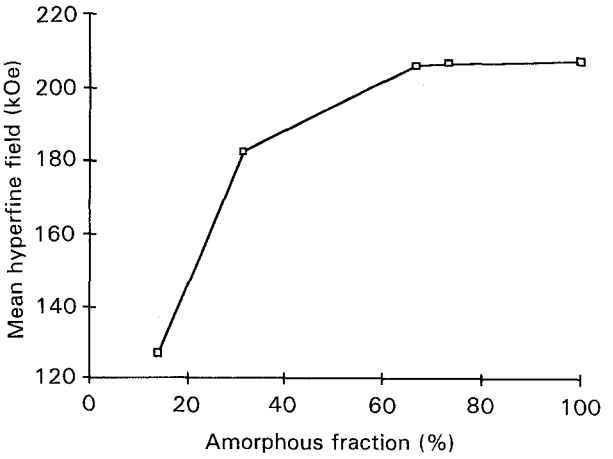

Figure 4 The mean hyperfine magnetic field at iron atoms in the amorphous phase as a function of the amount of the amorphous phase.

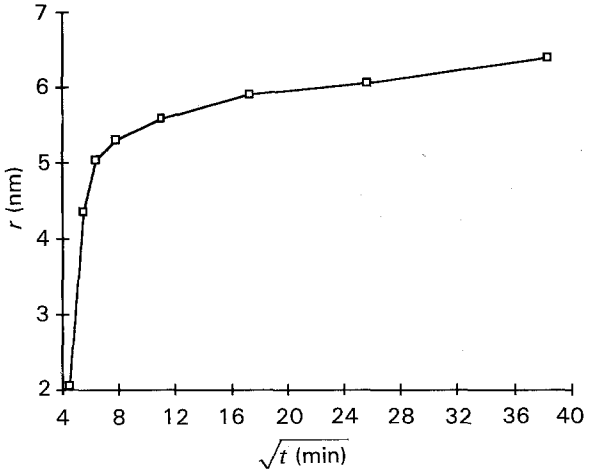

Figure 5 The average radii of the crystalline $D0_3$-FeSi alloy particles as a function of the square root of the annealing time at 793 K.

To obtain further information on the crystallization kinetics, the Johnson–Mehl–Avrami (JMA) equation was applied, which is generally used for description of solid-state nucleation and growth transformations [13–15]

$$X(t) = 1 - \exp[-(kt)^n] \quad (1)$$

where $X(t)$ is the fraction transformed after time t, n is a dimensionless parameter related to the reaction mechanism, k is the reaction rate constant, whose temperature dependence is generally expressed by the Arrhenius equation

$$k = k_0 \exp(-E_a/k_B T) \quad (2)$$

where k_0 is a frequency factor, E_a is the activation energy for a given process, k_B is the Boltzmann constant, and T the absolute temperature. The value of n can be obtained by plotting $\ln\{-\ln[1 - x(t)]\}$ against $\ln(t)$. Fig. 6 shows the results for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloys annealed at 750, 793 and 800 K for different times. The $X(t)$ crystalline fractions were obtained from the Mössbauer spectra by calculating the area ratio of the subspectra characterizing the crystalline and the

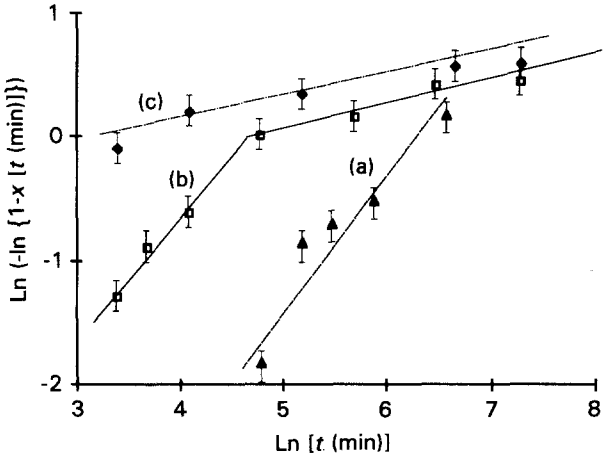

Figure 6 In $\{-\ln[1-x(t)]\}$ as a function of $\ln(t)$ for the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloys annealed isothermally at (a) 750, (b) 793 and (c) 800 K for different times.

amorphous phases. It was assumed that the Debye–Waller factors for all phases are the same.

At 750 K, the value of n is 1.00. The curve at 793 K contains two parts. The slope of the first part is almost the same as that at 750 K: $n = 0.98$. The slope of the other part is much lower: $n = 0.20$. At 800 K, n is a slightly lower than that for the second part of the curve at 793 K: the slope is 0.13.

It can be seen that the value of the Avrami exponent depends on the annealing temperature because the temperature affects the crystallization process. At 793 K, the value of n for the first part is near to 1.50, which is expected theoretically when the crystallization process is controlled by volume diffusion and the nucleation rate is zero (fixed number of quenched-in nuclei) [16]. The results of our X-ray diffraction measurements also suggest that the growth process is controlled by diffusion. The existence of quenched-in nuclei of a fixed number can also be expected, because the formation of such nuclei is probable during the quenching process. For longer annealing times, the value of n decreased to 0.20, which may be caused by suppression of the growth process of crystalline $D0_3$-FeSi grains. The reason for the suppression is probably the niobium, because the niobium atoms retard the diffusion of iron and silicon atoms because of their large atomic radii.

At 750 K, n was found to be 1.00. It seems as if the crystallization proceeded more slowly and the suppression of the growth followed only after a very long annealing time (more than 24 h). This could be the reason why only a straight line was obtained without a breakingpoint.

At 800 K, the value of n was very close to that belonging to the second part at 793 K. At this temperature, crystallization occurs more quickly than at 793 K, therefore, the suppression of growth can take place in a short time. Thus the data obtained reflect the state where the growth rate has already decreased.

The activation energy for crystallization was determined from Equation 2 using only the parts with slope $n \approx 1.0$. The slope of the $\ln k$–$1/T$ straight line is $-E_a/k_B$. The value of E_a obtained was about 143 kJ mol^{-1}.

4. Conclusion

From the Mössbauer and X-ray measurements, the phases formed in the annealed samples have been identified as $D0_3$-FeSi alloy and an amorphous phase enriched with niobium, boron and copper. The radii of the particles were found to follow a parabolic relationship with annealing time, which indicates that growth of the $D0_3$-FeSi alloy particles is controlled by volume diffusion. For longer annealing times, the growth rate decreased. This could be caused by the niobium atoms. The Avrami exponent was found to depend on temperature. The value of 1.00 also suggests that the crystallization process is controlled by diffusion and the nucleation rate is zero. The low n value ($n \approx 0.20$) may be associated with decrease of the growth rate, because of the effect of the niobium atoms.

The activation energy for the crystallization was found to be about 143 kJ mol^{-1}.

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