Crystallization kinetics of an Fe–Co based metallic glass

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Crystallization kinetics of the $Fe_{67}Co_{18}Si_1B_{14}$ metallic glass has been studied from electrical conductivity measurements. Results are interpreted on the basis of a modification of the Germain *et al.* model (*J. Non-Cryst. Solids* **23** (1977) 93). The characteristics of kinetics for different annealing temperatures are analysed and the activation energy is evaluated

1. Introduction

In recent years amorphous Fe–Co based alloys have been studied extensively [1–8] because of their potential use in replacing soft magnetic materials. Particularly, some of them are known to exhibit nearly zero magnetostriction. In a previous paper [9] we have reported some observations on the crystallization of the $Fe_{67}Co_{18}Si_1B_{14}$ alloy from electron microscopy studies.

Resistometric measurements are being used as a tool for the study of either crystallization or structural relaxation of amorphous samples, both being decisive in determining the practical abilities of these materials. The crystallized fraction can be obtained in a simple way from electrical conductivity measurements using Landauer's equation [10].

Germain and co-workers [11–14] proposed a simple model in which the time variation of crystallized fraction is interpreted in terms of surface (SIC) or bulk (BIC) induced crystallization. This model allows the determination of kinetic parameters and related characteristics such as the growth rate, size of the crystallites, etc. Applications of this model have been reported for germanium and silicon [13, 14], amorphous selenium [15], and metglasses [16]. The results agree well with those derived from TEM observations and other experimental measurements.

Recently, Kuo and Zhang [8] have studied the crystallization kinetics of amorphous $Fe_xCo_{78-x}Si_8B_{14}$ ribbons using resistivity measure-

ments. The results are interpreted on the basis to the Johnson–Mehl–Avrami relation and a value $n = 0.65$ is obtained for the Avrami exponent. It is obvious that a such value, a nearly half-integer one, cannot be explained by the simple Germain model. The aim of this paper is to propose a modification of the Germain model, which accounts for some limitations inherent in its approach, and apply it to describe the crystallization kinetics of the $Fe_{67}Co_{18}Si_1B_{14}$ metallic glass.

2. Theoretical details

Germain's model is basically supported by three hypotheses: (a) a linear growth rate law, (b) a homogeneous nucleation (steady state), and (c) a full consumption of amorphous matrix at the end of the transformation.

The crystallized fraction is defined as:

$$x(t) = 1 - \exp\left(- V_x(t)/V_0\right) \qquad (1)$$

where V_0 is the total volume and $V_x(t)$ is the extended crystallized volume [17].

From these hypotheses the following polynomial expressions of $\ln(1-x)^{-1}$ against t are found:

$$\ln\left(\frac{1}{1-x}\right) = \frac{p\pi}{S}\left(a_0 + v_g t\right)^2 + \frac{\pi}{3}n\, v_g^2 \left(t^3 - \tau^3\right)$$

$$+ \frac{\pi n}{3e} v_g^3 \tau^4 \ (t > \tau) \qquad (2)$$

TABLE I

Homogeneous nucleation: $n = $ constant

$$\ln\left(\frac{1}{1-x}\right) = \frac{C_\beta - C_\alpha}{C_0 - C_\alpha}\left[p\pi e\,(a_0 + Ct^{1/2})^2 + \tfrac{8}{15}\pi C^3 n t^{5/2}\right] \qquad t < \tau$$

$$\ln\left(\frac{1}{1-x}\right) = \frac{C_\beta - C_\alpha}{C_0 - C_\alpha}\left[p\pi e\,(a_0 + Ct^{1/2})^2 + \tfrac{8}{15}\pi C^3 n \tau^{5/2} + \frac{\pi e n C^2}{2}(t^2 - \tau^2)\right] \qquad t > \tau$$

Heterogeneous nucleation: $n = N_0\,\nu\,e^{-\nu t}$

$$\ln\left(\frac{1}{1-x}\right) = \frac{C_\beta - C_\alpha}{C_0 - C_\alpha}\left\{p\pi e\,(a_0 + Ct^{1/2})^2 + \tfrac{4}{3}\pi C^3 N_0\left(t^{3/2} - \frac{3t^{1/2}}{2\nu} + \frac{3}{2\nu^{3/2}}\right)F[(\nu t)^{1/2}]\right\} \qquad t < \tau$$

$$\ln\left(\frac{1}{1-x}\right) = \frac{C_\beta - C_\alpha}{C_0 - C_\alpha}\left\{p\pi e\,(a_0 + Ct^{1/2})^2 + \tfrac{4}{3}\pi C^3 N_0\left(\frac{\tau^{3/2}}{\nu} - \frac{3t^{1/2}}{2\nu}\right)e^{\nu(\tau-t)} - \frac{3}{2\nu^{5/2}}\,e^{\nu(\tau-t)}\,F[(\nu\tau)^{1/2}]\right\}$$

$$+ \pi e C^2 N_0\left\{\left[-\frac{1}{\nu} + t + \left(\frac{1}{\nu} - \tau\right)e^{\nu(\tau-t)}\right]\right\} \qquad t > \tau$$

$$\ln\left(\frac{1}{1-x}\right) = \frac{4}{3}\frac{\pi}{Se}(a_0 + v_g t)^3 + \frac{1}{3}\pi\frac{n}{e}v_g^3\,t^4$$
$$(t < \tau' < \tau) \qquad (3)$$

$$\ln\left(\frac{1}{1-x}\right) = \frac{p\pi}{S}(a_0 + v_g t)^2 + \frac{1}{3}\pi\frac{n}{e}v_g^3\,t^4$$
$$(\tau' < t < \tau) \qquad (4)$$

where τ is the mean time necessary for a growing crystallite to reach the film surface, e is the thickness of the film, v_g is the growth rate, τ' is such that $\tau' = (e - a_0)/v_g$, a_0 being the mean radius of the initial crystallites, p their number present at $t = 0$, and n the nucleation rate per unit of volume.

A fit of the experimental values gives the more prominent term, which reveals the preponderant crystallization mechanism. However, the main hypotheses of Germain's model are not perfectly realized in all cases and, for example, the expressions obtained cannot acount for half-integer exponents.

In the presence of a primary crystallization process, the following considerations must be done.

1. As shown elsewhere [18], for the assumption of a concentration-independent diffusion rate D, the radius of particles growing via a volume diffusion-controlled mechanism is proportional to $t^{1/2}$, $R = \alpha(Dt)^{1/2} = Ct^{1/2}$ where α is a dimensionless parameter evaluated from the compositions at the particle interface and the composition of the sample.

2. For many real systems heterogeneous nucleation is a more realistic assumption than homogeneous nucleation. Then, the nucleation rate can be expressed by the equation:

$$n = \frac{dN}{dt} = \nu\,(N_0 - N) \qquad (5)$$

where N_0 is the initial number of nucleation sites, $(N_0 - N)$ is the number of available sites at time t, and ν is the nucleation frequency. This assumption lead us to the exponential law:

$$n = N_0\nu e^{-\nu t} \qquad (6)$$

In particular, for $\nu \ll$: $n \simeq \nu N_0$, which corresponds to the steady state of the homogeneous nucleation.

3. Primary crystallization can be schematically expressed as: $\alpha_0 \to \alpha + \beta$, the ratio of α and β phases (transformed matrix and precipitated phase), of composition C_α and C_β respectively, being supplied from the lever-rule. Therefore, the amorphous matrix is not fully transformed in the course of an annealing treatment and, consequently, the crystallized fraction must be redefined as follows:

$$x'(t) = \frac{V_\beta(t)}{V_\beta(\infty)} = \frac{V_\beta(t)}{V_0}\frac{V_0}{V_\beta(\infty)} = x(t)\frac{C_\beta - C_\alpha}{C_0 - C_\alpha} \qquad (7)$$

We think that this approach is more advantageous than that proposed by Tóth [19], not applicable in our case because during the reheating, the polycrystalline configuration (e.g. size of grain) of the precipitated phase is modified and, consequently, the kinetic data are perturbed.

Table I summarizes the expressions obtained from the above hypotheses. Both situations, homogeneous and heterogeneous nucleation are contemplated and calculations are performed for
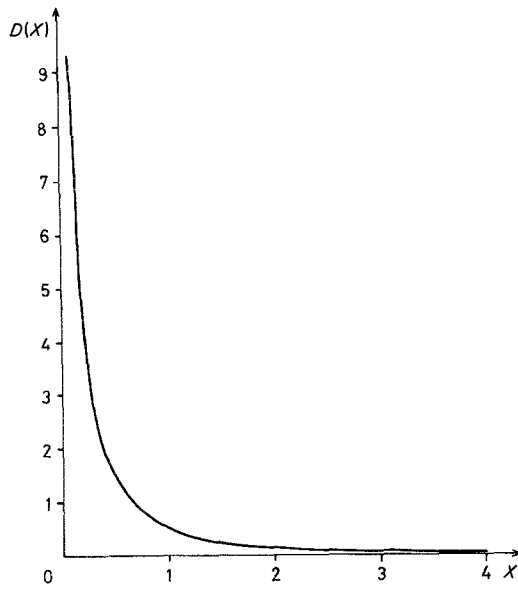
Figure 1 Modified Dawson's function, $D(x) = F(x^{1/2})/x^{3/2}$.

Figure 2 Electrical resistivity against temperature.

both $t < \tau$ and $t > \tau$. Some of the expressions use Dawson's function [20]:

$$F(u) = e^{-u^2} \int_0^u e^{s^2} \, ds \qquad (8)$$

The expressions obtained, more complex than those reported by Germain, include, as expected, half-integer exponent terms. For a much greater value of ν a simplified form of the above expressions is straightforward. For example, for $t < \tau$, the third and fourth terms are negligible (see Fig. 1) and the expression for the time dependent of $\ln[1/(1-x)]$ is:

$$\ln\left(\frac{1}{1-x}\right) = \frac{C_\beta - C_\alpha}{C_0 - C_\alpha} \left[p \, \pi e (a_0 + C t^{1/2})^2\right.$$
$$\left. + \tfrac{4}{3} \pi C^3 N_0 t^{3/2}\right] \quad (t < \tau) \qquad (9)$$

It can be noted that for many practical applications, the less complex $t < \tau$ equations are more useful than the $t > \tau$ equations. For example, MS-I crystallites nucleate copiously but grow slowly, and therefore, for $t > \tau$ further growth is difficult since the amorphous matrix is consumed.

3. Experimental details

Amorphous alloy of nominal composition $Fe_{67}Co_{18}Si_1B_{14}$ produced by Allied Chemical Co. was kindly supplied by Professor Hernando (University of Madrid, Spain). The ribbons were of $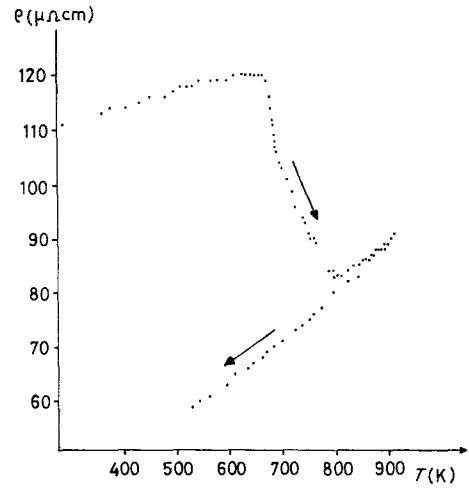100 \, \mu m$ thickness and 0.5 cm width. Electrical resistance was measured using a conventional d.c. method, and to assure good electrical contacts, sheets of copper of 0.3 mm width were pressed tightly on the sample. Temperatures were measured by a chromel−alumel thermocouple and the ensemble (sample, thermocouple, furnace, insulators . . .), which formed a compact whole device, was placed inside an evacuated system (10^{-3} Pa).

4. Results

Two types of experiments were carried out: (a) dynamic heatings, and (b) isothermal annealings at temperatures below the crystallization onset.

Fig. 2 shows the resistivity dependence with temperature during heating ($20 \, \text{K min}^{-1}$) up to $950 \, \text{K}$. Crystallization is evidenced as a single-step anomaly near $675 \, \text{K}$ and a drop of $37 \, \mu\Omega$ cm is observed. The measured value for the TCr is 2.7 $(1) \times 10^{-4} \, \text{K}^{-1}$. It should be also remarked that crystallization takes place through a broad temperature range (675 to $800 \, \text{K}$) and a reproducible anomaly near $700 \, \text{K}$ is detected as a weak slope change.

Fig. 3 shows the electrical resistivity as a function of the time for several isothermal annealings. It is remarkable to observe the differences in the asymptotic values of ρ. This feature is also present in the Kuo and Zhang results [8] and it is related to the different ratio of the remaining untransformed matrix.

Fig. 4 shows a plot of $\log\{\ln[1/(1-x)]\}$ against $\log t$ where the crystalline fraction has been calculated from the time variation of the resistance. In such a plot the slope of a straight line represents
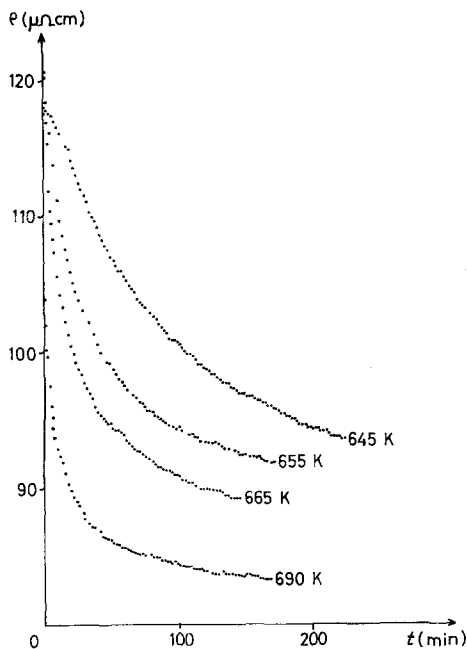
Figure 3 Time dependence of electrical resistivity at various annealing temperatures.

the power r of t:

$$\ln\left(\frac{1}{1-x}\right) = \lambda t^r \qquad (10)$$

The r values obtained for the different annealings are given in Table II.

A remarkable feature, in all the cases, is the absence of intervals with $r \simeq 2.5$. This fact exclude the existence of a dominant steady homogeneous
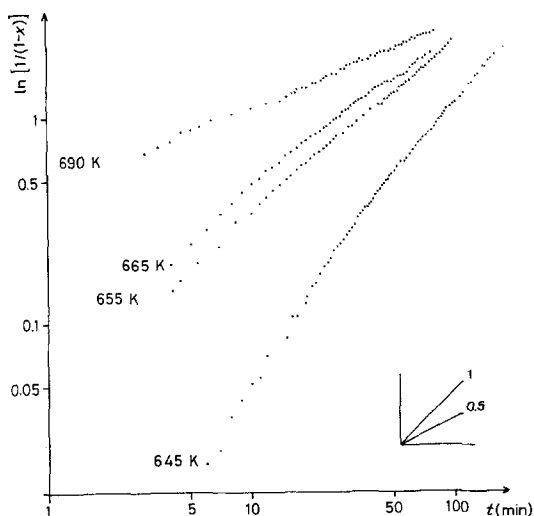

Figure 4 Log [ln $(1-x)^{-1}$] against log t with temperature as the parameter.

TABLE II

T (K)	r
645	1.2
655	0.8
665	1.1; 0.7
690	0.4

nucleation and so we can assume a high ν value. Moreover, this prominent feature was confirmed by means of electron microscopy observations in the course of *in situ* experiments [21], and agrees with the short induction time which can be estimated from the $x(t)$ curves.

Since the annealings were performed at temperatures near to the crystallization onset it can be assumed that the process is controlled mainly by the growth of the crystallites present at $t = 0$ (quenched-in nuclei or those produced in the course of heating up to the annealing temperature), i.e. p is much greater. This assumption is also supported by the absence of an interval with $r \simeq 1.5$. As a consequence, we can write:

$$\ln\left(\frac{1}{1-x}\right) \simeq \frac{C_\beta - C_\alpha}{C_0 - C_\alpha} \, p\pi e(a_0 + Ct^{1/2})^2 \qquad (11)$$

In the last equation the predominant term should be either the linear (t) or the parabolic $(t^{1/2})$, depending on the a_0/C ratio $(C = \alpha[D(T)]^{1/2})$. For the experiments carried out in the range 645 to 665 K, not too close to the crystallization onset, the size, a_0, of the grains formed when the temperature is raised must be small: $a_0 < C$. So, a linear dependence with time is expected, in agreement with experimental results. For the annealing performed at 690 K, close to the onset of crystallization, after a quick heating, the increase in a_0 is considerable [21], whereas the square-root of $D(T)$ only increases by a factor smaller than four (according to the activation energy, value obtained from Fig. 5) and a parabolic growth is expected.

In fact, the expression $\ln[1/(1-x)] = \lambda t^r$ corresponds to the classical Johnson–Mehl–Avrami equation, the overall reaction rate being $k = \lambda^{1/r}$. If an Arrhenius temperature dependence is assumed for k, a value for the overall activation energy of 2.4 (1) eV atom^{-1} is found. This value is lower than that reported for quaternary systems ($\simeq 3$ eV atom^{-1}). This result suggests a decreased stability for this quaternary glass in agreement
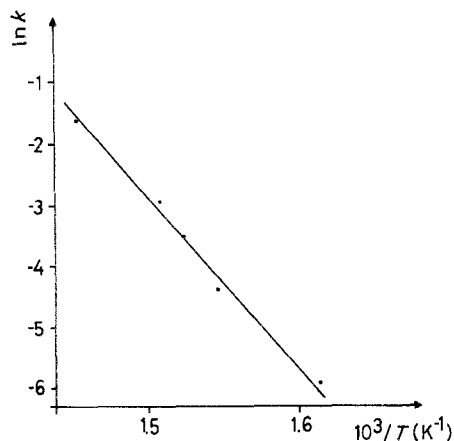
Figure 5 Arrhenius plot of the overall reaction rate, k.

with observations of Coleman [22]: the replacement of iron with cobalt lowers the activation energy and the crystallization onset.

Acknowledgement

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