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Crystallization kinetics study of Fe–B–Si metallic glasses in the theoretical frame of the JMA model

M.P. Trujillo [a,]*, A. Orozco [a], M. Casas-Ruiz [b], R.A. Ligero [b], R. Jimenez-Garay [a]

[a] *Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cádiz, Apartado 40, 11510 Puerto Real, Cádiz, Spain*

[b] *Departamento de Física Aplicada, Facultad de Ciencias Náuticas, Universidad de Cádiz, Apartado 40, 11510 Puerto Real, Cádiz, Spain*

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Abstract

The crystallization kinetics of Fe–B–Si metallic glasses, characterized by the effective activation energy E and the Avrami exponent n was studied by non-isothermal DSC technique. The data show values both for E and n in good agreement with the theoretical JMA model for the first crystallization stage, but not for the second.

1. Introduction

The wide interest in metallic glasses since their preparation for the first time by Paul Duwez in 1960 is quite justified because of their useful properties and applications.

Metallic glasses are soft magnetic materials, with a coercive field of about 10^3 Oe, and with a saturation magnetization of 1 T [1]. Ferromagnetic amorphous glasses are suitable for use in flux multipliers, because of their extremely soft magnetic behaviour and high resistivity, when compared with the corresponding crystalline phase [2].

Metallic glasses change by thermal treatment from their initial state to other states, closer to equilibrium. The transformation is revealed by a change in the microscopic parameters. The difficulty of the study is twofold: First, we do not know the atomic distribution of any metastable state, and, on the other hand, the atomic kinetic mechanisms, that is, the processes responsible of the individual or collective atomic displacements, are not known.

In this paper we will analyze the crystallization processes, by means of non-isothermal techniques, of the metallic glassy alloys $Fe_{78}B_{13}Si_9$ and $Fe_{79}B_{16}Si_5$.

2. Experimental

Glassy alloy foils 5 cm wide and 0.025 mm thick with densities of 7.18 g/cm^3 and 7.28 g/cm^3, and nominal compositions $Fe_{78}B_{13}Si_9$ and $Fe_{79}B_{16}Si_5$ respectively, were supplied by Goodfellow Metals Limited (UK). Continuous heating DSC experiments were carried out in a Perkin–Elmer DSC D7. Heating rates of 2, 4, 8, 16 and 32 K/min were used and the starting temperature was 537 K for all runs, using dry nitrogen as the purge gas. The samples, of about 2–3 mg weight, were heated up to the starting temperature at the maximum available rate (200 K/min) from room temperature to prevent unwanted annealing.

Fig. 1 shows the calorimetric curves for the different experimental runs. As we notice, both alloys present

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* Corresponding author.

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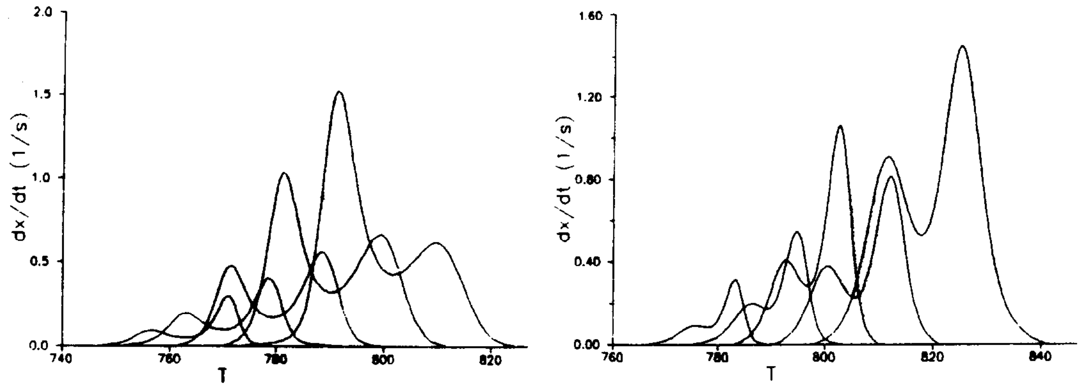

Fig. 1. DSC curves for the two alloys.

complex crystallization reactions, with two overlapping crystallization peaks for all the heating rates, indicating that the samples crystallize in, at least, two different phases.

In order to study separately the crystallization stages, a method is needed for separating the peaks. In this work we use a numerical procedure developed by Ligero et al. [3], making use of two associated functions belonging to the family of Gaussian functions.

3. Theoretical background

The crystallization kinetics of metallic glasses has been usually described in terms of the Johnson–Mehl–Avrami (JMA) equation [4],

$$x = 1 - e^{-(Kt)^n}, \tag{1}$$

where x is the transformed fraction, t is the time, n the Avrami index, and K is the rate constant, showing the temperature dependence of the reaction rate. It is usually described by the Arrhenius equation,

$$K(T) = K_0 \, e^{-E/RT}, \tag{2}$$

where K_0 is the pre-exponential factor, E the effective activation process, and R the gas constant.

However, it must be noticed that the JMA equation was developed under the following assumptions:

1. Isothermal transformation conditions.
2. Random nucleation.
3. The growth rate of the new phase depends just on the temperature, and not on the time.

Hence, its applicability to the description of non-isothermal processes is not well based from a theoretical point of view. However, it is a good approximation for the interpretation of nucleation and growth processes in a phenomenological way.

There are many methods to calculate the kinetic parameters and, in the present work, we use the method introduced by Yi Qun Gao et al. [5,6] in which, for the $E \gg RT$, the following relations are fulfilled

$$\beta \frac{E}{K_p R T_p^2} = 1, \tag{3}$$

$$\left(\frac{dx}{dt}\right)_p = 0.37 n K_p, \tag{4}$$

$$\frac{d\left[\ln\left(\frac{dx}{dt}\right)_p\right]}{d\left(\frac{1}{T_p}\right)} = -\frac{E}{R}, \tag{5}$$

where β is the heating rate and the index p refers to the values that the variables take at the maximum of the crystallization peak, that is, T_p is the temperature for maximum crystallization peak, K_p is the rate constant at the maximum crystallization peak, and $(dx/dt)_p$ is the rate of crystallization at the maximum crystallization peak.

If the values of $(dx/dt)_p$ can be identified in a series of exothermals taken at different heating rates, the plot of $\ln(dx/dt)_p$, versus $1/T_p$ should be a straight line with slope $-E/R$. The set of equations given by Eqs. (3) and (4) allows us to calculate the kinetic parameters n and K_0 as an average of the set of values obtained for the different heating rates.

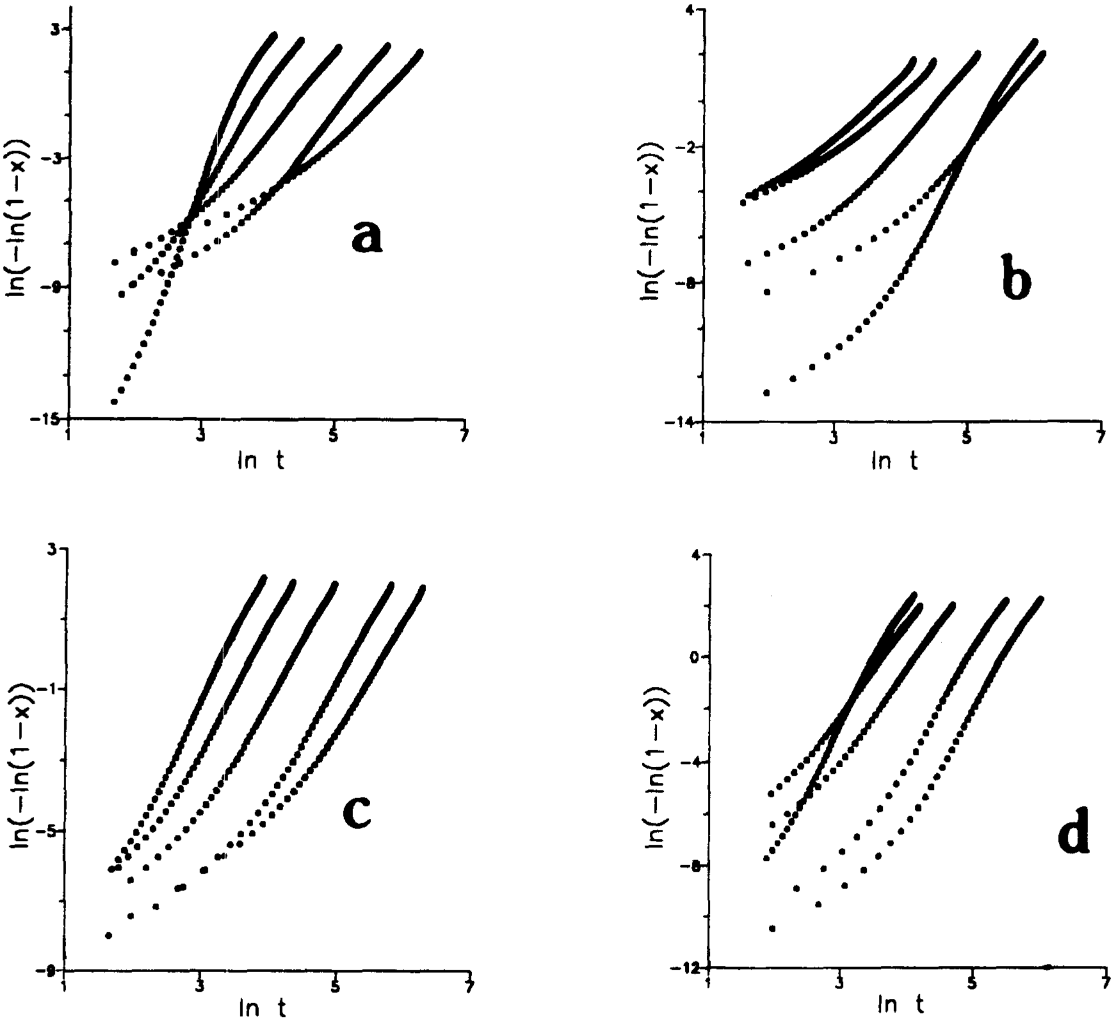

Fig. 2. Plots of $\ln[-\ln(1-x)]$ versus $\ln t$ for: (a) First crystallization peak of $Fe_{78}B_{13}Si_9$. (b) Second crystallization peak of $Fe_{78}B_{13}Si_9$. (c) First crystallization peak of $Fe_{79}B_{16}Si_5$. (d) Second crystallization peak of $Fe_{79}B_{16}Si_5$

Table 1
Calculated kinetic parameters

Sample	1st stage			2nd stage		
	E (kcal/mol)	n	K_0 (s^{-1})	E (kcal/mol)	n	K_0 (s^{-1})
$Fe_{78}B_{13}Si_9$	96.15	4.2	4.0×10^{24}	63.90	8.9	1.9×10^{15}
$Fe_{79}B_{16}Si_5$	97.85	4.3	6.8×10^{25}	50.55	7.1	6.6×10^{11}

4. Results and discussion

Eq. (1) for the crystallized fraction, which characterizes the JMA theoretical model, gives the following relation

$$\ln K + \ln t = \frac{1}{n}[\ln[-\ln(1-x)]] \qquad (6)$$

between the crystallized fraction and the effective crystallization time, pointing to the existence of a linear relationship.

This equation can be used as a test for the accuracy of the model. In fact: if the experimental data for a sample verifies the linear relationship, the theoretical model is justified. Otherwise, it should be wrong to try to describe the reaction kinetics in a theoretical frame that, a priori, the experimental data do not substantiate. Therefore, this criterion must be applied to the two studied alloys.

To do that, plots of experimental values of $\ln[-\ln(1-x)]$ versus $\ln t$ were made to check the linear behaviour of these quantities. In Fig. 2 it is noticed that, to a good approximation, the behaviour is linear in an adequately wide range of the crystallized fraction to consider that the model can be applied, although there are values out of this range but these represent such a very small quantity of the crystallized fraction that they are not significant. So, the following kinetic study is based on the JMA theoretical model.

The calculated kinetic parameters for the crystallization reactions are shown in Table 1.

To estimate the degree of accuracy of the obtained results, theoretical $x(t)$ functions have been generated, by substitution of the calculated kinetic parameters into the JMA equation, for both alloys and all the heating rates. After this, we calculated the root mean square between the experimental and theoretical curves. The results are collected in Table 2.

The values obtained for the Avrami index n in the first crystallization peak for the two alloys are explainable in the theoretical frame [7], but the values for the second crystallization stage raise problems when we try to interpret them in terms of a nucleation and growth process mechanism.

Regarding the activation energy obtained for the first peak in both samples, they are comparable with the values for this parameter obtained by Kissinger's method [8] (97.90 kcal/mol for $Fe_{78}B_{13}Si_9$ and 90.80 kcal/mol for $Fe_{79}B_{16}Si_5$).

Table 2
Root mean square between experimental and theoretical $x(t)$ curves

$Fe_{78}B_{13}Si_9$		$Fe_{79}B_{16}Si_5$	
1st peak	2nd peak	1st peak	2nd peak
0.1166	0.3460	0.1540	0.2540

This is not the case for the second peaks for the alloys. There is a disagreement between the values obtained and the ones calculated by Kissinger's method (84.87 and 83.8 kcal/mol for $Fe_{78}B_{13}Si_9$ and $Fe_{79}B_{16}Si_5$, respectively).

The values in Table 2 confirm that the accuracy of the theoretical data to the experimental ones is unsatisfactory. Besides, the values of n cannot be explained in terms of a nucleation and growth process.

The results suggest to us that the JMA model is adequate to explain the first crystallization process, however, in spite of its wide application in the analysis of thermoanalytical data for solid state reactions [9,10], it seems not adequate in describing the complete crystallization process in these alloys.

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