KINETICS OF CRYSTALLIZATION OF METALLIC GLASSES STUDIED BY NON-ISOTHERMAL AND ISOTHERMAL DSC

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A method for describing the lengths of induction periods at linear-heating measurements, is employed for the study of induction periods in the crystallisation of metallic glasses. For $Fe_{75}Si_{15}B_{10}$ glass, close values of the related kinetic parameters were obtained from isothermal and nonisothermal measurements. On the basis of the results obtained, the absence of induction period in the first crystallisation step of $Al_{90}Fe_7Nb_3$ glass in the isothermal DSC measurement has been elucidated.

Keywords: *induction period, isothermal DSC, kinetics of crystallization, metallic glass*

Introduction

Many processes exhibit an induction period (IP), in other words, the stage preceding the main process, where seemingly no chemical or physical action takes place. The transition of metallic glasses from amorphous to crystalline state belongs to this group.

In our previous paper, a theory for the kinetic description of induction periods for non-isothermal processes is outlined and a method is presented for obtaining the kinetic parameters of induction periods from the onset temperatures of non-isothermal DSC peaks with a linear increase of temperature [1]. The method has been employed for the study of induction periods of rubber compounds vulcanisation [2], oxidation of edible oils [1, 3], oxidation of polyolefines [1], recrystallisation of NiS [4], devitrification of silicate glass [5] and evaluation of antioxidant effectiveness in polyisoprene rubber [6, 7]. In this paper, the method is applied for the description of the length of induction periods in the devitrification of metallic glasses.

Experimental

The $Fe_{75}Si_{15}B_{10}$ and $Al_{90}Fe_7Nb_3$ glassy ribbons were studied by differential scanning calorimeter Perkin-Elmer DSC-7 with the Pyris software [8–11]. The absolute temperature of the DSC instrument was calibrated using the melting points of In and Zn standards for all heating rates. The non-isothermal DSC records were measured with heating rates of 5–80 K min^{-1}. The isothermal records were carried out at annealing temperatures, T_a, from 768 to 808 K for $Fe_{75}Si_{15}B_{10}$ and 508–658 K for $Al_{90}Fe_7Nb_3$ were used with heating ramp 40 K min^{-1}. Samples of 3–20 mg for linear heating and 20–40 mg for isothermal regime, were placed in open standard aluminium pans and covered with an aluminium lid. Nitrogen and argon were used as purge gases. The starting temperature of crystallisation, corresponding to the end of induction period, was determined as the onset temperature of the main peak in the case of the dynamic measuring regime. The standard deviation of a single measurement of the crystallisation onset temperature, determined from three measurements, was less than 0.5 K for all scans. The induction period of the isothermal crystallisation was determined as the onset temperature of the main peak in the case of the isothermal measuring regime. The standard deviation of IP determination was less than 0.2 min for all temperatures.

Treatment of experimental results

For a given constant temperature, the length of induction period can be expressed by an Arrhenius-like relationship [1]:

$$t_i = A\exp(B/T) \qquad (1)$$

where t_i is the length of induction period, A and B are constants and T is the absolute temperature. In the case of linear increase of temperature, the parameters A and B occurring in Eq. (1) can be obtained from Eq. (2):

$$\beta = \int_0^{T_i} \frac{\mathrm{d}T}{A\exp(B/T)} \qquad (2)$$

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where T_i is the onset temperature of the crystallization peak and β stands for the heating rate [1]. When knowing the parameters *A* and *B*, the length of induction period for any temperature regime can be calculated [1].

From the linear-heating measurements, the parameters *A* and *B* in Eq. (2) have been obtained by minimising the sum of squares between experimental and theoretical values of crystallization onset temperature using the simplex method [12]. The integration indicated in Eq. (2) has been carried out by the Simpson method. The standard deviations of *A* and *B* were calculated assuming a quadratic surface near the minimum [12].

Results and discussion

Both the isothermal and nonisothermal DSC measurements have been carried out. The records are shown in Figs 1 and 2.

For $Fe_{75}Si_{15}B_{10}$ ribbon, DSC linear-heating records show a dominant primary crystallisation peak of α-Fe(Si) followed by the crystallisation of the amorphous matrix [8, 9]. The agreement between experimental and fitted onset temperatures of the primary peak is demonstrated in Fig. 3. The resulting values of the parameters *A* and *B* are:

$$A=(1.3\pm0.9)\cdot10^{-32}\ \text{min},\ B=(60\pm2)\cdot10^{3}\ \text{K}$$

For the isothermal measurements, the temperature dependence of the length of induction period is shown in Fig. 4. It can be seen that the induction period steeply decreases with increasing temperature. In this case, the kinetic parameters *A* and *B* have been obtained by a direct comparison of experimental and theoretical values of induction periods using the program ORIGIN, where the theoretical values are given by Eq. (1). The values of *A* and *B* and their standard deviations obtained are:

$$A=(1.5\pm4.1)\cdot10^{-33}\ \text{min},\ B=(60\pm2)\cdot10^{3}\ \text{K}$$

It can be seen that the values of *B* obtained by the both methods are identical. The values of *A* differ by an order of magnitude although the intervals of *A* overlap so that their values determined by the both methods of measurements, i.e. isothermal and at linear heating, can be considered identical. The difference in the parameter *A* for the both methods is obviously caused by the linear heating ramp in the isothermal experiments. The lengths of induction periods calculated using the parameters from nonisothermal heating are hypothetical, corresponding to the case of immediate sample heating to the target temperature. So, it is necessary to take in mind that the isothermal

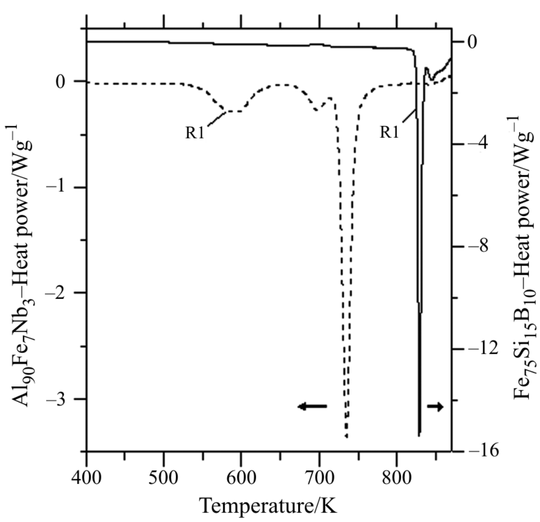

Fig. 1 Continuous heating at β=40 K min^{-1} DSC crystallization curves of the as-quenched glassy — – $Fe_{75}Si_{15}B_{10}$ and --- – $Al_{90}Fe_7NB_3$ ribbons

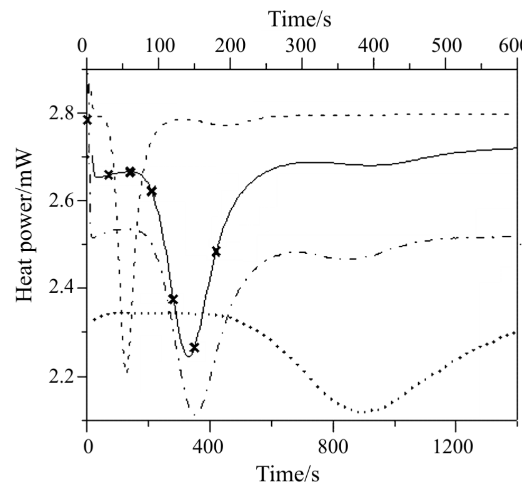

Fig. 2 Isothermal DSC crystallization curves at various temperatures T_a of the as-quenched glassy $Fe_{75}Si_{15}B_{10}$ ribbon. For --- – T_a=803 K and — – 793 K the upper time scale holds. For -·- – T_a=783 K and ··· – 773 K the bottom time scale holds

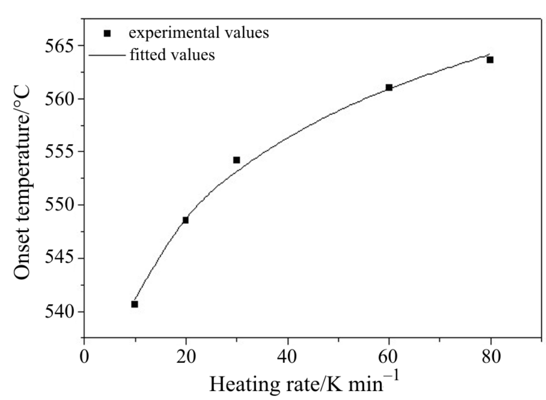

Fig. 3 Comparison of ■ – experimental and — – theoretical values of the onset temperature of transformation peak for various heating rates for the $Fe_{75}Si_{15}B_{10}$ glassy ribbon

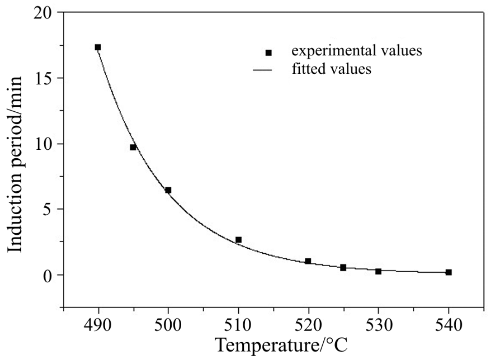

Fig. 4 Comparison of ▪ – experimental and — – theoretical values of the induction periods of the metallic glass transformation for various temperatures for the $Fe_{75}Si_{15}B_{10}$ glassy ribbon

measurements convey a systematic error arising in the linear heating of the metallic glass to the annealing temperature. The transition of metallic glasses from amorphous to crystalline state occurring during this linear ramp is not taken into account. Thus, the couple of kinetic parameters *A* and *B* obtained from non-isothermal measurements should be more correct.

For $Al_{90}Fe_7Nb_3$ glassy ribbon, the devitrification occurs in four individual transformation steps R1-R4. Hence, in DSC records with linear heating, four individual peaks are seen [10, 11]. It is quite surprising that no induction period is observed in the isothermal experiments for R1. We evaluated the length of the induction periods from non-isothermal measurements for the transformation stage R1. The parameters *A* and *B* were obtained using Eq. (2) and their values are:

$$A=(2.5\pm1.5)\cdot10^{-13}\ \text{min},\ B=(15\pm3)\cdot10^{3}\ \text{K}$$

For the temperature range 508–523 K, the lengths of induction periods calculated using Eq. (1) are within 1–4 min. The transformation obviously occurs during the linear heating ramp, taking about 4 min, and subsequent establishing of the steady state of the apparatus after switching to the isothermal regime, which also takes some time. In the isothermal DSC records, an exothermal process due to primary crystallisation of α-Al [10] is thus observed, but no induction period.

Conclusions

A method for obtaining the kinetic parameters from the linear heating measurements, describing the lengths of induction periods, is employed for the study of induction periods in the crystallisation of metallic glasses. For $Fe_{75}Si_{15}B_{10}$ glass, the method gives identical value of the parameter *B* as obtained from isothermal measurements. The parameter *A* obtained from linear heating measurements is higher by an order of magnitude than the one obtained from isothermal measurements. This difference is obviously caused by the linear heating ramp in the isothermal experiments where the transition of metallic glasses from amorphous to crystalline state occurring during this linear ramp is not taken into account. The method has been used for the elucidation of the absence of induction period in the first crystallisation step of $Al_{90}Fe_7Nb_3$ glass.

A DOS version of the program KINPAR for the treatment of linear-heating measurements using Eq. (2) is available on request from one of the authors (P. Šimon).

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