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Crystallization kinetics of amorphous $Fe_{75-x}Ag_xSi_9B_{16}$

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Abstract

The influence of Ag admixtures on the crystallization process of amorphous Fe–Si–B alloys of the series $Fe_{75-x}Ag_xSi_9B_{16}$ ($x = 0$, 1, 2, 3 and 4) was studied by differential scanning calorimetry (DSC) measurements at different heating rates. Two exothermic peaks were observed in the DSC trace when the Ag content was 2–4 at.% and one when it was 1 at.%, respectively. The activation energy was calculated both with Kissinger's and isoconversional Flynn, Wall and Ozawa methods. The possibility of analysis with the JMA model using the Avrami plot was investigated for the third stage of crystallization.

Keywords: Fe–Si–B; Crystallization; Activation energy; DSC

1. Introduction

During the last decade several experimental investigations have been conducted, aimed at the optimization of the soft ferromagnetic properties of the amorphous Fe alloys, which have important industrial application [1,2]. In this paper, the crystallization of the amorphous alloys having Ag admixtures is investigated by differential scanning calorimetry (DSC) measurements.

The observed complex behavior of the position of Curie temperature in such a small concentration range suggests, as noticed in a previous work [3], a rather inhomogeneous dispersion of admixtures throughout the amorphous material. Taking into account that the solid solubility of Ag in either Fe or B, or Si is insignificant even at very high temperatures [4], it was concluded that a random and homogeneous dispersion of the admixtures could be expected only at very low concentrations. On the contrary, as the concentration increases, there will be regions richer or poorer in Ag. Thus, the "effective" percentage of the admixtures (those that dictate the thermal behavior of the alloys) initially increases with the nominal concentration and then remains constant. If the Fe–Ag bonds favor the attenuation of the exchange interactions, one can explain the initial lowering of the Curie temperature and then the expected increase.

2. Experimental

Amorphous ribbons of $Fe_{75-x}Ag_xSi_9B_{16}$, where $x = 1$, 2, 3 or 4, were prepared by melt-spinning; the ingots were prepared by arc-melting 3N+ pure materials in the appropriate ratios. The composition of the ribbons was verified by SEM/EDAX as regards Fe, Ag and Si, whereas the atomic concentration of B was taken as equal to the value calculated during the preparation of the ingots.

The thermal behavior of $Fe_{75-x}Ag_xSi_9B_{16}$ was studied using a SETARAM DSC-131. Temperature and energy calibrations of the instrument were performed using the well-known melting temperatures and melting enthalpies of high purity zinc and indium supplied with the instrument. Ribbon-shaped specimens weighing about 7 mg, cut into small pieces, were crimped in stainless steel crucibles. An empty stainless steel crucible was used as reference. A constant flow of nitrogen was maintained in order to provide a constant thermal blanket within the DSC cell, thus eliminating thermal gradients, and ensuring the validity of the applied calibration standard from sample to sample.

A series of non-isothermal DSC experiments was carried out on the $Fe_{75-x}Ag_xSi_9B_{16}$ ribbons with continuous heating rates in the range 3–12.5 K min^{-1}.

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3. Results and discussion

Fig. 1 shows the DSC curves of rapidly quenched $Fe_{75-x}Ag_xSi_9B_{16}$ alloys containing 0, 1, 2, 3 and 4 at.% Ag obtained with a heating rate of $10\,K\,min^{-1}$ after the subtraction of the base line. None of the observed anomalies was reproduced in the subsequent DSC test carried out on the crystallized samples. Now, regarding the crystallization process, the measurements suggest that the presence of Ag admixtures induces an acceleration of the crystallization.

In comparing DSC curves, a distinct difference in the peak morphology can be noticed, i.e. the addition of Ag by replacing Fe resulted in the appearance of only one peak when the concentration of Ag is 1 at.%. Further increase in the Ag content leads to the appearance of another peak at lower temperatures, whose shape is shorter and wider than the one's at 1 at.% Ag. This peak's size becomes very small when the heating rate is lower than $10\,K\,min^{-1}$. This fact does not allow its evaluation with a satisfying accuracy for kinetic analysis. It is also observed that the increase in the Ag concentration from 2 to 4 at.% results to a slight shift in the position of the second, main, peak maximum towards higher temperatures. For the alloy without Ag, the crystallization occurs in a 60 °C temperature range. However, the admixture of Ag to a concentration greater than 1 at.% Ag, widens this range and shifts the phenomenon towards lower temperatures.

When the heating rate is $3\,K\,min^{-1}$, the second, main, exothermal peak takes place at 528.8, 524.2, 527.1, and 529.3 °C for the alloys with 1, 2, 3 and 4 at.% Ag correspondingly. These results are in good agreement with the ones obtained by measurements of the saturation magnetization [3].

From a previous work [3] and by measurements of the saturation magnetization during the heating of the alloys at constant temperatures it is known that, for the alloys with no Ag admixture, the crystallization procedure is completed in three stages. During these stages the following phenomenon take place [5,6] (a) the growth of dendritic b.c.c. Fe[Si] and the nucleation of b.c.t. Fe_3B, (b) the eutectic crystallization of b.c.c. Fe[Si] + b.c.t. Fe_3B and (c) the breaking of the metastable b.c.t. Fe_3B compound into b.c.c. Fe and b.c.t. Fe_2B. From these measurements in alloys having 1 at.% Ag, three stages are also discerned, the first two of which take place almost simultaneously during the first minutes of heating. For all the other alloys, with higher Ag concentration, only two stages are discernible. The fact that the third stage, for all the alloys, starts when their magnetization reaches a definite value, suggests that the presence of admixtures accelerates the second crystallization stage so that it takes place simultaneously with the first. The kinematics of the eutectic b.c.c. Fe[Si] + b.c.t. Fe_3B (second stage) depends on the B to Fe ratio in the remaining amorphous material. As the ratio increases, this stage is accelerated. The acceleration of the first crystallization stage results in a more rapid enrichment. Also, the replacement of the Fe atoms by Ag ones causes the ratio B/Fe to increase. The combination of these two effects results in the acceleration of the second crystallization stage with the Ag concentration.

A series of DSC experiments were carried out on 1 at.% Ag composition by continuous heating rates in the range $3–12.5\,K\,min^{-1}$, as shown in Fig. 2. It is evident that the peak temperature, T_p, shifts to higher temperatures with the increasing of the heating rate, while the peak height and the area under the crystallization exotherm increases at the same time.

On the basis of the dynamic DSC measurements at various heating rates the isoconversional [7] method of Flynn, Wall and Ozawa was used. This is a model free method which involves measuring the temperatures corresponding to fixed values of the fractional extent of reaction, α, from experiments at different heating rates, β, and plotting $\ln(\beta)$ against $1/T$

$$\ln(\beta) = \ln\left[Af(\alpha)\frac{d\alpha}{dT}\right] - \frac{E}{RT} \qquad (1)$$

and the slopes of such plots give $-E/R$. If the determined activation energy, E, is the same for the various values of α, the existence of a single-step reaction can be concluded with certainty. On the contrary, a change of E with increasing α is an indication of a complex reaction mechanism that invalidates the separation of variables involved in the OFW analysis [8].

Fig. 3 shows the variation of E with α, for all the compositions for the second, main peak. It is obvious that E is approximately the same for the compositions from 1 to 3 at.% Ag, it is constant for the range $0.1 < \alpha < 0.6$, whereas when the Ag composition is 4 at.% it has a slightly larger value for the range $0.1 < \alpha < 0.5$, while for values larger than 0.6 a small decrease in the value of E is observed.

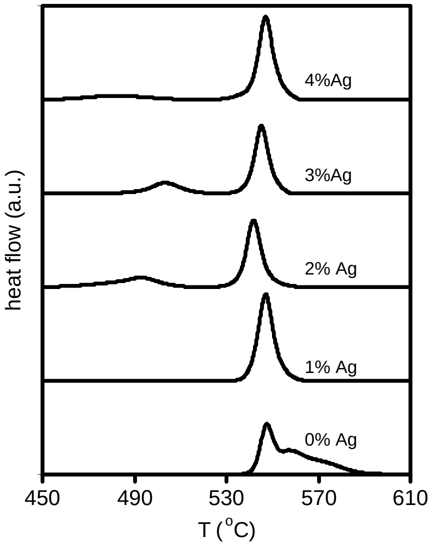

Fig. 1. DSC linear heating curves of $Fe_{75-x}Ag_xSi_9B_{16}$ at $10\,K\,min^{-1}$ heating rate and different at.% of Ag.

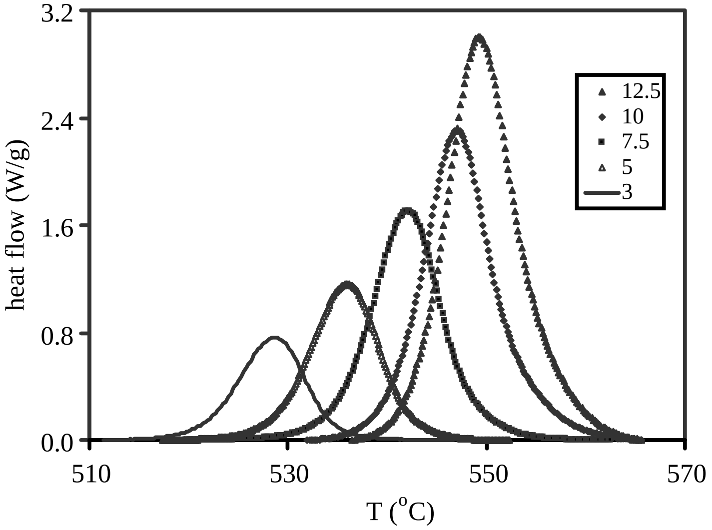

Fig. 2. Non-isothermal DSC crystallization curves of 1 at.% Ag under different heating rates (β, $\mathrm{K\,min^{-1}}$).

The activation energy of crystallization was also estimated by using the Kissinger's method [9], which relates the dependence of T_p on β (heating rate) by the following equation:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \frac{-E}{RT_p} + \ln\left(\frac{AR}{E}\right) \tag{2}$$

The value of E (kJ/mol) was obtained from the slope of $\ln(\beta/T_p^2)$ vs. $1/T_p$ plot given in Fig. 4 and also the pre-exponential factor A ($\mathrm{s^{-1}}$), from the intercept.

Table 1 shows the values of the activation energy and the pre-exponential factor for all the concentrations of Ag. The values of the activation energy, as they are calculated with the Kissinger's method, are slightly larger than the corresponding ones calculated with the method of Flynn, Wall and Ozawa for the peak temperature.

Table 1
Activation energy and pre-exponential factor for different concentration of Ag

Ag (at.%)	E (kJ/mol)	A ($\mathrm{s^{-1}}$)
1	361.9	8.9×10^{20}
2	356.9	5.9×10^{20}
3	357	5×10^{20}
4	366.7	1.8×10^{21}

The crystallization kinetics is usually interpreted in terms of the standard nucleation-growth model formulated by Johnson–Mehl–Avrami (JMA) [10,11]. Henderson [12,13] has shown that the validity of the JMA equation can be extended in non-isothermal conditions if the entire nucleation process takes place during the early stages of the transformation, and it becomes negligible afterward. One of the

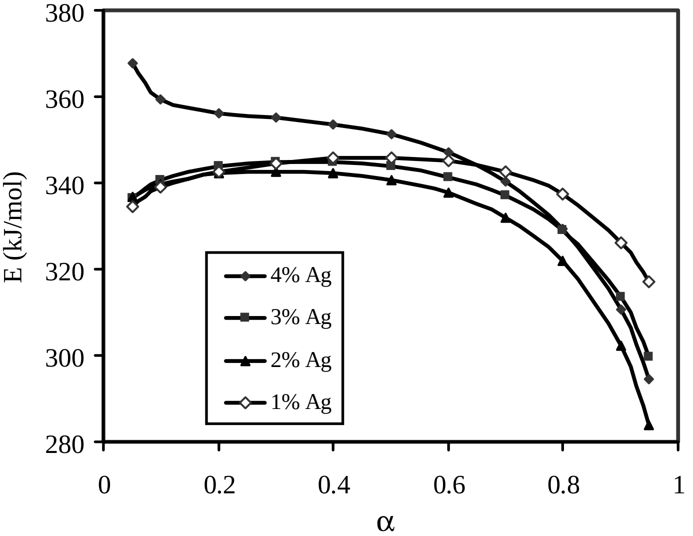

Fig. 3. The dependence of the activation energy (E) calculated by the isoconversional method of Ozawa on the degree of conversion (α).

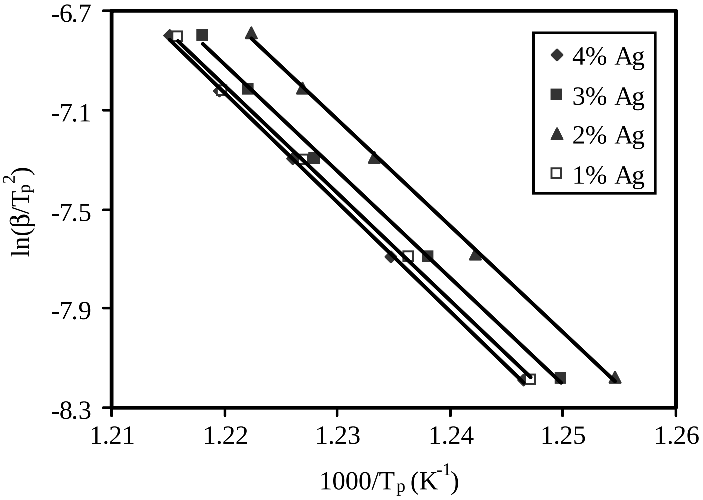

Fig. 4. The Kissinger plots of the heating rate shift in the DSC peak temperature.

testing methods for non-isothermal data is an inspection of the linearity of the Avrami (JMA) plot.

Matusita et al. [14,15] extending the use of the JMA equation, have suggested an equation, which is applicable for non-isothermal crystallization and is given by

$$\ln[-\ln(1-\alpha)] = -n\ln(\beta) - 1.052\frac{mE}{RT} + \text{const.} \qquad (3)$$

where m and n are numerical factors depending on the nucleation process and growth morphology. The plot of $\ln[-\ln(1-\alpha)]$ as a function of reciprocal temperature $1/T$ should be linear.

The plot of $\ln[-\ln(1-\alpha)]$ as a function of reciprocal temperature $1/T$ is shown in Fig. 5 for the second peak for all the concentrations and heating rate equal to 5 K min^{-1}. The appearance of two regions with a different slope has been noticed. This difference is generally small. The first region regards the slope of the lines when $0.05 < \alpha < 0.7$ and the second when $0.7 < \alpha < 0.95$ for the main peak. For the calculation of m, the value of the activation energy estimated by the Kissinger's method was used. The value of m ($= 5.4\pm0.3$) was calculated from the slope by least square method. This value of m is higher than the theoretically predicted by the JMA model, although the requirement of line formation is satisfied for a wide range of values of α.

The slope difference and the variation of the m values from the theoretically estimated ones, leads to the conclusion that the JMA model cannot be applied if a single-step reaction during crystallization is assumed, while the effect of at least two stages is included in every crystallization peak.

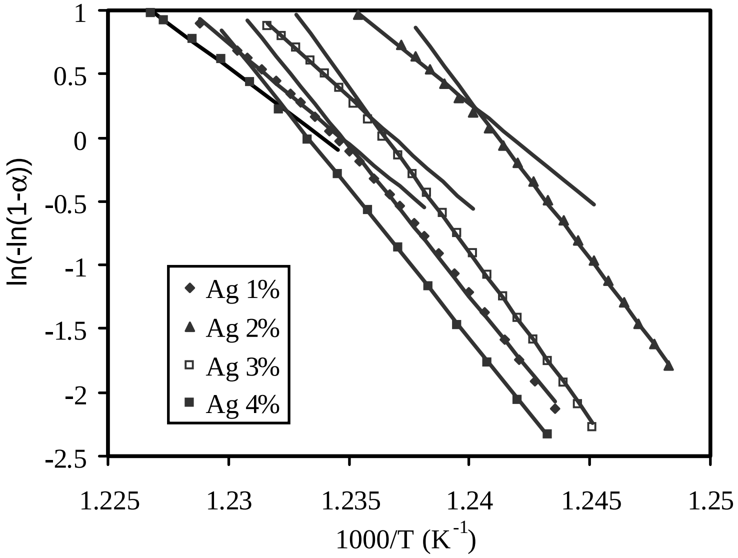

Fig. 5. Avrami plots of $\ln[-\ln(1-\alpha)]$ as a function of reciprocal temperature $1000/T$.

4. Conclusions

The activation energy, as estimated by using the Kissinger’s method for the second crystallization peak, is about the same for all the four values of Ag concentration and has a mean value 361 kJ/mol. The activation energy calculated with the isoconversional Flynn, Wall and Ozawa method is almost constant when $0.05 < \alpha < 0.6$ and exhibits a small monotical decrease when $\alpha > 0.6$. The dependence of $\ln(-\ln(1-\alpha))$ on $1/T$ exhibits two linear regions with a small slope difference, the values of m, when $0.05 < \alpha < 0.7$, are higher than the theoretically estimated ones suggesting that more than one transformation occurs during the crystallization of FeAgSiB amorphous alloys.

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