

CRYSTALLIZATION KINETICS OF AMORPHOUS Fe_{78-x}Mo_xSi₉B₁₃

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Abstract

In this work we study the influence of Mo admixtures on the crystallization process of amorphous Fe_{78-x}Mo_xSi₉B₁₃ ($x=1, 2, 3$ and 4) alloys by measurements of differential scanning calorimetry and on the soft ferromagnetic properties of the alloys by magnetic measurements. The addition of Mo by replacing Fe, results in magnetic hardening of materials. In DSC curves two peaks appear which are distinct when the concentration of Mo is 1 at.% and partly overlap when the Mo content is 2 at.%. Further increase in the Mo content leads to the appearance of just one peak. The activation energy was calculated both with Kissinger's and isoconversional Flynn, Wall and Ozawa methods.

Keywords: activation energy, crystallization, DSC, Fe–Si–B, model free kinetics, non-isothermal kinetics

Introduction

The influence of Mo admixtures with concentration less than 1%, (Fe_{0.99}Mo_{0.01})₇₈Si₉B₁₃, was studied by different techniques TEM, DSC, XRD [1, 2]. Admixtures of Mo [3] inhibit the crystallization of the amorphous Fe₇₈Si₉B₁₃ by displacing the whole crystallization procedure to higher temperatures and also attenuate the ferromagnetic properties of the amorphous alloy by decreasing both the saturation magnetization and the Curie temperature. Experimental results [3] from electric and magnetic measurements, as well as from TEM, show that the crystallization of the Fe_{78-x}Mo_xSi₉B₁₃ amorphous alloys takes place with up to three different kinds of reactions depending on Mo concentration.

As the amorphous material is heated, there grow bcc Fe(Si) dendrites. It is probable that the crystallites formed contain a small amount of Mo. During a second kind of reaction either the eutectic crystallization bcc Fe(Si)+Fe₃B, observed in the alloys with up to 2 at.% Mo, or the polymorphous crystallization of bct or orthorhombic Fe₃B, at higher concentrations take place. The Fe₃B compound is metastable and dissolves into bcc Fe and bct Fe₂B. The delay in the appearance of this reaction relatively to the initial one becomes shorter as the Mo concentration increases.

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The growth rate of crystallization during the first two reactions decreases gradually as the Mo concentration increases. Thus, the main volume of the crystallization is gradually moved into a third stage, that is the crystallization is completed with a third kind of reaction which takes place at higher temperatures and requires a longer heating time. During this reaction new phases appear. Electron diffraction patterns give some evidence of, among others, Fe₃Mo, Fe₂Mo and FeMo.

This work aims at the investigation of the influence of the Mo admixtures on the transformation process using differential scanning calorimetry (DSC) and on the soft ferromagnetic properties of the alloys by magnetic measurements.

Experimental procedure

Amorphous ribbons of Fe_{78-x}Mo_xSi₉B₁₃, 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 percentages. The composition of the ribbons was verified by SEM/EDAX as regards Fe, Mo and Si, whereas the atomic concentration of B was taken as equal to the value calculated during the preparation of the ingots.

B-H curves of the amorphous ribbons were traced by using a hysteresis loop tracer at 81 Hz.

The thermal behaviour of Fe_{78-x}Mo_xSi₉B₁₃ was studied using 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 and cut into small pieces, were crimped in stainless steel crucibles, an empty stainless steel crucible was used as reference. A series of non-isothermal DSC experiments was carried out on the Fe_{78-x}Mo_xSi₉B₁₃ ribbons with continuous heating rates in the range 3–12.5 K min⁻¹.

Results and discussion

The crystallization of the alloys starts at about 500°C, depending on the heating rate of the material, which is higher than the Curie temperature of the amorphous state. Figure 1 shows, for example, the DSC curves of the rapidly quenched Fe_{78-x}Mo_xSi₉B₁₃ alloys containing 1, 2, 3 and 4 at.% Mo with a heating rate of 7.5 K min⁻¹ without the subtraction of the base line. None of the observed anomalies was reproduced in the subsequent measuring run on the crystallized samples. We notice that the addition of Mo by replacing Fe, results in the appearance of two peaks which are distinct when the concentration of Mo is 1 at.% and partly overlap when the Mo content is 2 at.%. Further increase in the Mo content leads to the appearance of just one peak. According to literature [4, 5], during the examination of the Fe₇₈Si₉B₁₃ alloy two peaks are observed at lower temperatures than the corresponding ones for the alloys with Mo. According to TEM observations [3], the first peak for 1 at.% Mo content corresponds to the growth of bcc Fe(Si) dendrites. That also occurs in the alloy with 2 at.% Mo, where, however, there is a partial overlap with the

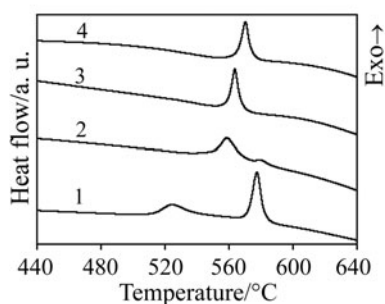


Fig. 1 DSC linear heating curves of $\text{Fe}_{78-x}\text{Mo}_x\text{Si}_9\text{B}_{13}$ with heating rate 7.5 K min^{-1} . 1 – 1 at.% Mo; 2 – 2 at.% Mo; 3 – 3 at.% Mo; 4 – 4 at.% Mo

second kind of reaction. When the concentration of Mo is more than 2 at.%, the growth of bcc Fe(Si) dendrites is not observed. The second crystallization reaction corresponds to the second exothermic peak for 1 at.% Mo, it is represented by the whole of the two overlapping peaks for 2 at.% Mo, and dominates in the single peak for the concentrations of 3 and 4 at.% Mo. By 600°C , for all the heating rates, the above described two crystallization reactions are over, still leaving some amorphous material. The fraction of the remaining amorphous material is very small for alloys with 1 at.% Mo, but rises significantly with the increase of the admixture.

A third crystallization reaction starts at about 600°C , where many new crystalline phases appear. That stage was not observed in the DSC curves, but it was observed by electron microscopy and measurements of magnetic saturation at constant temperature. It was defined magnetically, because the material which is paramagnetic becomes ferromagnetic, a transformation traceable by magnetic measurements.

A series of DSC experiments was carried out with continuous heating rates in the range $3\text{--}12.5 \text{ K min}^{-1}$, as shown in Figs 2 and 3 for the composition of 1 and 4 at.% Mo where two and one peaks are observed correspondingly. It is clear that the peak temperature, T_p , shifts higher with increasing heating rate, while at the same time the peak height increases and the area under the crystallization exotherm also increases.

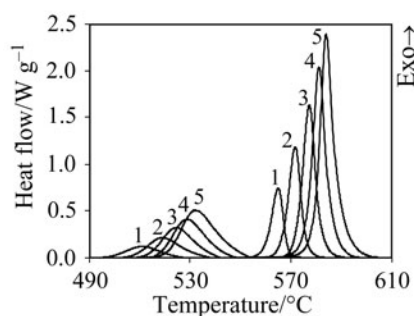


Fig. 2 Non-isothermal DSC crystallization curves of 1 at.% Mo with two exothermic peaks under different heating rates, $\beta/\text{K min}^{-1}$. 1 – $\beta=3$; 2 – $\beta=5$; 3 – $\beta=7.5$; 4 – $\beta=10$; 5 – $\beta=12.5$

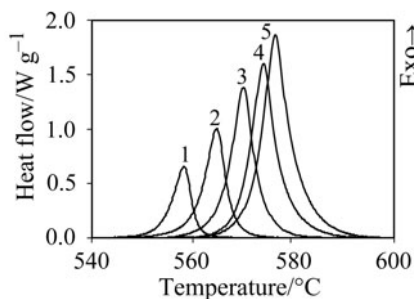


Fig. 3 Non-isothermal DSC crystallization curves of 4 at.% Mo with one exothermic peak under different heating rates, $\beta/\text{K min}^{-1}$. 1 – $\beta=3$; 2 – $\beta=5$; 3 – $\beta=7.5$; 4 – $\beta=10$; 5 – $\beta=12.5$

For the study of the crystallization kinetics we assume that each crystallization peak can be described by a kinetic equation of the form

$$d\alpha/dt = k(T)f(\alpha) \quad (1)$$

where

$$K(T) = A \exp[-E/(RT)] \quad (2)$$

is the Arrhenius temperature-dependent rate constant, E is the activation energy, A is the pre-exponential factor and $f(\alpha)$ characterizes the type of transformation mechanism.

On the basis of the dynamic DSC measurements at various heating rates the isoconversional method [6, 7] of Flynn, Wall and Ozawa [8, 9] was used. This is a model free method which involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rates, β , and plotting $\ln(\beta)$ vs. $1/T$

$$\ln(\beta) = \ln[Af(\alpha)d\alpha/dT] - E/RT \quad (3)$$

and the slopes of such plots give $-E/R$.

Figure 4 shows the variation of E with α for all the peaks, for the compositions 1, 3 and 4 at.% Mo. This variation is not shown for the composition 2 at.% Mo

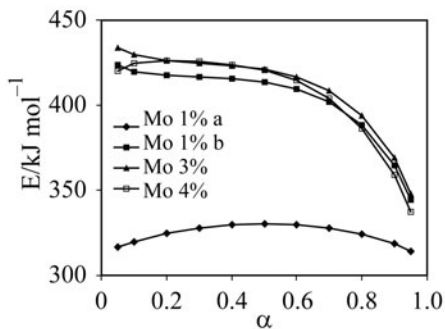


Fig. 4 The dependence of the activation energy calculated by the isoconversional method of Ozawa on the degree of conversion. a – first peak and b – second peak of 1 at.% Mo

because of the partial overlap of the two peaks. When the concentration is 1 at.% Mo, two curves are shown which correspond to the two independent peaks and present a significant difference in the activation energy. We notice that, for the peaks corresponding to the second crystallization reaction, E is approximately the same for these stoichiometries. It is constant for the range $0.1 < \alpha < 0.5$, whereas for values larger than 0.5 a small decrease in the value of E is observed. This kind of dependence results in the conclusion that we probably do not have a single-step reaction, that is only one kinetic equation, and this is an indication of a complex reaction mechanism.

The activation energy of crystallization (E) was also estimated using the Kissinger's method [10], which relates the dependence of T_p on β (heating rate) by the following equation

$$\ln(\beta/T_p^2) = -E/RT_p + \ln(AR/E) \quad (4)$$

The value of E (kJ mol^{-1}) was obtained from the slope of $\ln(\beta/T_p^2)$ vs. $1000/T_p$ plot given in Fig. 5, and the pre-exponential factor A (s^{-1}) from the intercept.

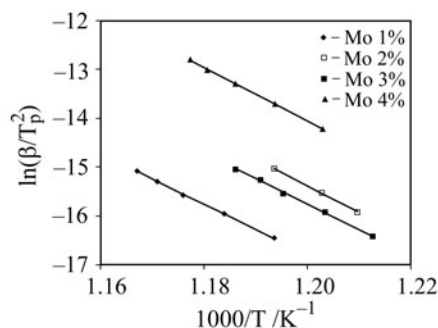


Fig. 5 The Kissinger plots of the heating rate shift in the DSC peak temperature

Table 1 Activation energy and pre-exponential factor for different concentrations of Mo

Mo concentration/at. %	$E/\text{kJ mol}^{-1}$	$\log A$
1 (peak 1)	353.1 ± 2.5	20.56 ± 4.78
1 (peak 2)	430.2 ± 5.4	24.38 ± 5.05
2 (peak 1)	455.5 ± 10	26.61 ± 5.26
3	435.0 ± 7.8	25.14 ± 5.21
4	457.3 ± 8	27.30 ± 5.16

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

As regards the magnetic properties of amorphous alloys, Table 2 presents the main parameters of the hysteresis loop of the amorphous alloys at room temperature. As the Mo concentration increases, the saturation magnetization decreases and the materials become magnetically harder.

Table 2 Coercive field (H_c), residual (M_r) and saturation (M_s) magnetization of the amorphous alloys at room temperature

Mo concentration/at. %	$H_c/A\ m^{-1}$	$M_r/kA\ m^{-1}$	$M_s/kA\ m^{-1}$
1	63	93	1065
2	127	83	1017
3	139	72	945
4	148	50	898

The decrease of the saturation magnetization observed in the amorphous alloys is also observed in the polycrystalline Fe–Mo alloys [11]. According to Jen and Chang [11], the presence of Mo admixtures in the Fe lattice brings about a broadening of the 3d band, resulting in an attenuation of both the atomic magnetic moments and the exchange interactions.

Polycrystalline Fe–Mo alloys also show a magnetic hardening [12] as the Mo concentration increases. This effect is attributed to the formation and precipitation of the ϵ phase (Fe₃Mo₂) that causes strong internal strains and inhibits the motion of the Bloch walls. The hardening in the amorphous alloys may be attributed to strains due to the fact that the atomic volume of Mo admixtures is 37% greater than that of Fe, and 71% greater than that of Si [13].

Conclusions

The activation energy as estimated with the Kissinger's method for the first exothermic peak of DSC curves, has a value of 353 kJ mol⁻¹ for 1 at.% Mo content. Also, it has a mean value of 444 kJ mol⁻¹ for the peaks that correspond to the second crystallization reaction. The activation energy calculated with the isoconversional Flynn, Wall and Ozawa method is almost constant when 0.05 < α < 0.5 and exhibits a small monotonical decrease when α > 0.5 for the peaks corresponding to the second crystallization reaction. This kind of dependence results to the conclusion that we probably do not have a single-step reaction and this is an indication of a complex reaction mechanism.

Although the dilution of Mo admixtures in amorphous Fe₇₈Si₉B₁₃ is good for their thermal stability, it is a disadvantage as regards their soft magnetic properties, because it produces a magnetic hardening and lessens both the saturation magnetization and the Curie temperature.

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