Kinetics and mechanisms of two-stage crystallization of Fe$_{85}$B$_{15}$ amorphous alloy

V I Tkatch, T N Moiseeva, S G Rassolov, V V Popov and V V Maksimov

A.A. Galkin Donetsk Institute for Physics & Engineering of NAS of Ukraine, 72 R. Luxemburg Str., 83114, Donetsk, Ukraine.

vit@depm.fri.ac.donetsk.ua

Abstract. The two-stage crystallization behavior has been experimentally identified in Fe$_{85}$B$_{15}$ metallic glass at isothermal and non-isothermal conditions involved appearance of primary α-Fe-based nanoscale particles in the first stage and polymorphic formation of Fe$_3$B crystals in the second step. An analytical model for description of two simultaneous processes in the Kolmogorov-Johnson-Mehl-Avrami formalism frameworks has been developed both for isothermal and constant rate heating conditions. The model is based on additivity of the extended volumes and on the assumption that growth of α-Fe nanoscale crystals is retarded due to diffusion field impingement. The calculated two-stage crystallization kinetic curves agree with those experimentally measured and the deduced values of free parameters are in reasonable accordance with the available ones.

1. Introduction

Materials with nanocomposite structures formed by primary (nano)crystallization of amorphous precursors posses an enhanced level of physical properties (e.g., [1]). However, primary crystallization is only the first stage of the full transition from amorphous to crystalline state and the development of the subsequent crystallization stages results in deterioration of the properties. Therefore, analysis of the transformation stages following the primary crystallization is important for good control of the partially crystallized structures with the improved characteristics.

Only a few attempts have been made to analyze the kinetics of several simultaneously occurring transformations [2-5]. The rigorous models developed in [2,3] in the frames of the classical Kolmogorov-Johnson-Mehl-Avrami (KJMA) formalism [6] assume additivity of the extended volumes of the phases formed at different stages of crystallization, while the models presented in [4,5] suggest that the total fraction of the volume transformed is the sum of the transformed volumes at each stage of crystallization. Such a way the latter approaches do not account the impingement of crystals which forms at different crystallization stages. On the other hand, the ratio between the volumes transformed in the at first and second crystallization steps in the models [2,3] is accounted by limitation of the time of the primary crystallization [2] or by introducing of the proportion between the volumes of different phases [3] which are a priori unknown.

The aim of this study is to elaborate an analytical model of two-stage crystallization process of metallic glasses in which the nanocomposite structure (nanocrystals in the residual amorphous matrix) forms in the first crystallization stage. In this case nanocrystallization retards due to the so-called soft impingement effects (overlapping of the diffusion fields around growing crystallites) [7] and the
relatively simple analytical model has been recently developed for description of this process [8]. The Fe\textsubscript{85}B\textsubscript{15} amorphous alloy has been chosen in this study because crystallization of this glass which has been widely studied (e.g., [9]) occurs in the two well separated stages: primary crystallization of nanoscale particles of the α-Fe(B) solid solution, followed by the formation of Fe\textsubscript{3}B crystals.

2. Experimental and results

Amorphous Fe\textsubscript{85}B\textsubscript{15} ribbons (2 mm wide and ~ 20 μm thick) were prepared by melt-spinning from a silica glass crucible on to a copper wheel in an Ar atmosphere. The structural characterization of the as-quenched and heat treated specimens was examined by X-ray diffraction (XRD) using Co Kα radiation in a DRON-3M diffractometer. The XRD patterns of the partially crystallized ribbons (α-Fe + residual amorphous phase) were deconvoluted and the structural parameters (the mean grain size, \(\langle L\rangle\), and volume fraction crystallized \(X\)) were determined. The value of \(\langle L\rangle\) was calculated from the half-width, \(B\), of α-Fe (110) diffraction peak using the known Scherrer formula \(\langle L\rangle = 0.9\lambda/(B\cos\theta_0)\) (where \(\lambda\) is the wavelength and \(\theta_0\) is the Bragg angle). The volume fraction of the nanocrystalline α-Fe phase formed at the first stage of crystallization, \(X_α\), was estimated from the relative areas of the deconvoluted amorphous and crystalline peaks accounting the compositional differences between the amorphous and crystalline phases [10]. The boron content in the nanocrystals, \(C_B\), was determined by comparison of the measured bcc lattice parameters with its concentration dependence [11]. From these parameters the values of the volume density of α-Fe nanocrystals, \(N_{Fe}(\approx 6X/(\pi\langle L\rangle^3))\) and the average interparticle spacing, \(2R_S(\approx \sqrt[3]{6/\pi N_{Fe}})\) were estimated.

The crystallization kinetics was studied by both electrical resistivity measurement method (a standard dc four-probe technique) and differential scanning calorimetry (a Perkin-Elmer DSC-7 calorimeter). The constant rate heating measurements were performed at scan rates 10 and 40 K/min while the isothermal annealing was carried out at 720 ± 0.5 K in a salt bath.

The XRD data showed that the as-quenched specimens of Fe\textsubscript{85}B\textsubscript{15} alloy had amorphous structure. The changes of the relative resistance both at the constant temperature and under continuous heating as well as the DSC scans clearly indicate the two-stage crystallization process with the well separated stages which is typical for this glass [9]. The detailed analysis of the X-ray data has shown that during the first crystallization stage nanocomposite structures are formed with parameters listed in Table 1.

| Heat treatment          | \(\langle L\rangle\)(nm) | \(C_B\) (at.%) | \(X_α\)   | \(N_{Fe}(\text{m}^3)\) | \(R_S\)(nm) |
|-------------------------|--------------------------|----------------|-----------|------------------------|-------------|
| Annealing at 720 K for 600 s | 81 ± 3                    | 4.5            | 0.26 ± 0.005 | 9.3×10\textsuperscript{20} | 63.5        |
| Heating at 10 K/min up to 727 K | 80 ± 3                    | 4.0            | 0.24 ± 0.005 | 8.9×10\textsuperscript{20} | 64.4        |
| Heating at 40 K/min up to 761 K | 92 ± 3                    | 4.0            | 0.24 ± 0.005 | 5.9×10\textsuperscript{20} | 74.0        |

The X-ray diffraction patterns of the fully crystallized samples revealed the presence of the additional peaks belonging to the Fe\textsubscript{3}B. Using the experimentally determined values of the volume fraction crystallized at the first crystallization stage and assuming that the volume fraction transformed at each stage of crystallization is proportional to the normalized change in resistivity [12], the both isothermal (together with the data of Walter et al. [13]) and non-isothermal kinetic crystallization curves of the Fe\textsubscript{85}B\textsubscript{15} metallic glass have been plotted (figures 1, 2).
The results of the kinetic studies and structural characterization of the partially crystallized samples were used for analysis of two-stage crystallization using the analytical model presented below.

3. Model
As it follows from the above reported results crystallization of the Fe\textsubscript{85}B\textsubscript{15} metallic glass occurs via two steps: the former is primary crystallization of supersaturated \(\alpha\)-Fe solid solution while the latter is polymorphic formation of the Fe\textsubscript{3}B compound. These stages are well separated at isothermal and non-isothermal annealing conditions (Figures 1, 2) which allows analyzing them separately.

In the present study for description of glass crystallization the classical KJMA equation [6] was used which can be written as

\[
X(t) = 1 - \exp\left[-\left(\frac{\pi}{3}\right)/\Upsilon_t^4 t^4\right]
\]

in the case when crystallization occurs by nucleation and three-dimensional growth of crystals and

\[
X(t) = 1 - \exp\left[-\left(\frac{4\pi}{3}\right)\Upsilon_t^3 t^3\right]
\]

when the process takes place by the growth of the pre-existing nuclei. Here, \(I\) and \(U\) are the rates of crystal nucleation and growth, respectively, and \(N_+\) is the volume density of the pre-existing nuclei.

As it has been recently shown [8] kinetics of the first crystallization stage of Fe\textsubscript{85}B\textsubscript{15} amorphous alloy can be satisfactory described by equation (3) derived under assumption that a dominating role in this process plays growth of the pre-existing nuclei under the condition of diffusion field impingement

\[
X_{\alpha}(t) = 1 - \exp\left[-\left(\frac{4\pi}{3}\right)N_+ R_{H}^3(t)\right],
\]

where \(R_H\) is the radius of growing crystal

\[
R_H(t) \approx \sqrt{2/3\lambda_H R_S \left[1 - \exp\left(-3\lambda_H D_{al}t / R_S^2\right)\right]}^{1/2},
\]

with \(D_{al}\) being the volume diffusion coefficient governing the growth and \(\lambda_H\) being a dimensionless constant depending on the solute concentration in the particle, \(C_P\), and those in the matrix at, \(C_I\), and far, \(C_M\), from the interface

\[
\lambda_H = \left[(C_I - C_M) / (C_I - C_P)\right]^{1/3}
\]

In view that evaluated concentration of boron in the residual amorphous matrix approaches 25 at.% at the end of primary crystallization the homogeneous nucleation and interface controlled growth mechanism interface has been supposed for formation of the second phase (Fe\textsubscript{3}B crystals).
The following classical expressions for description of the temperature dependencies of the nucleation and growth rates were used [7]:

$$I_\beta = \left( N_0 D_\beta / a^3_0 \right) \exp\left[ -16\pi \sigma^2 V^2_m / (3kT\Delta G^2) \right],$$

(5)

and

$$U_\beta = (D_\beta / a_0) [1 - \exp\left[ -\Delta G / (RT) \right]],$$

(6)

where $N_0$ is the number of atoms per unit volume, $D_\beta$ is the crystal-glass interface diffusion coefficient, $a_0$ is the average atomic diameter, $\sigma$ is the interfacial energy per unit area between the crystal and glass (liquid), $V_m$ is the molar volume, $\Delta G$ is the molar Gibbs free-energy difference between the glassy and crystal phases, $k$ is the Boltzmann constant and $R$ is the universal gas constant.

In order to calculate the thermodynamic driving force of transformation the well-established equation proposed by Thompson and Spaepen [14] was used and kinetics of the second ($\beta$) phase formation process was approximated with equation (1).

In view that the crystallization stages of the glass investigated are well separated and the volume fraction crystallized of the primary ($\alpha$) phase (equation (3)) is limited due to soft impingement, for description of the overall kinetic transformation the following equation (based on the additivity of the extended volumes) was proposed:

$$X(t) = X_\alpha(t) + \left[ 1 - X_\alpha(t) \right] X_\beta(t).$$

(7)

As it known [6], the rigorous analytical description of the non-isothermal crystallization kinetics is possible only in the case if the rate of transformation is invariant under any thermal conditions. Nevertheless, as it has been shown [5] the glass crystallization processes at constant rate heating, $q$, both the interface and volume diffusion controlled can be satisfactory approximated by the analytical equations which formally coincide with the isothermal ones if the parameter $T^2(qQ)$ (with $Q$ ($\rightarrow$ $T$) being the activation energy of the diffusivity expressed in kelvins) was used instead of the real time $t$. This parameter has dimension of seconds and may be considered as a certain effective time, $t_{eff}$ of thermally activated process at constant rate heating.

4. Modeling and discussion

To verify the validity of the proposed kinetic approach to the two-stage glass crystallization process the fitting of the experimental kinetic curves for the Fe$_{80}$B$_{15}$ glass with equation (7) has been performed. As it is evident from Section 3 the equations (3)-(7) contain a relatively large number of parameters, but only the diffusivities which control the growth of the primary crystals, $D_\alpha$, and the interface-limited nucleation and growth processes, $D_\beta$, as well as the specific interfacial crystal-glass energy, $\sigma$ are the model (adjustable) variables.

The simplest case for modeling is isothermal formation of primary $\alpha$-Fe crystals because as it follows from equations (3) and (4) the parameters except $D_\alpha$ are the structural parameters which have been determined from the XRD studies (Table 1). Because the main objective of these calculations was to test the validity of equation (7) for description of the two-stage crystallization process rather then quantitative agreement with the experimental data we used the experimentally determined crystal growth rates of the interface controlled crystallization of Fe$_{80}$B$_{20}$ metallic glass [15] to approximate the $D_\beta$ values for the second crystallization stage. In view that the crystallization of this glass occurs by growth of the eutectic colonies which consist of about 95 % Fe$_3$B phase this approximation seems to be reasonable. The reported in Ref. [15] values of $U(T)$ in the temperature range 573-673 K were approximated by an Arrhenius law and using equation (6) we have obtained for $D_\beta(T)$ $[m^2/s] = 0.615\exp(- 29320 K/T)$. For calculations of the $\Delta G(T)$ for Fe$_3$B nucleation the values of $T_m$ and $\Delta H_m$ were taken to be 1424 K [16] and 1.2RT$_m$, respectively.

Such a way in order to match the experimental isothermal kinetic curve presented in figure 1 only the values of $D_\alpha$ and $\sigma$ for the first and the second crystallization stages, respectively, were required. The result of fitting procedure shown by the dashed curve in figure 1 has been obtained for $D_\alpha$ and $\sigma$ being $1.5\times10^{-19}$ $m^2/s$ and 0.234 J/m$^2$, respectively. As can be seen from figure 1 the calculated kinetic
curves well agree with the experimental ones except the deviation of the second crystallization step with the data [14] which may be attributed to the approximate nature of the model.

It should be noted that the value of the specific interfacial energy for Fe$_3$B deduced from the fitting procedure is close to that of 0.256 J/m$^2$ found for Fe$_85$B$_{17}$ undercooled melt [17]. Besides, a comparison of the value of $D_a$ at 720 K with those estimated from analysis of primary crystallization kinetics of Fe$_85$B$_{15}$ glass at several temperatures in the range of 628-667 K [8] has shown that all these data are well approximated by the common Arrhenius-type dependence in the form $D_a(T)$ [m$^2$/s] = $2.9 \times 10^3 \times \exp[-(32050 \pm 1100) \text{K}/T]$. These values are about two order of magnitude higher that the values of $D_a$ governing the interface controlled nucleation and growth of Fe$_3$B crystals and are close both to the diffusion coefficients extracted by Köster et al. [18] from measurements of the sizes of α-Fe crystals growing in Fe-B amorphous alloys at 493-693 K and to the extrapolated values of the iron grain boundary diffusivity in crystalline Fe-B alloys measured at 973-1173 K [19].

The value of the specific interfacial energy and the $D_a(T)$ dependence deduced from analysis of two-stage crystallization at 720 K as well as the $D_a(T)$ values were used in calculations of the kinetic crystallization curves at heating with 10 and 40 K/min. In these calculations the experimental kinetic data were modeled by substituting the parameter of $T^2/(qQ_{1,2})$ with $Q_1$ and $Q_2$ being 32050 and 29320 K for the first and second crystallization stages, respectively, instead of $t$ in the expressions (1) and (4) entering in equation (7) and using the experimentally determined values of $C_B$, $N_{1,2}$ and $R_4$ listed in Table 1. The results of these calculations are shown by the lines in figure 2. Note, that for the better coincidence between the calculated and experimental $X(T)$ curves at 10 K/min the value of the specific interfacial energy was the slightly corrected, i.e. 0.237 J/m$^2$ was used instead of 0.234 J/m$^2$.

In summary, a good correspondence between the calculated and experimental kinetic curves of α-Fe and Fe$_3$B crystals formation in amorphous Fe$_85$B$_{15}$ alloy as well as the reasonable values of the deduced model parameters provide an evidence for the validity of the proposed analytical model for description of two-stage crystallization of metallic glasses.

References

[1] Willard M A, Laughlin D E and McHenry M E 2000 J. Appl. Phys. 87 7091
[2] Yu G and Lai J K L 1996 J. Appl. Phys. 79 3504
[3] Kasuya T, Ichikawa K and Fuji M and Bhadeshia K D H 1999 Mater. Sci. Technol. 15 471
[4] Kristiakova K and Svec P 2001 Mater. Sci. Eng. A304-306 343
[5] Tkatch V I, Moiseeva T N and Popov V V and Kameneva V Yu 2001 Phys. Met. Metallogr. 91 53
[6] Christian J W 1975 The Theory of Transformations in Metals and Alloys (Oxford: Pergamon Press)
[7] Clavaguera-Mora M T, Clavaguera N and Crespo D and Pradel T 2002 Progr. Mater. Sci. 47 559
[8] Tkatch V I, Rassolov S G and Moiseeva T N and Popov V V 2005 J. Non-Cryst. Solids 351 1658
[9] Köster U and Herold U 1981 Glassy Metals, Applied Physics eds H J Günterodt and H Beck (New York: Springer-Verlag) part I pp 225-271
[10] Blazquez J S, Franco V and Conde C F and Conde A 2003 JMMM 254-255 460
[11] Vorob’ev G M, Bashiev V F and Bol’shakov V I 1998 Phys. Met. Metallogr. 85 223
[12] Gangopadhyay A K, Croat T K and Kelton K F 2000 Acta Mater. 48 4797
[13] Walter J L, Bartram S F and Mella I 1978 Mater. Sci. Eng. 36 193
[14] Thompson C V and Spaepen F 1979 Acta Metallurg. 22 1855
[15] Greer A L 1982 Acta Metal.lur. 30 171
[16] Palumbo M, Cacciamani G, Bosco E, Baricco M 2001 CALPHAD 25 625
[17] Battezzati L, Antonione C, Baricco M 1997 J. Alloys Comp. 247 164
[18] Köster U, Herold U and Hillerbrand H-G and Denis J 1980 J. Mater. Sci. 15 2125
[19] Borisov V T, Golikov V M and Shcherbedinskii G V 1964 Fiz. Met. Metalloved. 17 1855