Crystallization of amorphous Fe\textsubscript{78}Si\textsubscript{9}B\textsubscript{13} alloy

E. Jakubczyk \textsuperscript{a}, A. Krajczyk \textsuperscript{b}, M. Jakubczyk \textsuperscript{c}

\textsuperscript{a} Institute of Physics, Jan Długosz University, Al. Armii Krajowej 13/15, 42-200 Częstochowa, Poland
\textsuperscript{b} Institute of Materials Science and Applied Mechanics, Wrocław University of Technology, Smoluchowskiego25, 50-371 Wrocław, Poland
\textsuperscript{c} Institute of Chemistry and Environmental Protection, Jan Długosz University, Al. Armii Krajowej 13/15, 42-200 Częstochowa, Poland

e-mail: e.jakubczyk@ajd.czest.pl

Abstract. The crystallization process of Fe\textsubscript{78}Si\textsubscript{9}B\textsubscript{13} metallic glass was investigated by DSC, X-ray diffraction, electrical resistivity, Hall effect and TEM methods. The investigations proved two-stages crystallization. By means of non-isothermal DSC experiments the activation energy and the Avrami exponent were determined for both stages. The created phases: $\alpha$-Fe(Si) and (Fe,Si)\textsubscript{2}B were identified on the basis of X-ray and TEM investigations. However, TEM observations showed also a little amount of the FeB\textsubscript{49} phase as well as some rest of the amorphous phase. The electrical and Hall resistivities decrease abruptly after the creation of the phases out of the amorphous matrix.

1. Introduction
The rapid solidification applied to produce the metallic glasses makes their as-quenched state a metastable one. The metastability motivates to the structural evolution by the phase transformations into the stable equilibrium [1, 2]. The structural changes cause the modification of the physical properties [3, 4]. Knowledge of these changes is especially important from the point of view of the application [5]. The stability of the amorphous structure of the metallic glasses depends on quenching conditions, the composition and subsequent thermal history [6, 7]. The various thermal treatment can cause the changes in short (structural relaxations) or/and in long range ordering (crystallization) [4, 8, 9].

In this paper we report the result of crystallization investigations of the Fe\textsubscript{78}Si\textsubscript{9}B\textsubscript{13} metallic glass. The studies of crystallization were performed by differential scanning calorimetry (DSC), X-ray diffraction (XRD), transmission electron microscopy (TEM), electrical resistivity and Hall effect methods. The aim of these studies was description of the crystallization kinetics and determination of the influence of the crystallization on the electrical properties.
2. Experimental

The metallic glass Fe₇₈Si₉B₁₃ was prepared by the roller quenching method in the Institute of Materials Engineering of Warsaw Technical University in Poland. DSC measurements were carried out using an STA-409 NETZSCH apparatus at the continuous heating. Heating rates of 5, 10, 15 and 20 K/min were used. The scanning temperature was from room temperature up to 900 K and with precision ± 0.1 K. High purity argon was used as inert atmosphere. The mass of sample was typical (22-25 mg).

The Hall voltage was measured by a constant current method in the field up to 3.26 T. The electrical resistivity was also measured within d.c. regime. The samples for the measurements of the Hall and electrical resistivities were prepared by selective etching using photolithography.

XRD were done at the room temperature for the as-received as well as isochronally (4 h) annealed samples at various temperatures (573-823 K). The X-ray studies were performed using a DRON-2.0 diffractometer with a horizontal goniometer of GUR-5 type. The X-ray tube had a molybdenum target \( \lambda = 0.71069 \times 10^{-10} \text{ m} \) and a graphite monochromator in the primary beam.

3. Results and discussion

The crystallization process of Fe₇₈Si₉B₁₃ metallic glass was investigated by means of the standard technique which is the DSC method. The measurements of non-isothermal crystallization were carried out at the continuous heating rates of 5, 10, 15 and 20 K/min. All the DSC curves display two clearly separate exothermic peaks and it allows to conclude that the transformation from the amorphous to the crystalline state proceeds through two main stages. The position on the temperature axis of both peaks put forward with the increase of the heating rate. Knowledge the peaks of the temperature allows to determine the activation energy \( E_a \) for the crystallizing phases according to the Kissinger equation \([10, 11]\)

\[
\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + \ln\left(\frac{K_0 R}{E_a}\right)
\]

(where: \( \beta = \frac{dT}{dt} \) is heating rate, \( T_p \) peak of the temperature, \( R \) the gas constant and \( K_0 \) frequency factor).

On the basis of the Kissinger plots: \( \ln\left(\frac{\beta}{T_p^2}\right) \) vs. \( 1/T_p \) for both stages the values \( E_a \) are received from the approximately straight line by least-squares fitting. The calculated values are listed in Table1.

The isothermal solid state transformation is strictly described by the Johnson-Mehl-Avrami (JMA) equation \([11]\)

\[
x(t) = 1 - \exp\left(- (Kt)^n\right)
\]

where: \( x \) is the volume fraction transformed after time \( t \), \( n \) a dimensionless quantity called the kinetics exponent, and \( K \) the reaction rate constant. The temperature dependence of \( K \) is generally expressed by the Arrhenius equation:

\[
K(T) = K_0 \exp\left(-\frac{E_a}{RT}\right)
\]

The twice logarithm of the equation (2) leads to:

\[
\ln\left[\ln(1-x)\right] = n \ln K + n \ln t
\]
and then values of $n$ and $K$ are determined from expression (4) by least-squares fitting of $\ln[-\ln(1-x)]$ versus $\ln t$. Next, the activation energy $E_a$ and the frequency factor $K_0$ can be evaluated from the logarithmic form of equation (3). However, it is very interesting to generalize the JMA equation to experiments in which the rate of heating $\beta = dT / dt$ is constant. Assuming that progress of crystallization and mechanism do not change with temperature, the volume fraction transformed after time $t$ is described as [11]:

$$x(t) = 1 - \exp\left[-\left(\frac{1}{n} \int K[T(t')]dt'\right)^n\right] = 1 - \exp(-I^n)$$

(5)

where: $K[T(t')]$ is expressed by the Arrhenius formula (3), $T(t')$ is the temperature at the time $t'$. The determination of the maximum crystallization rate from equation (5) leads to:

$$nK_p(I^n) = \beta E_I / RT_p^2 + (n-1)K_p$$

(6)

( where subscript $p$ denote the magnitude values at the maximum crystallization rate). The integral I can be represented by the alternating series and thus it is obtained [11]

$$I = RT^2K(\beta E_a)^{-1}\left(1 - 2\frac{RT}{E_a}\right)$$

(7)

Because, almost always: $E_a / RT \gg 1$ (usually $E_a / RT \geq 25$) then for the maximum crystallization rate $I = I_p = RT_p^2K_p(\beta E_a)^{-1}$ and on the base (6) $I_p = 1$.

Finally, the kinetics exponent $n$ is described by the equation

$$n = (dx / dt)_pRT_p^2(0.37\beta E_a)^{-1}$$

(8)

Although the JMA equation was deduced for the isothermal case, it is widely applied also by many authors to the non-isothermal crystallization process [11-15]. The JMA equation is used in a variety of mathematical analysis of the non-isothermal solids state transformation. Here, we calculated the Avrami kinetics exponent $n$ from the equation (8) developed at the first time by Y.Q. Gao and W.Wang [13].

Figure 1. Crystallization rate, $dx/dt$, vs. temperature, $T$, for the Fe$_{78}$Si$_9$B$_{13}$ metallic glass at different heating rates for the first stage of crystallization.

Figure 2. Crystallization rate, $dx/dt$, vs. temperature, $T$, for the Fe$_{78}$Si$_9$B$_{13}$ metallic glass at different heating rates for the second stage of crystallization.
The crystallized fraction $x$ at any temperature $T$ is given as $x = \frac{A_x}{A}$, where $A$ and $A_x$ are total and part (at generic temperature $T$) area of exothermic peak, respectively. The crystallization rates versus temperature for both stages are presented in Fig. 1 and Fig. 2. The maximum crystallization $(dx/dt)_p$ for each heating rate gives $n$, according to the equation (8). Mean values of the kinetics exponent $n$ are included in Table 1. The values $n$ indicate that at the first and second stages of the crystallization process there are crystal growth controlled by diffusion and by interface, respectively [16].

Table 1
Parameters of crystallization kinetics and of elementary cells of created phases

| Parameters | I stage | II stage |
|------------|---------|----------|
| $E_a$ [kJ/mol] | 341 | 410 |
| $n$ | 2.49 | 4.93 |
| phase | $\alpha - \text{Fe(Si)}$ cubic ($\text{Im}^3\text{m}$) $a = 2.856$ Å | $(\text{Fe, Si})_2\text{B}$ tetragonal ($I4/\text{mcm}$) $a = 5.105$ Å $c = 4.228$ Å |

The range of the structural changes is determined by parameters of the annealing. Therefore, the samples of the alloy were annealed at various temperatures in order to obtain respective changes and determine the influence of these changes on the electrical resistivity and Hall effect. Fig. 3 shows the relative changes of the electrical resistivity (related to the resistivity of the as-received state) vs. the annealing temperature. The $\Delta\rho/\rho_0$ values show an increase in the initial range of annealing, which is connected with the structural changes of the short range ordering (SRO) type [4]. The decrease of the electrical resistivity during the crystallization is caused by the increase of the free path of the carriers in the ordered structure.

Figure 3. The relative electrical resistivity $\Delta\rho/\rho_0$ as a function of annealing temperature $T$ for the samples of Fe$_{78}$Si$_9$B$_{13}$ alloys.
The Hall resistivity $\rho_H$ as a function of external magnetic field $B_0$ for samples in as-received state and samples annealed isochronally at different temperatures are presented in Fig. 4. Each curve ($\rho_H = f(B_0)$) is of the typical shape as for the ferromagnetic materials and is described by means of the formula [17-20]

$$\rho_H = R_0 B_0 + \mu_0 M$$

(9)

where: $R_0$ and $R_s$ are ordinary and spontaneous Hall coefficient respectively, and $M$ is the magnetization of the sample. This demonstrates that during the crystallization process the macroscopic ferromagnetic ordering of the alloy is conserved. The first term of the equation (9) is the ordinary Hall resistivity ($\rho_{H0} \propto B_0$). It is related to the action of the Lorentz force on the carriers and it corresponds to the slowly growing part of the $\rho_H = f(B_0)$ curve above the magnetization saturation. The second term is the spontaneous Hall effect ($\rho_{HS} \propto M$) and is represented by the initial part of the $\rho_H = f(B_0)$ curve. The $\rho_{HS}$ is connected with a ferromagnetic state and determined by following mechanisms: a spin-orbit interaction, a skew scattering and a side jump [18]. Due to these mechanisms the mean free path of carriers decreases. For the initial part of the $\rho_H = f(B_0)$ curves the spontaneous Hall coefficient $R_s$ was calculated using the linear regression $R_s = (\partial \rho_H / \partial B_0)_{B_0 \rightarrow 0}$. Berger and Bergmann gave the relationship between the spontaneous Hall coefficient $R_s$ and the electrical resistivity $\rho$ [20]

$$R_s = a\rho + b\rho^2$$

(10)

where: $a$ and $b$ are constants roughly independent of temperature.
The first term of equation (10) is responsible for the classical asymmetric scattering of charge carriers and the second term describes the quantum effect and corresponds to the lateral displacement of the charge carrier trajectory at the point of scattering, i.e. the side jump. The dependence of $\lg R_s$ on $\lg \rho$ gives the exponent $k$ in relation $R \propto \rho^k$ and by it we can conclude which type of scattering is the dominant one for the spontaneous Hall effect. The calculated exponent $k$ is 1.91 and this value $k$ allow to accept that during the crystallization process the charge carriers are mainly scattered by nonclassical mechanism, i.e. side jump. In order to identify the crystalline phases formed in the amorphous matrix the X-ray and TEM investigations were performed. The X-ray diffraction patterns are presented in Fig. 5 for the as–received as well as the annealed samples. The investigations of the X-ray diffraction prove that the first and second stages of the crystallization occur after the annealing at the temperature 723 K and 773 K, respectively. By means of the qualitative analysis it was established that at the first and second stages are formed $\alpha$-Fe(Si) and (Fe,Si)$_2$B phases, respectively [21, 22]. The parameters of the elementary cells of the created phases are listed in Table 1.

Figure 5. X-ray diffraction patterns for the samples of Fe$_{78}$Si$_9$B$_{13}$ alloy annealed at different temperatures.

TEM and SAED studies of Fe$_{78}$Si$_9$B$_{13}$ specimen heated at 823 K for 4 h verify the creation of the $\alpha$-Fe(Si) and (Fe,Si)$_2$B phases stated by X-ray diffraction measurements. A representative micrograph of the $\alpha$-Fe(Si) particles with corresponding diffraction pattern is shown in Fig. 6. The diffraction data indicate the presence of spots characteristic for $\alpha$-Fe(Si), which are dominant. Also, additional spots (situated inside nearly ring marked “1”) are visible, which could be indexed as phase of Fe$_2$B type [23, 24]. Additionally, TEM observations showed the presence of a needle-like cuboid shaped large crystalline particles, typically between 20 and 50 nm in shorter, and even to 500 nm in elongated sizes. TEM and HRTEM micrographs with the corresponding fast Fourier transforms (FFT) of such
Figure 6. TEM image and SAED pattern of $\alpha$-Fe particles in Fe$_{78}$Si$_9$B$_{13}$ specimen heated at 823 K for 4 h.

Figure 7. TEM (A) and HRTEM (B,C) images with the corresponding FFT ($B^I$, $C^I$) of the FeB$_{49}$ particles in Fe$_{78}$Si$_9$B$_{13}$ specimen heated at 823 K for 4 h. Crystallites are shown in Fig. 7 (A-C). Indexing the SAED patterns and FFT analysis of the HRTEM images allowed to identify the crystallites as FeB$_{49}$ phase [PDF Number: 00-039-0418]. The particles
with 0.742 nm and 0.547 nm lattice fringes (Fig. 7 B and C) are characteristic for [1 1 2] and [2 1 0], respectively, of the FeB_{49} compound. However, some amount of the amorphous phase was also observed after the applied treatment of the specimen.

4. Conclusions
Investigation of the thermal stimulated crystallization of Fe_{78}Si_{9}B_{13} metallic glass leads to the following conclusions:
- DSC studies clearly indicate that the transformation from the amorphous to the crystalline state proceeds through two main stages and the activation energy for the second stage is bigger than for the first one.
- The determined Avrami kinetics exponents agree to the theoretical considering of D. Kashchiev.
- X-ray and TEM studies identify the created phases: α – Fe(Si), (Fe, Si)_{2}B in first and second stage, respectively.
- TEM observations prove also the presence of FeB_{49} phase and some part of the amorphous phase after annealing at 823 K for 4 h.
- The formation of the crystalline phases causes the abrupt decrease of the electrical as well as the Hall resistivities.
- During the process of the crystallization the ferromagnetic state is conserved.

References
[1] Köster U., 1993, Phase transformations in rapidly solidified alloys, Key Eng. Mat., 81-83, 647-662.
[2] Kulik T., 2001, Nanocrystallization of metallic glasses, Journal of Non-Crystalline Solids 287, 145-161.
[3] Jakubczyk E. Stępień Z. Jakubczyk M., 2005, Influence of the composition of M_{70}Si_{9}B_{13} metallic glasses on their structural stability, Optica Applicata 35, No.3. 339-346.
[4] Komatsu T., 1990, Structural relaxation and related processes in metallic glasses, Res. Mechanica 31, 263 – 283.
[5] Hasegawa R., 2004, Applications of amorphous magnetic alloys, Materials Science and Engineering, A 375-337, 90 – 97.
[6] Muñiz P., De Toro J.A., Riveiro J.M., 2004, Influence of the quenched-in nuclei on the crystallization of amorphous Ni_{80}B_{20}, Journal of Magnetism and Magnetic Materials, 272-276, e1129-e1130.
[7] Zaluska A., Matyja H., 1983, Crystallization characteristics of amorphous Fe-Si-B alloys, 18, 2163-2172.
[8] Sietsma J., Thijse B.J., 1995, Characterization of free volume in atomic models of metallic glasses, Physical Review B, 52, No. 5, 3248-3255.
[9] Bourrous M., Moser N., Kronmüller H., 1989, Reversibility and annealing of magnetic after-effect in ferromagnetic amorphous alloys, phys. stat. sol. (a), 112, 181-188.
[10] Kissinger H.E., 1957 Reaction kinetics in differential thermal analysis, Anal. Chem., 29, 1702-1706.
[11] Vázquez J, López-Alemany P.L., Villaes P, Jiménez-Garay R., 1998, A study on non-isothermal transformation kinetics, Application to the crystallization of Sb_{0.20}As_{0.32}Se_{0.48} alloy, J. Alloy Comp., 270, 179.
[12] Kashchiev D., Sato K., Kinetics of crystallization preced by metastable-phase formation, J. Chem. Phys., 109, 1998, 8530-8540.
[13] Gao Y.Q., and Wang W.,1986, On the activation energy of crystallization in metallic glasses, J. Non-Cryst. Solids, 81, 129 –134.
[14] Mehta N., Kumar A.,2006, A study of thermal crystallization in glassy Se_{80}Te_{20} and Se_{80}In_{20} using DSC technique, J. Therm. Anal. Cal., 83, 401-405.
[15] Shanker Rao T.L., Lad K.N., Pratap A.,2004, Study of non-isothermal crystallization of amorphous Cu_{80}Ti_{50} alloy, J. Therm. Anal. Cal., 78, 769-774.
[16] Christian J.W.,1965, The Theory of Transformation in Metals and Alloys, Pergamon Press, Oxford.
[17] Hurd C.M.,1972, The Hall Effect in Metals and Alloys, Plenum Press, New York – London.
[18] Berger L., Bergmann G., 1980, The Hall effect of ferromagnets, (The Hall Effect and Its Applications, C.L. Chien, C.R. Westgate (Eds.), Plenum Press, New York).
[19] Mc Guire T. R., Gambino R. J. and O’Handley R. C.,1980, Hall effect in amorphous metals, (The Hall Effect and Its Applications, C.L. Chien, C.R. Westgate (Eds.), Plenum Press, New York).
[20] Stobiecki T. and Przybylski M.,1986, Spontaneous Hall effect and magnetization of Fe-(B,Zr) and Co-Mo amorphous film, phys. stat. sol. (b), 134, 131-139.
[21] Tomaszewski P. E., 2002, Golden Book of Phase Transitions, Wroclaw.
[22] Havinga E.E., Damsma H., Hokkeling P.,1972, Compounds and pseudo-binary alloys with the CuAl_{2}(C16)-type structure, I. Preparation and X-ray results, Journal of the Less-Common Metals, 27, 169-186.
[23] Spence J.C.H.,2003, High Resolution Electron Microscopy, Oxford Univ. Press, New York, ed.3.
[24] Amelinckx S., GeversR., Van Landuyt J.,1979, Diffraction and Imaging Techniques in Material Science, Nort-Holland Publishing Company, Amsterdam, New York.Oxford.