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THE ACTIVATION ENERGY OF PRIMARY CRYSTALLIZATION OF $Fe_{95}Si_5$ METALLIC GLASS

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K e y w o r d s: metallic glass, energy activation, crystallization kinetics parameter, DSC.

A b s t r a c t

The primary crystallization process of $Fe_{95}Si_5$ metallic glass was investigated by DSC and *X*-ray diffraction methods. The crystalline phase α-Fe(Si) was identified during the primary crystallization process. The activation energy of crystallization E_a has been calculated in the frame of two models: Kissinger and Ozawa. The activation energy for primary crystallization of amorphous $Fe_{95}Si_5$ alloy are determined as 235.2 and 247.3 kJ mol^{-1} by means of the Kissinger and Ozawa equations, respectively.

ENERGIA AKTYWACJI KRYSTALIZACJI PIERWOTNEJ SZKŁA METALICZNEGO $Fe_{95}Si_5$

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S ł o w a k l u c z o w e: szkło metaliczne, energia aktywacji, parametr kinetyki krystalizacji, skaningowa kalorymetria różnicowa.

A b s t r a k t

Proces krystalizacji pierwotnej szkła metalicznego $Fe_{95}Si_5$ badano metodą różnicowej kalorymetrii skaningowej (DSC) oraz dyfraktometrii rentgenowskiej. Zidentyfikowano fazę powstającą podczas pierwszego etapu krystalizacji jako α-Fe(Si). Obliczono energię aktywacji przemiany krystalicznej na podstawie dwóch modeli: Kissingera oraz Ozawy. Energia aktywacji obliczona z równań Kissingera i Ozawy wyniosła odpowiednio 235,2 oraz 247,3 kJ mol^{-1}.

Introduction

The excellent soft magnetic properties of metallic glasses have found use in many industrial applications and new glasses and their properties are continually being explored (LI et al. 2008, SAHINGOZA et al. 2004, NOBUYUKI et al. 2007).

The amorphous alloys are metastable materials. On increase of temperature, such non-crystalline alloys transform into crystalline state in course of time. From the technological application point of view, the thermal stability of the amorphous alloys is of considerable importance.

The thermal stability of metallic glasses is a subject of considerable interest, since the properties of these engineering materials may be significantly changed by the onset of crystallization (LIU et al. 2004, BHATTACHARYA et al. 2009, SANTOS et al. 2001).

The crystallization behaviour of various metallic glasses has been studied using a variety of techniques, such as ferromagnetic resonance, differential scanning calorimetry (DSC), Mössbauer spectroscopy, *X* ray diffraction, and electrical resistance variations. (RIBEIRO et al. 2004, JAKUBCZYK et al. 2007).

The study of crystallization kinetics in glass-forming liquids has often been limited by the elaborate nature of the experimental procedures that are employed. The increasing use of thermoanalytical techniques such as differential thermal analysis (DTA) or differential scanning calorimetry (DSC) has, however, offered the possibility of obtaining useful data with simple methods.

Many authors for example (RIBEIRO et al. 2004, JAKUBCZYK et al. 2007, MINIĆ et al. 2009, SOLIMAN et al. 2004) characterized the thermal stability and effective activation energies *Ea* using differential scanning calorimetry (DSC) by isothermal and non-isothermal methods.

The present work concerns studies on activation energy E_a for the $Fe_{95}Si_5$ metallic glass in primary crystallization.

Theory

The study of crystallization kinetics of glassy materials can be calculate the one of three kinetic parameters – activation energy E_a. In calorimetric measurements, isothermal and non-isothermal methods can be used. Most methods is based on Johnson-Mehl-Avrami (JMA) equation of isothermal transformation kinetics (MÁLEK 2000):

$$x(t) = 1 - \exp(-Kt^n) \tag{1}$$

where: $x(t)$ is volume fraction transformed after time t, n is Avrami kinetics exponent (the exponent which reflects the nucleation rate and the growth morphology), K is the reaction rate constant. The temperature dependence is usually assigned from Arrhenius equation:

$$K = K_0 \exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

where: E_a is the activation energy for the crystallization reaction, K_0 is the frequency factor and R is the gas constant.

The non-isothermal crystallization, is characterized by a constant heating rate. The relation between the sample temperature T and the heating rate β can be written:

$$T = T_0 + \beta t \tag{3}$$

A popular non-isothermal analysis method developed by KISSINGER (1957) and OZAWA (1970). Their methods is based on JMA theory and logarithmic form of equation 2. The Kissinger and Ozawa models are considered that on the top of crystallization peak DSC the amount of crystallized fraction is $x_p = 0.63$. Using the highest rate of a transformation at maximum peak approximations interpreted in this equations, respectively:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \frac{-E_a}{RT_p} + \ln\left(\frac{K_0 E_a}{R}\right) \tag{4}$$

$$\ln(\beta) = \frac{-E_a}{RT_p} + \ln\left(\frac{K_0 E_a}{R}\right) \tag{5}$$

where: T_p the temperature of a peak, $\beta = dT/dt$ heating rate.

The partial $\ln(K_0R/E_a)$ and $\ln(K_0E_a/\mathrm{R})$ in equations 4 and 5 are constant. From the slope and the intercept of the straight line (Eq. 4, 5) it is possible to derive the value of the activation energy E_a and the pre-exponential factor K_0 of the crystallization process, respectively.

Experimental

The amorphous samples were obtained by rapid solidification from the melt using the melt-spinning method. The obtained ribbon was 20 mm wide and and 0,03 mm thick, with nominal composition of $Fe_{95}Si_5$.

The crystallization process was investigated by differential scanning calorimetry (DSC) in nitrogen atmosphere using a NETZSCH DSC 204 instrument. The sample masses used for DSC measurements were about several milligrams. Te samples where heated from 340 K to 840 K using different rates β = 2, 5, 10, 20 and 30 K min^{-1}.

The structural characterization was carried out by an *X*-ray diffraction. The sample of amorphous alloy $Fe_{95}Si_5$ annealed at different temperature 753 K in a stream of nitrogen during 30 min. The *X*-ray diffraction measurements were performed on DRON 4.07 diffractometer using $CoK\alpha$ radiation, over a 2Θ angle range of 35 ÷ 105 degrees with a step of 0.05 deg min^{-1}. The voltage was set at 31 kV and the current set at 21 mA.

Results and discussion

The kinetics of non-isothermal crystallization of $Fe_{95}Si_5$ amorphous alloy was investigated by DSC method. Figure 1 shows DSC curves for $Fe_{95}Si_5$ amorphous metallic alloys, obtained at a heating rate of 2, 5, 10, 20 and 30 K min^{-1}. Samples of the alloy present two distinct exothermal peaks, and this behavior is independent of the applied heating rate, suggesting a crystallization process with two distinct exothermal reactions. When the heating rate increases, the position of both peaks was shifted to the higher temperatures.

Figure 2 presents XRD pattern for the sample of $Fe_{95}Si_5$ alloy annealed at 753 K temperature during 30 min. On the basis *X*-ray diffraction analysis after crystallization (see Fig. 2) the $Fe_{95}Si_5$ metallic glass primary crystallizes into phase the *bcc*-α-Fe(Si) of lattice constant a = 2.867 Å. It is corresponds to literature data about of kinetic crystallization of Fe-Si-X amorphous alloys for example (Li et al. 2008, Sahingoza et al. 2004, Jakubczyk et al. 2007, Ribeiro et al. 2009).

The activation energy E_a of primary crystallization of metallic glass $Fe_{95}Si_5$ has been calculated by Kissinger and Ozawa method. For this purpose, the plots $\ln(\beta/T_p^2)$ vs. $10^3/T_p$ (Fig. 3) and $\ln(\beta)$ vs. $10^3/T_p$ (Fig. 4) are plotted for the present metallic glass.

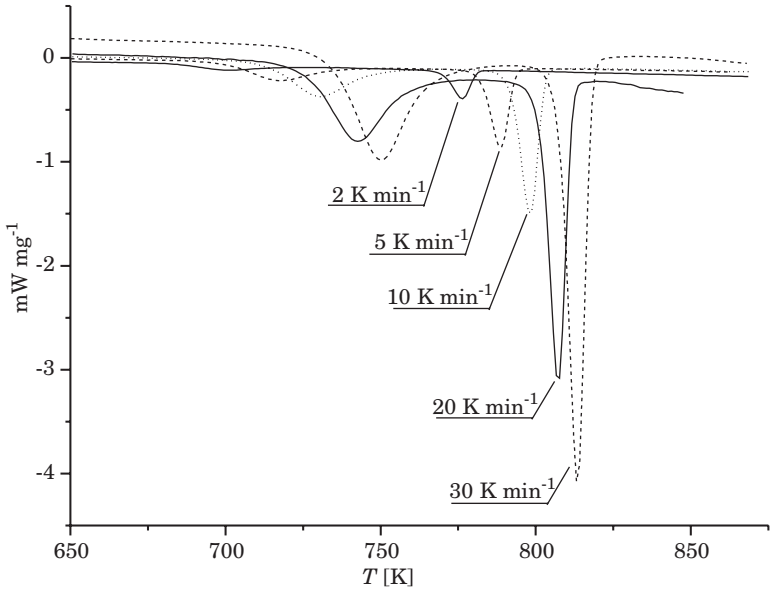

Fig. 1. DSC curves of $Fe_{95}Si_5$ for several heating rates showing the primary crystallization process (first peak) and secondary crystallization (second peak)

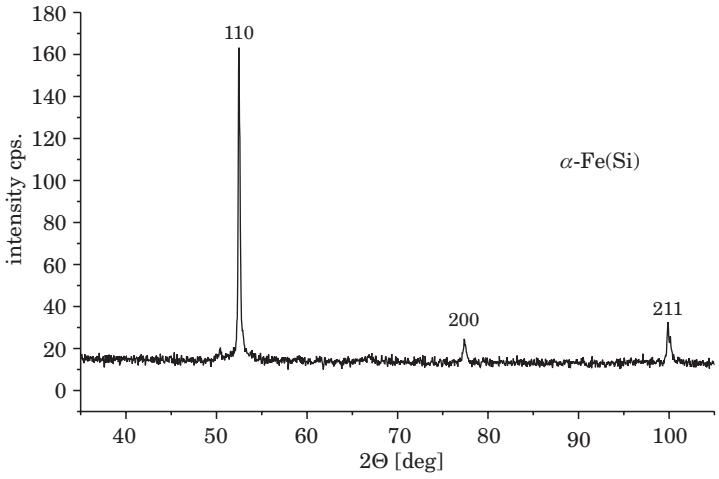

Fig. 2. *X*-Ray diffractogram of the $Fe_{95}Si_5$ metallic glass annealed at 753 K during 30 min

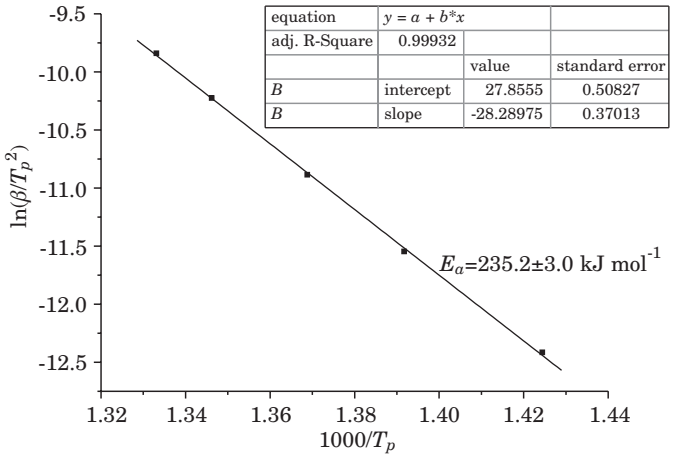

Fig. 3. Kissingers plot for determination of the activation energy *Ea* from a set of DSC scans with different heating rates (2, 5, 10, 20 and 30 K min^{-1}). In the case of the Fe-Si alloy. This analysis was performed for first observed exothermal reaction from DSC

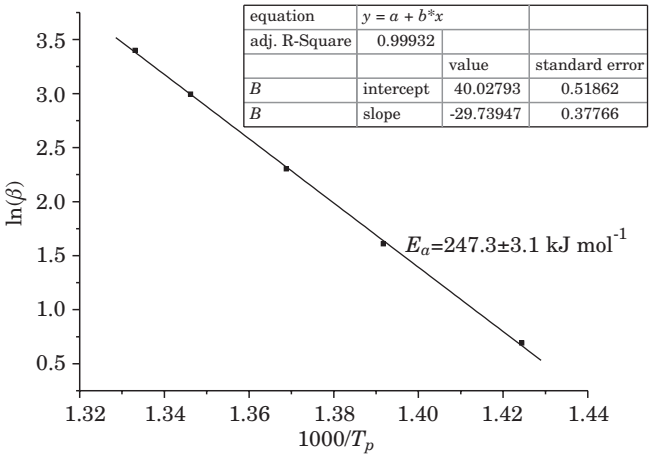

Fig. 4. Ozawa plot for determination of the activation energy E_a from a set of DSC scans with different heating rates (2, 5, 10, 20 and 30 K min^{-1}). In the case of the Fe-Si alloy. This analysis was performed for first observed exothermal reaction from DSC

From the slope $(-E_a/R)$ of the line activation energy E_a of an amorphous alloy can be obtained. A best fit for the results was calculated by the least-square method. The arithmetic mean as well as the standard deviation were calculated for the activation energies.

The primary crystallization parameters are presented in Table 1.

Table 1

Primary crystallization parameters of $Fe_{95}Si_5$

Heating rate β [K min^{-1}]	2	5	10	20	30
Temperature max. peak T_p [K]	702.1	718.6	730.6	742.9	750.2
Enthalpy phases transformation [J g^{-1}]	32.78	43.61	41.95	42.54	41.42
Energy activation E_a (by Kissinger equation) [kJ mol^{-1}]	235.2 ± 3.0				
Energy activation Ea (by Ozawa equation) [kJ mol^{-1}]	247.3 ± 3.1				
Phasecubic	α-Fe(Si) (Im3m) a = 2.856 Å				

The activation energy E_a is one of the most important kinetic parameters for the crystallization of an amorphous alloy.

The values of the kinetic parameters determined according to the Kissinger method are some higher than ones determined by applying the Ozawa method, but the differences between the values determined by the two methods are under 6%. Similar results received authors (MINIĆ et al. 2009, WANG 2003) when they studied crystallization kinetics of $Fe_{89.8}Ni_{1.5}Si_{5.2}B_3C_{0.5}$ and $Zr_{70}Cu_{20}Ni_{10}$ metallic glasses.

Conclusions

The activation energies connected with the first peak temperature in the continuous heating DSC curves of the amorphous $Fe_{95}Si_5$ alloy have been calculated using different methods. These are determined as 235,1 and 247,2 kJ mol^{-1} when using the Kissinger and Ozawa equations, respectively. The Ozawa equation gives the largest value of activation energy.

To compare the activation energy of different amorphous alloys, the same equation or model should be utilized.

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References

BHATTACHARYA S., LASS E.A., POON S.J., SHIFLET G.J. 2009. *High thermal stability of soft magnetic (Fe,Co)–Mo–B-C–P–Si metallic glasses*. Journal of Alloys and Compounds, 488: 79–83.

JAKUBCZYK E., KRAJCZYK A., JAKUBCZYK M. 2007. *Crystallization of amorphous $Fe_{78}Si_9B_{13}$ alloy*. Journal of Physics: Conference Series, 79.

KISSINGER H. E. 1957. *Reaction kinetics in differential thermal analysis*. Analytical Chemistry, 29: 1702–1706.

LI H.X., JUNG H.Y., YI S. 2008. *Glass forming ability and magnetic properties of bulk metallic glasses* $Fe_{68.7-x}C_{7.0}Si_{3.3}B_{5.5}P_{8.7}Cr_{2.3}Mo_{2.5}Al_{2.0}Co_x$ (x = *0-10*). Journal of Magnetism and Magnetic Materials, 320: 241–245.

LIU D.Y., SUN W.S., WANG A.M., ZHANG H.F., HU Z.Q. 2004. *Preparation, thermal stability, and magnetic properties of Fe–Co–Zr–Mo–W–B bulk metallic glass*. Journal of Alloys and Compounds, 370: 249–253.

MÁLEK J. 2000. *Kinetic analysis of crystallization processes in amorphous materials*. Thermochimica Acta, 355: 239–253.

MINIĆ D.M., GAVRILOVIĆ A., ANGERERB P., MINIĆ D.G., MARIČIĆ A. 2009. *Thermal stability and crystallization of* $Fe_{89.8}Ni_{1.5}Si_5.2B_3C_{0.5}$ *amorphous alloy*. Journal of Alloys and Compounds, 482: 502–507.

NOBUYUKI N., KENJI A., AKIHISA I. 2007. *Novel applications of bulk metallic glass for industrial products*. Journal of Non-Crystalline Solids, 353: 3615–3621.

OZAWA T. 1970. *Kinetic analysis of derivative curves in thermal analysis*. Journal of Thermal Analysis, 2: 301–324.

RIBEIRO R. M., SANTOS D. S., BIASI R. S. 2004. *Crystallization kinetics of the* $(Fe_{50}Co_{50})_{73.5}Ag_1Nb_3Si_{13.5}B_9$ *amorphous alloy*. Journal of Alloys and Compounds, 363: 232–235.

RIBEIRO R.M., BIASI R.S., SANTOS D.R., SANTOS D.S. 2009. *Nanocrystallization of Fe-based amorphous metallic alloys studied by non-isothermal and isothermal techniques*. Journal of Alloys and Compounds, 483: 495–498.

SAHINGOZA R., EROLA M., GIBBS M.R.J. 2004. *Observation of changing of magnetic properties and microstructure of metallic glass* $Fe_{78}Si_9B_{13}$ *with annealing*. Journal of Magnetism and Magnetic Materials, 271: 74–78.

SANTOS D.R., SANTOS D.S. 2001. *Crystallization Kinetics of Fe–B Based Amorphous Alloys Studied in-situ using X-rays Diffraction and Differential Scanning Calorimetry*, Materials Research, 4(1): 47–51.

SOLIMAN A.A., AL-HENITI S., AL-HAJRY A., AL-ASSIRI M., AL-BARAKATI G. 2004. *Crystallization kinetics of melt-spun* $Fe_{83}B_{17}$ *metallic glass*. Thermochimica Acta, 413: 57–62.

WANG H.R, GAO Y.L., YE Y. F., MIN G.H., CHEN Y., TENG X.Y. 2003. *Crystallization kinetics of an amorphous Zr–Cu–Ni alloy: calculation of the activation energy*. Journal of Alloys and Compounds, 353: 200–206.