*Proc. 2nd Saudi Sci. Conf.,Fac. Sci , KAU, 15-17 March 2004, **Part II,*** pp. 223-230 (2005 A.D./1425 A.H.)

Calorimetric and Kinetic Studies of Crystallization of $Fe_{83}B_{17}$ Metallic Glass

A. AL-HAJRY[1*], S. AL-HENITI[2], A.A. SOLIMAN[1] and M. AL-ASSIRI[1]
[1] *Physics department, Faculty of Science, King Khalid University, Abha, Saudi Arabia*
[2] *Physics department, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia*

ABSTRACT. The crystallization of melt-spun $Fe_{83}B_{17}$ metallic glass was obtained by using differential scanning calorimetry (DSC) under non-isothermal conditions. The fraction of crystallized material, calculated using the partial area analysis, revealed that the crystallization process of the $Fe_{83}B_{17}$ metallic glass was a bulk growth in two dimensions. The crystallization activation energy (E_c) was calculated from the DSC thermograms using different models.

Keywords: $Fe_{83}B_{17}$, metallic glasses, crystallization, thermal analysis

1. Introduction

The melt-spinning technique allows the rapid solidification of metallic alloys to produce amorphous or nano-crystalline materials. Amorphous Fe- and B- based materials have good soft magnetic properties, and have been the subject of much scientific research over the past few decades. They are used in diverse applications, such as transformers, information handling technology and magnetic sensors (Cowley *et al.*, 1983 & 1991; Cowlam, 1996; Wildes *et al.*, 1998, 2001, Al-Heniti *et al.*, 1999).

Crystallization kinetics can be described by three kinetic parameters, namely; the activation energy for crystallization (E_c), the Avrami exponent (n) which reflects the characteristics of nucleation and the growth processes, and the frequency factor (K_o). Studies of the crystallization of a glass upon heating can be performed in several ways. In calorimetric measurements, two basic methods can be used, isothermal and non-isothermal. In the isothermal method, the sample is brought quickly to a temperature above the glass transition temperature (T_g) and the heat produced during the crystallization

* Corresponding author e-mail: ahajry@kku.edu.sa

process at a constant temperature is recorded as a function of time. In the second method, the sample is heated at a fixed rate (α), and the heat produced is recorded as a function of temperature or time.

Recently (Soliman *et al.,* 2004), the crystallization activation energy (E_c) of the $Fe_{83}B_{17}$ metallic glass was obtained to be in the range 221-235 kJ/mol from DSC thermograms under non-isothermal conditions using the Kissinger (Kissinger, 1956 & 1957) and Augis-Bennett (Yinnon & Uhlmann, 1983) methods while the Avrami exponent n=3.25 was obtained from the modified Johnson-Mehl-Avrami (JMA) equation (Matusita & Sakka, 1979a & 1979b), revealing that the crystallization process of the $Fe_{83}B_{17}$ metallic glass was a bulk growth in two dimensions.

The aim of the present work is to obtain the crystallization kinetics of $Fe_{83}B_{17}$ metallic glass using Ozawa-Chen (Ozawa, 1971; Chen, 1978) and Coats-Redfern-Šestăk (Yinnon & Uhlmann, 1983; Šestăk, 1974) methods to confirm the earlier results (Soliman et al, 2004).

2. Experimental

Parent ingots of pure Fe rod (99.98%) and B crystalline pieces (99.7%) from Aldrich Chemicals Ltd. of appropriate at.% proportions were melted and thoroughly mixed in an argon-arc furnace. The metallic glass ribbon was produced by conventional chill-block melt-spinning (Al-Heniti, 1999), using a steel wheel with a rim speed of approximately 50 m s^{-1}, under an atmosphere of helium. For structural measurements, the resulting ribbon ($\approx$ 25μm thick and $\approx$ 1mm wide) was wound onto a flat plate and then X-ray investigations were performed on a Philips-PW1710 vertical goniometer with a curved crystal monochromator using molybdenum K_α radiation λ=0.711 Å. For scanning electron microscope (SEM) examinations, ribbons surfaces were coated by a thin Au layer using fine coat JFC-100E ion sputter Jeol type, for 10 minutes at 10 mA. The surface microstructure was studied by a Jeol type JSM-1200 scanning electron microscope.

Differential scanning calorimetry (DSC) measurements were performed using a Shimadzu DSC-50 instrument on samples of $\approx$ 20 mg encapsulated in platinum pans in an atmosphere of dry nitrogen at a flow of 30 ml/min. Powdered Al_2O_3 was used as a reference material. The temperature and energy calibrations of the instrument were performed using the well known melting temperatures and melting enthalpies of high purity tin, lead, zinc and indium supplied with the instrument, giving an accuracy of $\pm$ 0.1 K for the temperature and $\pm$ 0.02 mW for the energy. Non-isothermal DSC curves were obtained with selected heating scan rates 5-30 K/min in the range from room temperature to beyond the crystallization exotherm.

The fraction of crystallized materials, χ, at any temperature T is given by $\chi=(A_T/A)$ where A is the total area of the exotherm between the temperature T_1 where crystallization just begins and the temperature T_2 where the crystallization is completed; A_T is the area between T_1 and T as shown by the hatched portion in (see Fig.1).

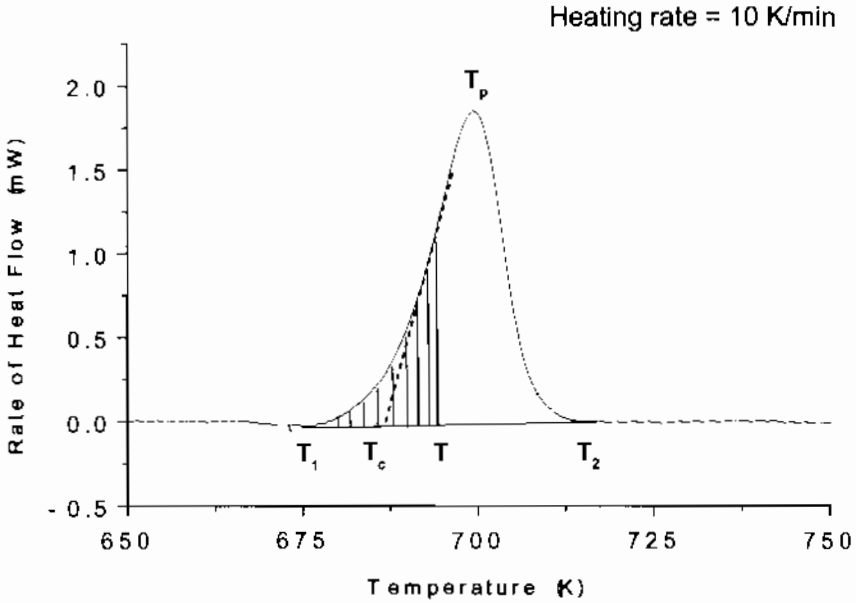

Fig.1. Typical DSC trace of as-quenched $Fe_{83}B_{17}$ metallic glass at a heating rate of 10 K/min.

3. Results and Discussion

From the analysis point of view, the DSC curve of the investigated $Fe_{83}B_{17}$ metallic glass is indicated by one exothermic crystallization peak (T_p) corresponding to the crystallization process as shown in Fig 1. The onset temperature of crystallization (T_c) has been defined as a temperature corresponding to the intersection of two linear portions adjoining the transition elbow of the DSC trace in the exothermic direction (See Fig.1). The peak temperature of crystallization (T_p) is the temperature at which the overall crystallization rate attains its maximum value. Values of T_c and T_p for the investigated $Fe_{83}B_{17}$ metallic glass are given in Table 1 as a function of heating rates α. The table reveals that these values are shifted to higher values by increasing the heating rates.

Table 1. Transition temperatures of $Fe_{83}B_{17}$ metallic glass as a function of heating rates.

	Heating rate α K/min					
	5	10	15	20	25	30
T_c/K	676	686	694	699	705	706
T_p/K	688	700	707	712	716	718

The activation energy of crystallization E_c for the investigated $Fe_{83}B_{17}$ metallic glass has been estimated using the following methods.

1. Ozawa-Chen method (Ozawa, 1971; Chen 1978) this method relates the dependence of the crystallization temperature T on the heating rate α at different crystallization fractions by the equation

$$\ln(\alpha/T^2) = -E_c/RT + \text{const} \qquad (1)$$

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. If a plot of $\ln(\alpha/T^2)$ versus 1/T yields a straight line, then E_c can be evaluated. Fig. 2 shows $\ln(\alpha/T^2)$ plotted against 1/T at different crystallization fractions for the present $Fe_{83}B_{17}$ metallic glass. Before the second method (Coats-Redfern-Šestăk method) can be applied to evaluate the activation energy of crystallization E_c, the order of the crystallization reaction

n (Avrami exponent) must be determined. Using Ozawa (Ozawa, 1971) method, the value of n can be determined at any fixed temperature as the slope of the relation.

$$\text{Log}[-\ln(1-\chi)] = \text{const} - n \ln\alpha \qquad (2)$$

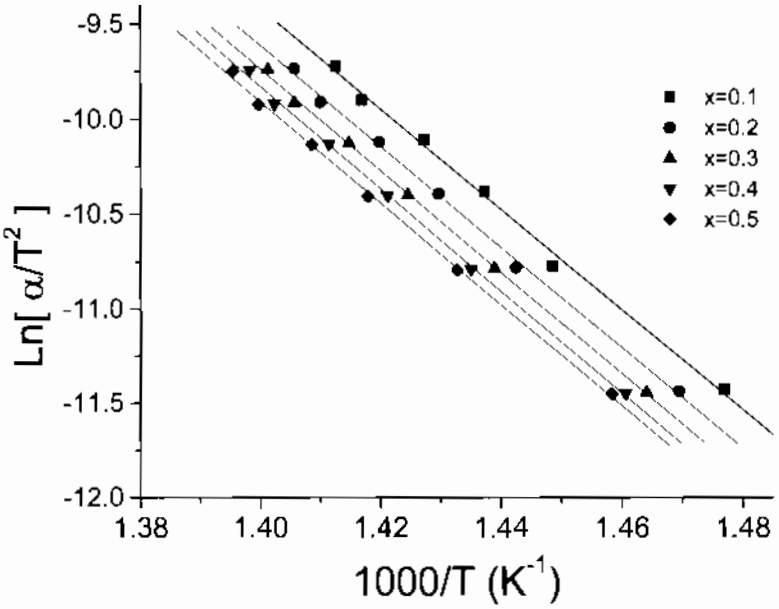

Fig.2. Ozawa-Chen plot of $\ln(\alpha/T^2)$ versus 1000/T at five constant volume fractions for $Fe_{83}B_{17}$ metallic glass.

Figure 3 shows the plots of $\text{Log}[-\ln(1-\chi)]$ versus $\ln\alpha$ for the investigated $Fe_{83}B_{17}$ metallic glass at three different temperatures, namely 695, 700 and 705 K. The average deduced value of n is equal to 3.65 ± 0.05. The calculated value of n is not an integer, which means that the crystallization process of the present glass occurs with two mechanisms (Mahadevan *et al.*, 1986). The obtained value for n indicates that the crystallization process of $Fe_{83}B_{17}$ metallic glass can be carried out by a bulk growth in two dimensions (Soliman et al, 2004).

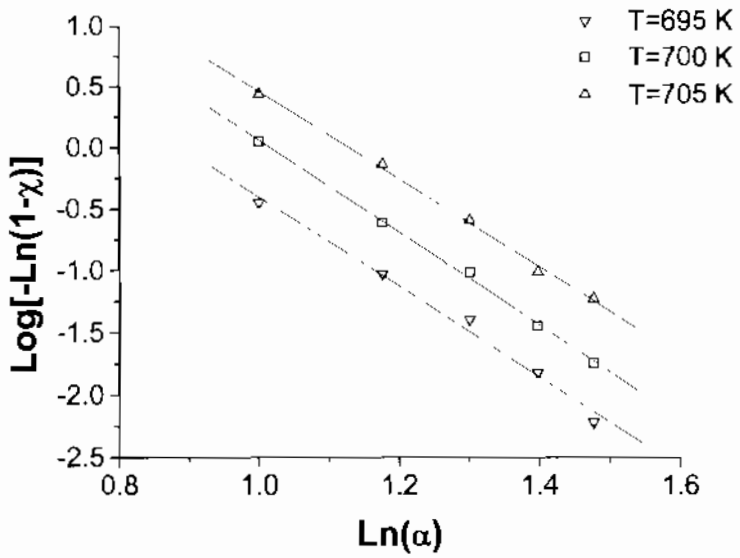

Fig.3. Ozawa plot of $\ln[-\ln(1-\chi)]$ versus $\ln\alpha$ at three different temperatures for $Fe_{83}B_{17}$ metallic glass.

2. *The Coats-Redfern-Šestăk method* (Yinnon & Uhlmann, 1983; Šestăk, 1974) determines the influence of temperature on the crystallization fraction χ for a particular heating rate. In this method the following equation is used

$$\ln[-\ln(1-\chi)/T^{2n}] = -nE_c/RT + \text{eonst} \quad (3)$$

The plot of $\ln[-\ln(1-\chi)/T^{2n}]$ versus 1/T at a heating rate 10 K/min is shown in Fig.4, and the E_c value was determined to be 234 ± 6 kJ/mol.

The slight differences in the value of E_c evaluated by different formulations may be attributed to the different approximations that have been adopted while arriving at the final equation of the various formalisms. It may be mentioned that the activation energy obtained from Matusita et al model in our previous work on this $Fe_{83}B_{17}$ metallic glass system (Soliman *et al.*, 2004)) is more accurate than those obtained from other methods. This is due to the fact that the activation energy in this method has been derived from the variation of the temperature that scans the whole curve starting from the beginning of the crystallization process till approximately its end. Besides, it allows the determination of the dimensionality of growth and the crystallization mechanism involved in amorphous materials. Table 2 shows the values of the effective activation energies of crystallization E_c calculated by means of different models.

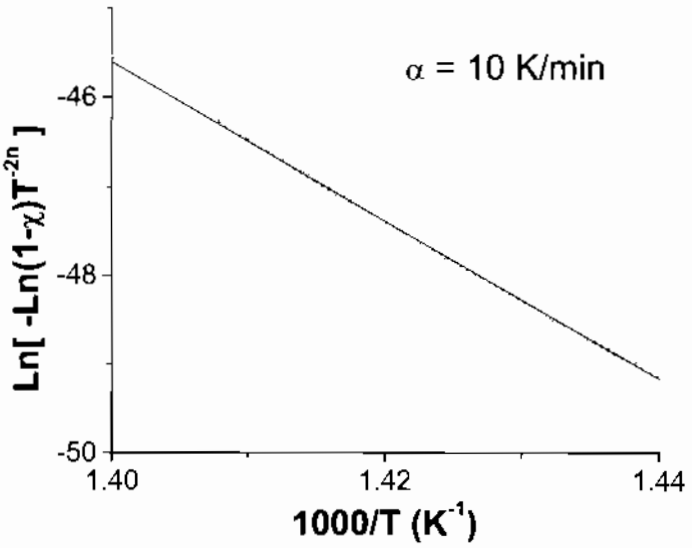

Fig.4. Coast-Redfern-Šestăk plot of $\ln[-\ln(1-\chi)/T^{2n}]$ versus 1000/T at a heating rate of 20 K/min for the $Fe_{83}B_{17}$ metallic glass.

The activation energies to be considered in a crystallization process are the activation energy for nucleation (E_n), activation energy for crystal growth (E_G) and that for the whole process of crystallization, called the activation energy for crystallization denoted by E_c. The thermal analysis methods enable the determination of E_c (Ranganathan & Heimendahl, 1981). It has been pointed out (Illekova, 1984) that in non-isothermal measurements, generally due to a rapid temperature rise and large differences in the latent heats of nucleation and growth, the crystallization exotherm characterizes the growth of the crystalline phase from the amorphous matrix; nucleation is more or less calorimetrically unobservable at temperatures below the crystallization exotherm, or it takes place very rapidly and immediately after overheating of the material in the initial stages of the crystallization exotherm, which results in the deformed beginning of the measured exotherm. consequently, the obtained values of E_c (listed in Table 2) can be taken to

represent the activation energy of growth, E_G of this melt-spun $Fe_{83}B_{17}$ metallic glass. Inspection of table 2 shows that the values of E_c are found to be in the range 224-235 kJ/mol with an average value of 229 ± 5 kJ/mol. These values of E_c confirm our earlier results and in a good agreement with other melt spun $Fe_{80}B_{20}$ metallic glasses (Davis *et al.*, 1976; Luborsky & Liebermann, 1978; Matsuura, 1979; Leake & Greer, 1980).

Table 2. The values of activation energy of crystallization of $Fe_{83}B_{17}$ metallic glass as determined by different models.

Method	Relation	E_c(kJ/mol)
Kissinger	$Ln(\alpha/T_p^2)$ vs. 1/T	224 ± 4
Augis-Bennett	$Ln[\alpha/(T_p-T_0)]$ vs. 1/T	226 ± 5
Ozawa-Chen	$Ln(\alpha/T^2)$ vs 1/T	228 ± 3
Matusita et al	$Ln[-Ln(1-\chi)]$ vs. 1/T	235 ± 4
Coats-Redfern- Šestāk	$Ln[-Ln(1-\chi)/T^{2n}]$ vs. 1/T	234 ± 6

4. Conclusions

The crystallization behavior of $Fe_{83}B_{17}$ metallic glass was studied using a non-isothermal analysis method. The DSC results indicate that the crystallization reaction begins to occur from 676 ~ 706 K and the temperature at maximum crystallization is 688 ~ 718 K for the different heating rates. Several thermal analysis models were used in this investigation to confirm the reliability of the estimated value of the activation energy of crystallization for the $Fe_{83}B_{17}$ metallic glass which was found to be in the range of 224 - 235 kJ /mol. Some of these models have advantage over the others because they can provide more information about the mechanism of the growth and crystallization. The obtained parameters of some models have shown that the crystallization proeess of the $Fe_{83}B_{17}$ metallic glass is carried out by a bulk crystallization growth in two dimensions.

References

Al-Heniti, S., Cowlam, N. and **Wildes, A.R.,** A study of the structures of some (FeRu)B metallic glasses by x-ray and neutron scattering, *J. Phys.: Condens. Matter,* **11,** (1999) 9139-9150.

Al-Heniti, S., *Structural studies of some metallic glasses using x-ray and neutron diffraction methods,* Ph.D Thesis, University of Sheffield, UK (1999).

Chen, H.S., A method for evaluating viseosities of metallie glasses from the rates of thermal transformations, *J. Non-Cryst. Solids,* **27,** (1978) 257.

Cowlam, N., Metallic glasses: Structure and properties, *J. Non-Cryst. Solids,* **205-207,** (1996) 567.

Cowley, R.A., Patterson, C., Cowlam, N., Ivison, P.K., Martinez, J. and **Cussen, L.D.,** Non-collinear magnetic structures of Fe-based amorphous alloys, *J. Phys.: Condens. Matter,* **3,** (1991) 9521.

Cowley, R.A., Paul, Mck.,D., Stirling, W.G. and **Cowlam, N.,** Polarized neutron seattering from the amorphous ferromagnet, $Fe_{83}B_{17}$, *Physica,* **120B,** (1983) 373.

Davis, L.A., Ray, R., Chou, C.P., and **O'Handley, R.C.,** Mechanical and thermal properties of $Fe_{80}B_{20}$ glass, *Sc. Metall.,* **10,** (1976) 541.

Illekova., E., On the various activation energies at crystallization of amorphous metallie materials, *J. Non-Cryst. Solids,* **68,** (1984) 153.

Kissinger, H.E., Reaction kinetics in differential thermal analysis, *Anal. Chem.*, **29,** (1957) 1702.

Kissinger, H.E., Variation of peak temperature with heating rate in differential thermal anaylsis, *J. Res. Nat. Bur. Stand.*, **57,** (1956) 217.

Leake, J.A. and **Greer, A.L.,** An examination of the sources of variation in the measured properties of $Fe_{80}B_{20}$ glass, *J. Non-Cryst. Solids,* **38/39,** (1980) 735.

Luborsky, F.E. and **Liebermann, H.H.,** *Crystallization kinetics of Fe-B amorphous alloys,* Report No. 78 CRD 133, General Electric Company (July 1978).

Mahadevan, S., Giridhar, A. and **Singh, A.K.,** Calorimetric Measurement on As-Sb-Se Glasses, *J. Non-Cryst. Solids,* **88,** (1986) 11.

Matusita, K. and **Sakka, S.,** Study on crystallization kinetics in glass by differential thermal analysis, *Thermochim. Acta,* **33,** (1979) 351.

Matusita, K. and **Sakka, S.,** Kinetic study of the crystallization of glass by differential scanning calorimetry, *Phys. Chem. Glasses,* **20,** (1979) 81.

Matsuura, M., Crystallization kinetics of amorphous Fe-B alloys by DTA, *Solid State Commun.*, **30,** (1979) 231.

Ozawa, T., Kinetics of non-isothermal crystallization, *Polymer,* **12,** (1971) 150.

Ranganathan, S. and **von Heimendahl, M.,** The activation energies with isothermal transformations - application to metallic glasses, *J. Mat. Sci.,* **16,** (1981) 2401.

Šestăk, J., Thermophysical properties of solids, their measurements and theoretical analysis, Elsevier, Amsterdam, 1984. **15,** (1974) 137.

Soliman, A.A., Al-Heniti, S., Al-Hajry, A., Al-Assiri, A.M. and **Al-Barakati, G.,** Crystallization kinetics of melt-spun $Fe_{83}B_{17}$ metallic glass, *Thermochim. Acta,* **413,** (2004) 57.

Wildes, A.R., Cowley, R.A., Al-Heniti, S., Cowlam, N., Kulda, J. and **Lelièvre-Berna, E.,** The magnetic structure of $(Fe_{80-x}Ru_x)B_{20}$ metallic glasses, *J. Phys.: Condens. Matter,* **10,** (1998) 2617.

Wildes, A.R., Cowlam, N., Al-Heniti, S., Kiss, L.F. and **Keměny, T.,** Non-Collinear ferromagnetism in Fe-Zr metallic glasses, *J. Magn. Mater.*, **226-230,** (2001) 1470.

Yinnon, H. and **Uhlmann, D.R.,** Applications of thermoanalytical techniques to the study of crystallization kinetics in glass-forming liquids, part I: Theory, *J. Non-Cryst. Solids,* **54,** (1983) 253.

دراسة كالورمتريه (حرارية) لتبلور المعدن الزجاجي $Fe_{83}B_{17}$

علي الحجري[1] ، صالح الحنيطي[2] ، علاء سليمان[1] و محمد عسيري[1]

[1] *قسم الفيزياء، كلية العلوم ، جامعة الملك خالد ، أبها – المملكة العربية السعودية*

[2] *قسم الفيزياء، كلية العلوم ، جامعة الملك عبد العزيز*

جـــــدة – المملكة العربية السعودية

المستخلص. اهتم هذا البحث بدراسة بعض الخصائص الحرارية المرتبطة بتبلـــور عينة المعدن الزجاجي $Fe_{83}B_{17}$ ذات التركيب غير البلوري و المحـــضرة بطريقـــة التبريد السريع (Fast Quenching). لقـــد تم دراسة عملية التبلور بواســـطة الطـــرق التالية: المسح التفاضـــلي الكـــالورمتري (DSC) وحيـــود الأشـــعة الـــسينية (XRD) والميكروسكوب الإلكتروني (SEM). وتم تحديد النسبة الجزئية للتبلور و كذلك تعيـــين طاقة تحفيز النمو باستخدام طرق مختلفة. وقد وجد أن عملية نمو التبلور تـــتم فـــي بعدين (Two Dimensions).