

Crystallization Kinetics of Amorphous $\text{Fe}_{77}\text{B}_{16}\text{Si}_5\text{Cr}_2$ Metallic Glass

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ABSTRACT: Differential Scanning Calorimetry (DSC) experimental data under non-isothermal conditions for metglas 2605S3A ($\text{Fe}_{77}\text{B}_{16}\text{Si}_5\text{Cr}_2$) metallic glass ribbons are reported and discussed. The DSC thermograms at 2, 4, 6, 8 and 10 K/min heating rates showed two step crystallization processes and are interpreted in terms of different models (Kissinger, Ozawa, Bosewell, Augis & Bennett, Gao & Wang and Matusita & Sakka) developed for non-isothermal conditions. From the heating rate dependence of the on-set temperature (T_o) and the crystallization peak temperature (T_p), the kinetic triplet (activation energy of crystallization (E_c), Avrami exponent (n) and the frequency factor (A) were determined. The evaluated values of the Avrami exponent, n (for peak I is 3.8 and for peak II is 4.2) which indicate three dimensional growths, which is responsible for the amorphous-crystalline transformation. The determined E_c for peak I is 425 ± 1.7 kJ/mol and for peak II is 384 ± 1.9 kJ/mol, respectively.

KEYWORDS: Crystallization kinetics, Activation energy of crystallization, Non isothermal methods, Metallic glasses.

I. INTRODUCTION

Bulk metallic glasses have several scientific and technological uses. One of these uses is connected with the production of amorphous alloys with soft magnetic properties, by which the chemical composition of the alloys has thoroughly been modified and investigated. They have emerged as a new technological materials and a great variety of alloys with different elemental compositions and magnetic properties. The technological applications of these amorphous alloys have been restricted to low-working temperatures because of their mechanical properties, which become brittle in the crystalline state. Thus, the brittleness problem of these Fe-based amorphous alloys greatly depends on the elemental nature of the alloy and the presence of crystalline phases [1-4]. Study of crystallization kinetics using DSC is easy and widely applied and discussed in the literature [5-9]. Thermally stimulated solid state processes can be analyzed in two methods, namely, isothermal and non-isothermal [10-14]. In isothermal method the sample is brought quickly to a glass transition temperature (T_g) and the heat liberated during the crystallization process is recorded as a function of temperature, whereas in the non-isothermal method the sample is heated at a constant heating rate and the heat evolved is measured as a function of time or temperature.

The disadvantage in isothermal method is reaching the required temperature instantaneously and taking the readings at that point. This drawback is eliminated in the non-isothermal method [15]. We have employed non isothermal calorimetric studies at different heating rates for evaluating the kinetic parameters. DSC, Positron annihilation lifetime spectroscopy, X-ray diffraction and Vickers micro-hardness were studied by López-Morales et al [1,2], whereas non-isothermal crystallization kinetics studies were not reported in the literature.

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II. EXPERIMENTAL METHODS

Specimens of amorphous (2605S3A) $Fe_{77}B_{16}Si_5Cr_2$ ribbons were procured from Metglas, USA. DSC measurements were performed for the as-quenched samples using Mettler Toledo instrument (Temp Precision: ± 0.02 °C, energy sensitivity: better than $0.1\mu W$). Non-isothermal DSC curves were obtained with selected heating rates 2, 4, 6, 8 and $10 Kmin^{-1}$ from room temperature to beyond second crystallization exotherm in air. The fraction of crystallized material, at any temperature T is given by $\alpha = (S_T/S)$ where S 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; S_T is the area between T_1 and T as shown by the hatched portion in Fig.1. But the 'α' is given by the software attached with the DSC set up. .

III. RESULTS

The DSC thermograms of $Fe_{77}B_{16}Si_5Cr_2$ bulk amorphous alloy at $6K/min$ heating rate is shown in Fig.1. All the DSC traces have double exothermic peaks in the temperature scanned, and an extended supercooled liquid region before the onset of the crystallization. The onset and peak temperatures (T_o and T_p) for crystallization, are given in the Table I. It is noticed that the T_p shifted to high temperatures with increasing heating rate. This indicates that the crystallization behaves in a marked kinetic feature. This shift in the peak forms the basis for determination of the activation energy. Due to increase in the sensitivity, the peak height also increases with increasing heating rate. The non-isothermal crystallization data of DSC have been analyzed using different methods of kinetic analyses as discussed below. The plots of α versus T for different heating rates for both the peaks are shown in fig.2 & 3. Their shapes are quite typical sigmoidal. The sigmoidal plot exhibits the bulk crystallization and excludes the chance of surface crystallization.

Table I: Transition temperatures of $Fe_{77}B_{16}Si_5Cr_2$ metallic glass as a function of heating rates.

Heating Rates (β) K/min	Peak I		Peak II	
	T_o (K)	T_p (K)	T_o (K)	T_p (K)
2	765.3	774.1	783.9	793.2
4	772.4	782.0	791.1	801.9
6	777.0	786.8	795.9	807.5
8	781.1	790.2	800.6	811.5
10	781.5	792.4	803.2	813.6

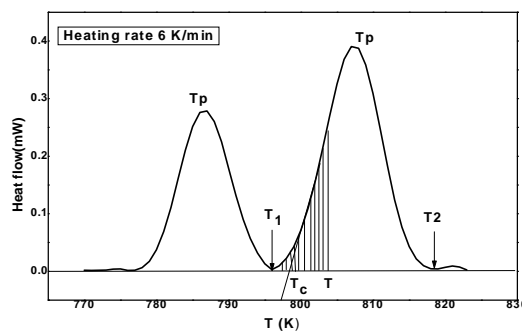


Fig. 1 DSC Thermogram of the $Fe_{77}B_{16}Si_5Cr_2$ at the heating rate $6 K/min$.

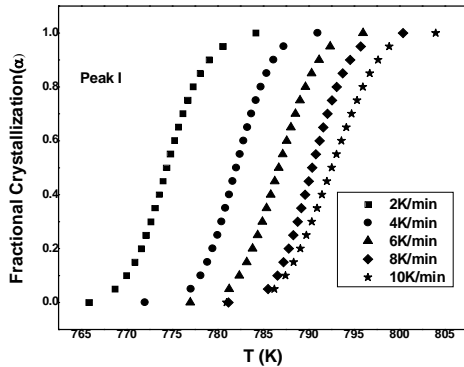


Fig. 2 Sigmoidal plot for Fe₇₇B₁₆Si₅Cr₂ at different heating rates.

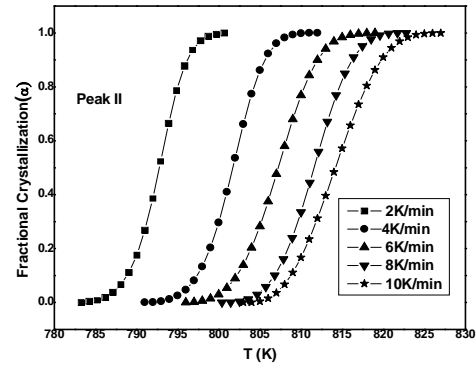


Fig. 3 Sigmoidal plot for Fe₇₇B₁₆Si₅Cr₂ at different heating rates.

The activation energy of crystallization E_c , frequency factor, A and Avrami exponent, n for the investigated Fe₇₇B₁₆Si₅Cr₂ metallic glass has been estimated using the following methods.

A. KISSINGER METHOD:

Using Kissinger's Equation [16]

$$\ln(\beta/T_p^2) = -E_c/RT_p + \ln(AR/E_c) \tag{1}$$

Where β is the heating rate and R is the universal gas constant, the value of E_c can be obtained from the heating rate dependence of the peak temperature of crystallization. Fig. 4 shows $\ln(\beta/T_p^2)$ vs $1000/T_p$ relationship. The value of E_c for crystallization and the frequency factor (A) are obtained from the slope and intercept of the plot and are given with the correlation coefficient in the Table II & III respectively.

B. OZAWA METHOD:

According to Ozawa [17], the change of $\ln(1/T_p^2)$ with β is negligibly small compared to the change of $\ln(\beta)$ and therefore, the Kissinger's equation can be written as

$$\ln \beta = -1.0516 E_c / RT_p + \text{const} \tag{2}$$

Plotting $\ln \beta$ vs $1000/T_p$ (Fig.5), E_c is calculated (Tables II & III.)

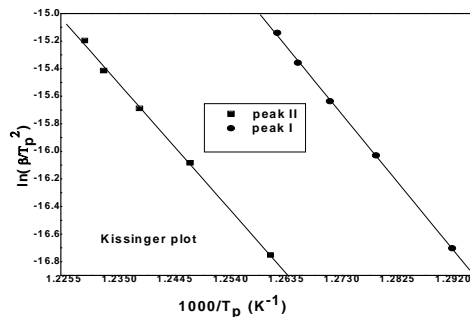


Fig. 4 $\ln(\beta/T_p^2)$ versus $1000/T_p$ plot for Fe₇₇B₁₆Si₅Cr₂

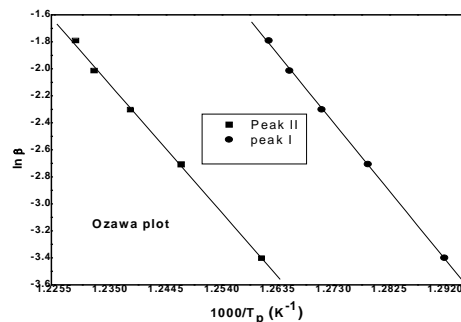


Fig. 5 $\ln \beta$ versus $1000/T_p$ plot for Fe₇₇B₁₆Si₅Cr₂

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C. BOSEWELL METHOD [18]:

In order to determine the activation energy, Bosewell uses the following equation

$$\ln(\beta/T_p) = -E_c/RT_p + \text{const} \tag{3}$$

The slopes of the graph (Fig.6) give the activation energy and are given in Tables II & III.

D. AUGIS AND BENNETT METHOD [19] :

The equation given by Augis and Bennett is

$$\ln(\beta/(T_p - T_o)) = -E_c/RT_p + \ln A \tag{4}$$

Where T_p and T_o are the peak and the onset crystallization temperature respectively. Fig.7 shows the plot $\ln(\beta/(T_p - T_o))$ vs $1000/T_p$ and gives the E_c and A values for crystallization and are given in Tables II & III.

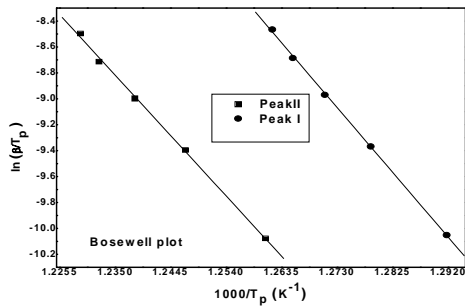


Fig. 6 $\ln(\beta/T_p)$ versus $1000/T_p$ plot for $Fe_{77}B_{16}Si_5Cr_2$

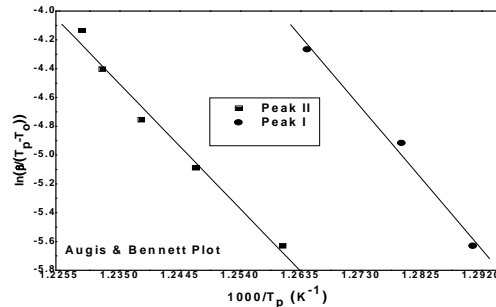


Fig. 7 $\ln[\beta/(T_p - T_o)]$ versus $1000/T_p$ plot for $Fe_{77}B_{16}Si_5Cr_2$

E. GAO AND WANG METHOD [9] :

This method uses the following expressions to determine E_c and A and Avrami exponent n . Fig. 8 gives the plot of $\ln[\beta(d\alpha/dT)_p]$ versus $1000/T_p$. The slope gives E_c and are given in the Table II & III for peaks I & II.

$$\ln\left[\beta\left(\frac{d\alpha}{dT}\right)_p\right] = -E_c/RT_p + \text{const.} \quad \text{where } \beta = dT/dt \tag{5}$$

$$K_p = \beta E_c / RT_p^2 \quad \text{Where } K_p = A e^{-E/RT_p} \tag{6}$$

$$n = \left(\frac{d\alpha}{dt}\right)_p / 0.37 K_p \tag{7}$$

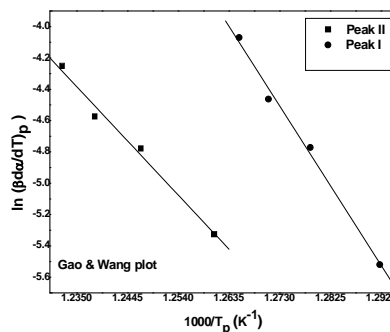


Fig. 8 $\ln(\beta d\alpha/dT)_p$ versus $1000/T_p$ plot for $Fe_{77}B_{16}Si_5Cr_2$

F. MATUSITA AND SAKKA METHOD [20] :

Matusita and Sakka suggested the following equation specifically for non-isothermal data

$$\ln[-\ln(1-\alpha)] = -n \ln\beta - 1.052 mE_c/RT + \text{const} \tag{8}$$

Where m is an integer depends on the dimensionality of the crystallization and n the Avrami exponent depends on the nucleation process. When the nuclei formed during the heating $n = m+1$ and when nuclei formed during any previous heat treatment prior to thermal analysis then $n = m$ [21-23]. Fig.9 and Fig. 10 shows the variation of $\ln(-\ln(1-\alpha))$ with $\ln\beta$ at six constant temperatures for peaks I and II , whose slope gives the value of n . The average value of n for the peak I is found to be 3.9 and for peak II is 4.2 and given in the Table II & III. The n value, which indicates a three dimensional surface crystallization. According to Eq. 8, the plot of $\ln(-\ln(1-\alpha))$ versus $1000/T$ at a constant heating rate should give a straight line. Figs.11 and 12 shows such plots at different heating rates for the peaks I and II and the average value of mE_c for peak I and II are 1502.2 and 1701.5 kJ/mol respectively. Taking $m=3.7$ for peak I and 4.1 for peak II, the E_c values 406 and 415 kJ/mol are obtained (Table I & II). The plots are almost linear over most of the temperature range. At high temperature region where large crystallization occurs, deviation is more pronounced from linearity. This is attributed to the saturation of nucleation sites in the final stage of crystal growth due to small particle size [24]

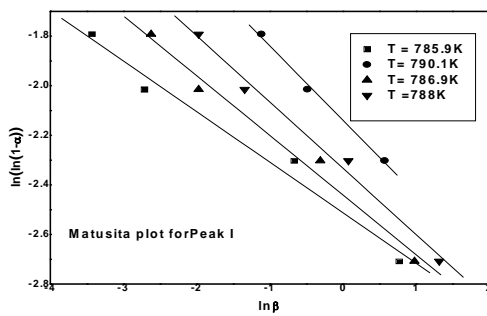


Fig.9 $\ln(-\ln(1-\alpha))$ versus $\ln\beta$ for $Fe_{77}B_{16}Si_5Cr_2$.

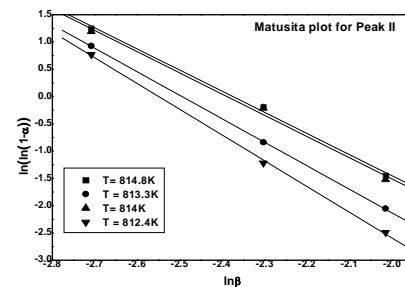


Fig. 10 $\ln(-\ln(1-\alpha))$ versus $\ln\beta$ for $Fe_{77}B_{16}Si_5Cr_2$.

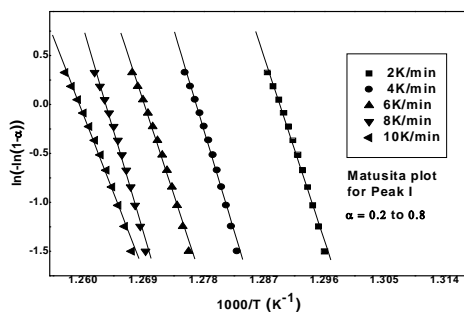


Fig. 11 $\ln(-\ln(1-\alpha))$ versus $1000/T$

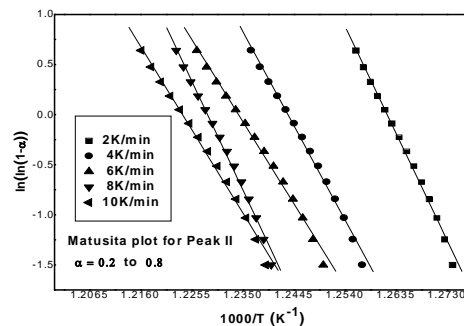


Fig. 12 $\ln(-\ln(1-\alpha))$ versus $1000/T$

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Table II: E_c , A and n for Peak I from various methods

Method	Activation energy(kJ/mol)	r	Frequency factor(A) (sec ⁻¹)	Avrami exponent (n)
Kissinger	430.7±0.7	0.99974	3.4×10^{26}	
Ozawa	422.0±0.7	0.99975		
Bosewell	437.3±0.7	0.99975		
Augis & Bennett	406.6±2.8	0.99671	9.7×10^{24}	3.9
Gao & Wang	445.6±3.2	0.99655	3.2×10^{27}	3.7
Matusita & Sakka	406.0±2.4	0.99560		3.7

Table III: E_c , A and n for Peak II from various methods

Method	Activation energy (kJ/mol)	r	Frequency factor(A) (sec ⁻¹)	Avrami exponent (n)
Kissinger	401.6±1.1	0.9992	6.72×10^{23}	
Ozawa	394.4±1.1	0.99923		
Bosewell	408.2±1.1	0.99925		
Augis & Bennett	379.1±3.5	0.99148	3.4×10^{22}	4.3
Gao & Wang	304.3±2.8	0.99424	2.4×10^{17}	
Matusita & Sakka	415.0 ±1.8	0.99781		4.1

IV. DISCUSSION

The differences in the value of E_c determined by different methods may be attributed to the different approximations that have been adopted while arriving at the final equation of the various methods. It may be mentioned that the E_c determined from Matusita et al model for this $Fe_{77}B_{16}Si_5Cr_2$ metallic glass system is more accurate than those determined from other methods. This is due to the fact that the E_c 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 the growth and the crystallization mechanism involved in amorphous metallic glasses. Tables II and III for both the peaks show the values of the effective E_c , frequency factor (A) and Avrami exponent (n) calculated by different methods.

The activation energies for the crystallization process are the combination of the activation energy for nucleation(E_n) and the activation energy for growth(E_G) and that for the whole process of crystallization, called the activation energy for crystallization denoted by E_c [25]. It has been pointed out[26] that in non-isothermal measurements, due to rapid temperature rise and large differences in the latent's of nucleation and growth, the crystallization thermogram characterizes the growth of the crystalline phase from the amorphous matrix ; nucleation is more or less calorimetrically unobservable at temperatures below the crystallization. Hence the determined values of E_c (listed in Tables II & III) can be taken to represent the activation energy for growth, E_G of this metallic glass. Inspection of Tables 2 & 3 shows that the values of E_c for peak I are found to be in the range 406-445.6 kJ/mol with average value of nearly 425 kJ/mol and for peak II in the range 304.3-415 kJ/mol with average value of nearly 384 kJ/mol .Our reported E_c values are in agreement with the values obtained by isoconversional and model fitting methods[27]. It is seen that the E_c of peak I is

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greater than peak II, which has been already observed in Fe-Si-B metallic glasses [28,29]. Avrami exponent, n , an important parameter, can reflect the crystallization mode directly. The evaluated values of the Avrami exponent (n) for peak I (3.8) and for peak II (4.2), indicate three dimensional growth, which is responsible for the amorphous-crystalline transformation.

The frequency factor explains the atomic collision probability and gives the measure of the probability that an atom having energy E_c will participate in a crystallization process. Thus the frequency factor up to certain extent, expresses the mobility of the atom and stability of the amorphous phase. It is observed that the value of A , for peak I is greater than peak II.

V. CONCLUSION

The crystallization kinetics of amorphous 2605S3A ($Fe_{77}B_{16}Si_5Cr_2$) metallic glass is studied using DSC in non-isothermal conditions. The DSC results indicate that the onset of crystallization occur from 765.3-781.5K for the peak I and 783.9-803.2K for the peak II and the temperature at maximum crystallization is 774.1-792.4K for peak I and 793.2-813.6K for the peak II for the different heating rates. Several kinetic methods are used in this investigation to estimate the values of E_c for the $Fe_{77}B_{16}Si_5Cr_2$ metallic glass and its average values are nearly 425 ± 1.7 kJ/mol and 384 ± 1.9 kJ/mol for peak I & II respectively. The Avrami exponent, n for peak I is found as 3.8 and for peak II is 4.2. The frequency factor, A for peak I & II are also evaluated.

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REFERENCES

- [1] A.López-Morales, A.Cabral-Prieto, F.García-Santibáñez, J.Ramírez, J.López-Monroy, J.Orozco-Velazco, Micro-structural changes in the amorphous Fe-based alloy 2605S3A prior to crystallization, Part 1, Internet Electronic Journal ,Nanociencia et Moletrónica Julio 8 (2010)1445
- [2] A. López-Morales, A. Cabral-Prieto, F. García-Santibáñez, J. Ramírez, J. López-Monroy, Micro-structural changes in the amorphous Fe-based alloy 2605S3A prior to crystallization, Part 2, Internet Electronic Journal Nanociencia et Moletrónica Julio 8 (2010)1473
- [3] A.Brener,G.E.Riddell, J. of Research of the National Bureau of Standards, 37(1946)31
- [4] P.Allia,P.Tiberto,M.Baricco,F.Vinai, Improved Ductility of nanocrystalline $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$ obtained by direct-current joule heating , Appl. Phys. Lett. 83(1993)2759
- [5] A.H.Moharram, M.Abu El-Oyoun ,Pre-crystallization kinetics of $Bi_{10}Se_{90}$ glass, J.Phys.D:Appl.Phys.33 (2000) 700
- [6] A.H.Moharram,M.S. Rasheedy, A simple method for crystallization kinetics determination and its application to $Ge_{10}Te_{35}As_{55}$ glass, Phys.Stat. Sol. A 169 (1998) 33
- [7] J.Vazquez,C.Wagner, P.Villares, R.Jimenez-Garay,Glass Transition and Crystallization Kinetics in $Sb_{0.18}As_{0.34}Se_{0.48}$ glassy alloy by using non-isothermal techniques, J.Non-Cryst.Solids 548(1998) 235
- [8] J.Vazquez, C.Wagner, P.Villares,R. Jimenez-Garay,A theoretical method for determining the crystallized fraction and kinetic parameters by DSC, using non-isothermal techniques, *Acta Mater.*44 (1996) 4807
- [9] Y.Q.Gao ,W.Wang ,On the Activation Energy of Crystallization in Metallic Glasses, J. Non-Cryst.Solids 81(1986)129
- [10] R.A. Ligeró, J.Vazquez, P.Villares, R.Jimenez-Garay,Crystallization kinetics in the As-Se-Te system, *Thermochim Acta* 162(1990) 427
- [11] A.H.Moharram, M.Abu El-Oyoun , A.A. Abu-Sehly,J.Phys. D: Appl. Phys 34 (2001)1
- [12] N. Rysava ,T. Spasov ,L. Tichy ,Isothermal DSC method for evaluation of the kinetics of crystallization in the Ge-Sb-S glassy system, J. Therm Anal. and Calorimetry ,32 (1987) 1015
- [13] A. Giridhar , S.Mahadevan ,Studies on the $As_xSb_{15}Se_{85-x}$ glass system, J. Non-Cryst Solids 51 (1982) 305
- [14] N. Afify , Kinetics study of non-isothermal crystallization in $Se_{0.7}Ge_{0.2}Sb_{0.1}$ chalcogenide glass, J. Non- Cryst. Solids 128 (1991) 279
- [15] M.J. Starink ,A.M. Zahra ,Determination of the transformation exponent s from experiments at constant heating rate, *Thermochim.Acta* 298 (1997)179
- [16] H.E.Kissinger , Reactions Kinetics in Differential Thermal Analysis, *Anal.Chemistry*, 29 (1957)1702
- [17] T.Ozawa ,A New Method of Analysing Thermogravimetric Data, *Bull. Chemical Society of Japan*, 38 (1965)1881
- [18] P.G.Bosewell ,On the Calculation of Activation Energies using a Modified Kissinger Method, *J. Thermal Analysis*, 18 (1980) 353
- [19] J.A.Augis and J.E.Bennett,Calculation of the Avrami Parameters for Heterogenous Solid State Reactions Using a Modification of the Kissinger Method, *J. Thermal Analysis*, 13 (1978) 283

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

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- [20] K.Matusita , S.Sakka ,Kinetic Study on Crystallization of Glass by Differential Thermal Analysis –Criterion on Application of Kissinger Plot, Phys.Chem.Glasses, 20 (1979) 81
- [21] S.Mahadevan,A.Giridhar and A.K.Singh, J. Non-Cryst.Solids 81(1986)11
- [22] N.Afify,M.A.Abdel-Rahim,A.S. Abdel-Rahim and M.M.Hafiz, Kinetics study of non-isothermal crystallization in $Se_{0.7}Ge_{0.2}Sb_{0.1}$ chalcogenide glass J. Non-Cryst.Solids 128(1991)269
- [23] A.A.Abu-sehyl,Study of Kinetics of Non-Isenthal Crystallization in $Ge_{20}Te_{80}$ Chalcogenide Glass,PhysicsB,325(2003)372
- [24] J.Colmenero and J.M.Barandiaran,Crystallization of $Al_{23}Te_{77}$ glasses, J. Non-Cryst.Solids 30(1979)263
- [25] S.Ranganathan and M.von Heimendahl,The activation energies of crystallization of in the amorphous alloy METGLASS 2826A, J.Mat.Sci, 16 (1981)2401
- [26] E.Illekova,Crystallization behavior of $Co_{100-1(x+y)}Nb_xB_y$ amorphous alloys, J. Non-Cryst. Solids 68(1984) 53
- [27] T.Shanker Rao and T.Lilly Shanker Rao, A survey on isoconversional and model fitting methods for Fe-based metallic glass, International Journal of Innovative Research in Science,Engineering and Tecnology (online) Vol 5,Issue 9,September 2016.
- [28] C.F. Chang, J. Marti, Crystallization of metallic glass $Fe_{80}B_{12}Si_8$, J. Mater. Sci. 18 (1983) 2297.
- [29] P.Tomic, M.Davidovic, The study of relaxational properties and crystallization of the metallic glass $Fe_{80}Si_{10}B_{10}$ J. Non-Cryst. Solids. 204(1996)32