Research & Reviews: Journal of Material Sciences
DOI: 10.4172/2321-6212.1000163

e-ISSN: 2321-6212
p-ISSN: 2347-2278

Calculation of Activation Energy, Frequency Factor and Avrami Exponent of Amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ Alloys on the Basis of Crystallization Kinetics

Bhanu Prasad B* and Rajya Lakshmi N

Department of Sciences & Humanities, M.V.S.R. Engineering College, Nadergul, Hyderabad, Hyderabad, India

Research Article

Received: 04/01/2017
Accepted: 04/03/2017
Published: 14/03/2017

***For Correspondence**

Bhanu Prasad B, Department of Sciences & Humanities, M.V.S.R. Engineering College, Nadergul, Hyderabad, India, Tel: 40-24530846.

E-mail: bbpproofphys56@gmail.com

Keywords: Differential scanning calorimetry; Activation energy; Crystallization temperature; Frequency factor

ABSTRACT

The activation energy of crystallization (E_a), Frequency factor(k_0) and Avrami exponent (n) of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys have been calculated by three methods namely Kissinger, Augis-Bennet and Matusita-Sakka on the basis of crystallization kinetics using Differential Scanning Calorimetry (DSC). The average activation energy for primary crystallization of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys using the above three methods is determined as 389.67 kJouls/mole and 578.59 kJouls/mole, respectively. The frequency factor of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys using Kissinger method is found to be 4.542×10^{19} $(sec)^{-1}$ and 8.5×10^{31} $(sec)^{-1}$, respectively. Similarly, the Avrami exponent of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys is found to be 1.67 and 0.831, respectively.

INTRODUCTION

The Thermal stability of amorphous alloys is a subject of considerable interest, since the properties of these engineering materials may be significantly changed by the onset of crystallization. The crystallization is associated with nucleation and growth process. Activation energy (E_a) is one of the important parameters describing the transformation kinetics. E_a values are found to be larger at higher temperatures in crystallization. These features probably originate from the crystallization micro-mechanism. Thus, crystallization kinetics of amorphous materials was investigated by explaining the crystallization mechanism and the crystallization activation energy in terms of isothermal and non-isothermal methods with different approaches. Different thermal analysis techniques used in crystallization kinetics were reported and a correlation between kinetic and structural investigations were made to determine the crystallization mechanism in these materials [1,2]. Therefore, the investigation of crystallization kinetics is important since it quantifies the effect of the nucleation and growth rate of the resulting crystallites [1]. In this paper, we present the Calculation of activation energy, frequency factor and Avrami exponent of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys on the basis of crystallization kinetics using Differential Scanning Calorimetry (DSC).

EXPERIMENTAL SECTION

Specimens of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ ribbons prepared by single roller melt spinning technique under inert atmosphere were procured from our other researchers. The alloy ribbons were about 1 mm wide and about 30 μm thick. The amorphous nature of ribbons was confirmed by X-ray diffraction (XRD). The as-quenched samples of $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Pr_4B_{20}$ ribbons were heated in DSC (DSC-50, Shimadzu, Japan) at four linear heating rates (10, 20, 30 and 40 Kelvin/min) from room temperature to 1000 K. The DSC scans were recorded by a thermal analyzer interfaced to a computer.

RESULTS AND DISCUSSION

The DSC curves of as-quenched samples of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys at four heating rates of crystallization are shown in **Figure 1**.

e-ISSN: 2321-6212
p-ISSN: 2347-2278

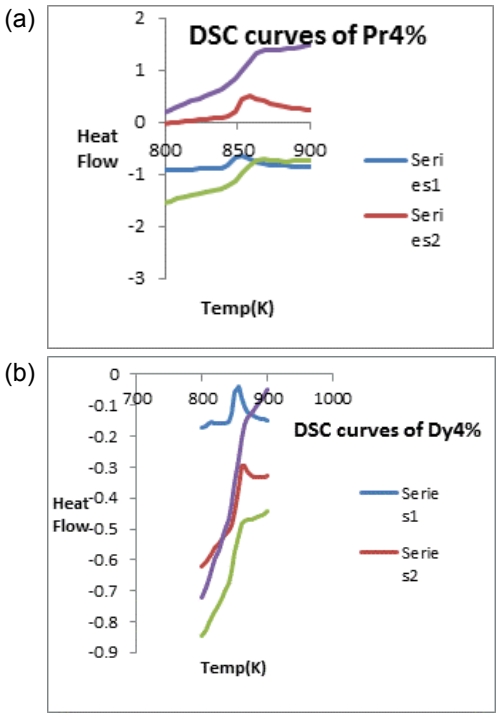

Figure 1. The DSC curves of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys at four heating rates of crystallization in the temperature range 800 K–940 K (Blue - 10 K/min, Red - 20 K/min, Green - 30 K/min and Violet-40 K/min).

The activation energy for crystallization of an amorphous alloy under a linear heating rate can be estimated using Kissinger's peak shift method [3], which relates the peak temperature, T_p, with heating rate (β) through the equation.

$$\ln(\beta/T_p^2) = -(E_a/RT_p) + \ln(k_0R/E_a) \quad (1)$$

Where E_a is the activation energy for crystallization, k_0 the frequency factor which is defined as the number of attempts made by the nuclei per second to overcome the energy barrier and and R is the universal gas constant. **Figure 2** shows the graph of $\ln(\beta/T_p^2)$ vs $1000/T_p$ of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys, which is a straight line with a slope $(-E_a/R)$ and an intercept of $\ln(k_0R/E_a)$. The activation energy and the frequency factor k_0 for crystallization peak calculated using Kissinger's peak shift method for the given samples are given in **Table 1**.

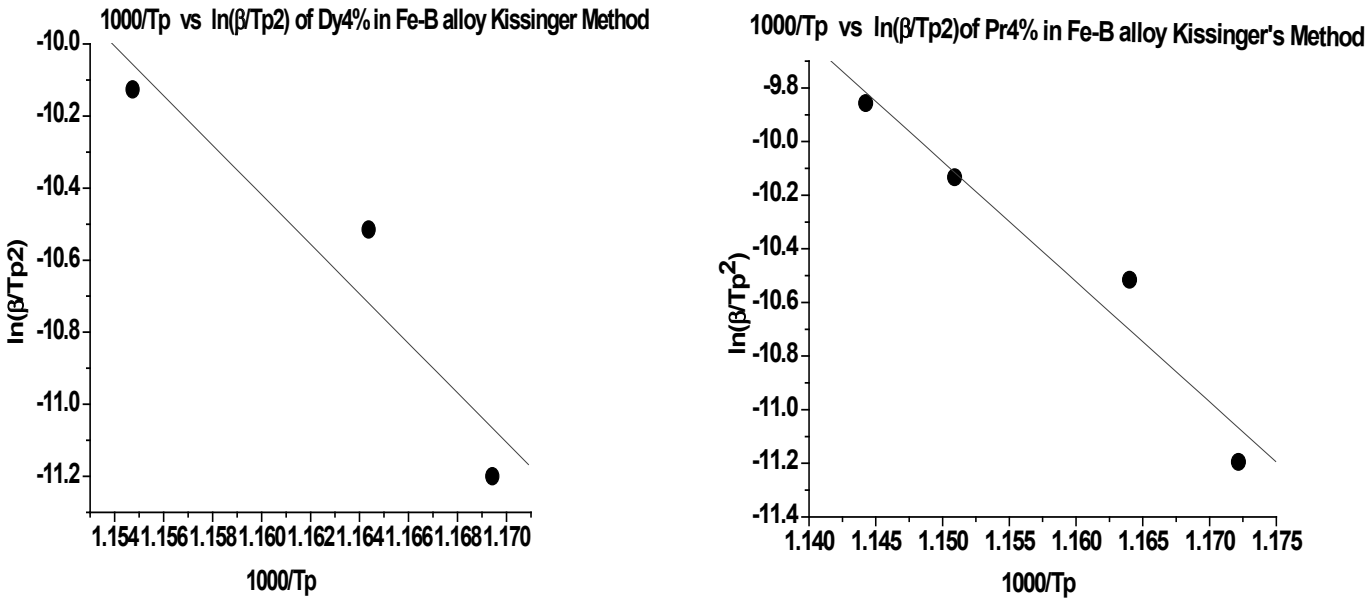

Figure 2. ln (β/Tp2) vs. (1000/Tp) of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys.

e-ISSN: 2321-6212
p-ISSN: 2347-2278

The activation energy for crystallization of an amorphous alloy under a linear heating rate can also be estimated using Matusita-Sakka's peak shift method [4], which relates the peak temperature, T_p, with heating rate (β) through the equation.

$$\ln(\beta) = -(E_a/RT_p) + \text{constant} \quad (2)$$

where E_a is the activation energy for crystallization and R is the universal gas constant. **Figure 3** shows the graph of ln (β) vs $1000/T_p$ of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys, which is a straight line with a slope $(-E_a/R)$. The activation energy calculated using Matusita-Sakka's peak shift method for the given samples, is given in **Table 1**.

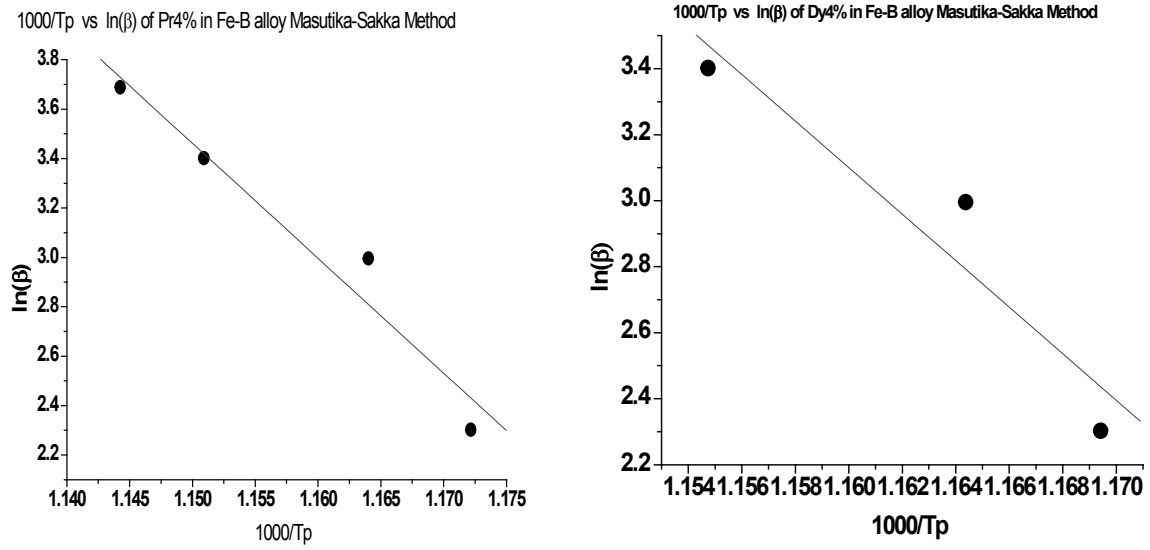

Figure 3: ln (β) vs. (1000/Tp) of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys.

The activation energy for crystallization of an amorphous alloy under a linear heating rate can be estimated using Augis & Bennett method [5], which relates the peak temperature, T_p, with heating rate (β) through the equation.

$$\ln(\beta/T_p) = -E_a/RT_p + \ln k_o \quad (3)$$

Where E_a is the activation energy for crystallization, R is universal gas constant and k_0 the frequency factor. **Figure 4** shows the graph of $\ln(\beta/T_p^2)$ vs. $1000/T_p$ of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys, which is a straight line with a slope $(-E_a/R)$ and an intercept of $\ln k_0$. The activation energy E_a and the frequency factor k_0 for crystallization peak using Augis & Bennett method for the given samples are also given in **Table 1**.

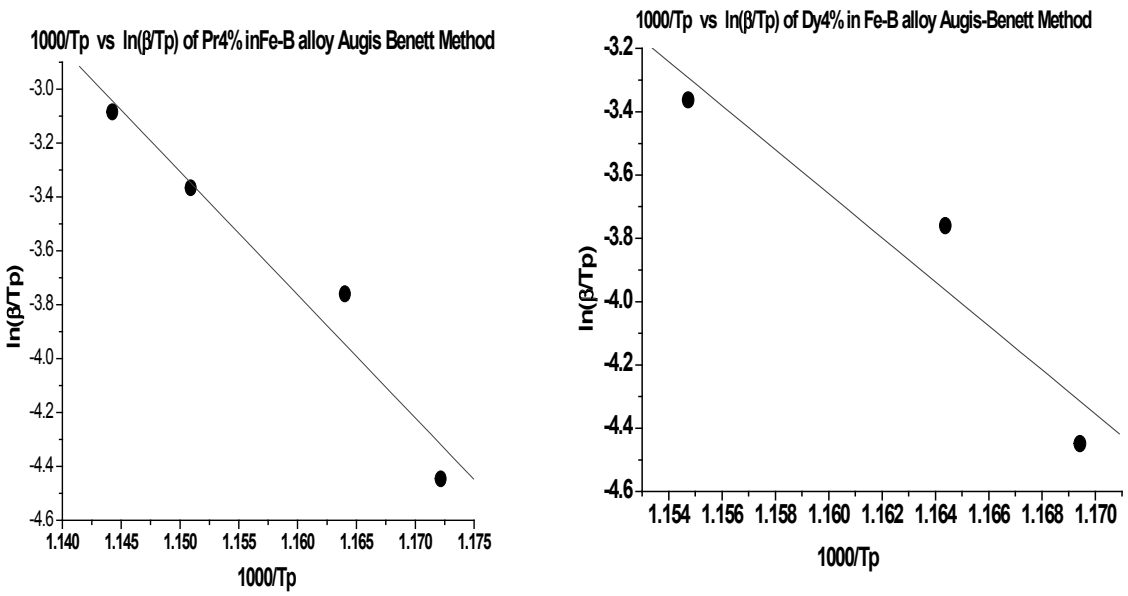

Figure 4: ln (β) vs. (1000/Tp) of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys.

e-ISSN: 2321-6212
p-ISSN: 2347-2278

Table 1: Composition, Activation Energy, Ea (kJouls/mole) and Frequency factor, ko (sec)-1 of amorphous Fe76Pr4B20 and Fe76Dy4B20 alloys.

Composition	Activation Energy, E_a (kJouls/mole)				Frequency factor, k_o $(sec)^{-1}$	
	Kissinger's Method	Augis-Bennet's Method	Matusita-Sakka's Method	Average (kJouls/mole)	Kissinger's Method	Augis-Bennet's Method
$Fe_{76}Pr_4B_{20}$	372.625	409.315	387.09	389.67	4.542×10^{19}	2.37×10^{21}
$Fe_{76}Dy_4B_{20}$	571.3	578.488	586.08	578.59	8.5×10^{31}	2.92×10^{33}

Table 1 also gives the average value of activation energy of the samples. Thus, the average activation energy for primary crystallization of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys using a Kissinger's Method, Augis-Bennet's Method and Matusita-Sakka's Method is determined as 389.67 kJouls/mole and 578.59 kJouls/mole, respectively. The activation energy increases as the atomic number increases. It is observed that the activation energies of amorphous alloys calculated by means of the different theoretical models differ slightly from each other which may be attributed to the different approximations used in the models. The frequency factor k_o of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys using Kissinger method is found to be 4.542×10^{19} $(sec)^{-1}$ and 8.5×10^{31} $(sec)^{-1}$, respectively. Also, the frequency factor k_o of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys using Augis-Bennet's method is found to be 2.37×10^{21} $(sec)^{-1}$ and 2.92×10^{33} $(sec)^{-1}$, respectively.

Avrami [6] expresses that x is the volume fraction transformed after time t as:

$$x=1 - \exp(-kt^n) \quad (4)$$

Where n is called "the Avrami 'n' or a dimensionless quantity called the kinetics exponent".

The kinetics exponent n is described by the equation

$$n=(dx/dt)_p \, RT_p^2 \, (0.37\beta E_a)^{-1} \quad (5)$$

Values of Avrami exponent, *n* and the reaction rate constants *k* can be determined by least square fits of the experimental data. The Avrami kinetics exponent n was calculated from the above equation developed by Gao and Wang [7]. The crystallization rates, (dx/dt) versus temperature (T) of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys are presented in **Figure 5**. The maximum crystallization $(dx/dt)_p$ for each heating rate gives n, according to the equation $n=(dx/dt)_p \, RT_p^2 \, (0.37\beta E_a)^{-1}$. Thus, mean values of the kinetics exponent, <n> of $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys are included in **Table 2**. Form **Table 2**, the Avrami exponent (or) mean values of the kinetics exponent, <n> of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys is found to be 1.67 and 0.831, respectively. The Avrami exponent decreases as the atomic number increases.

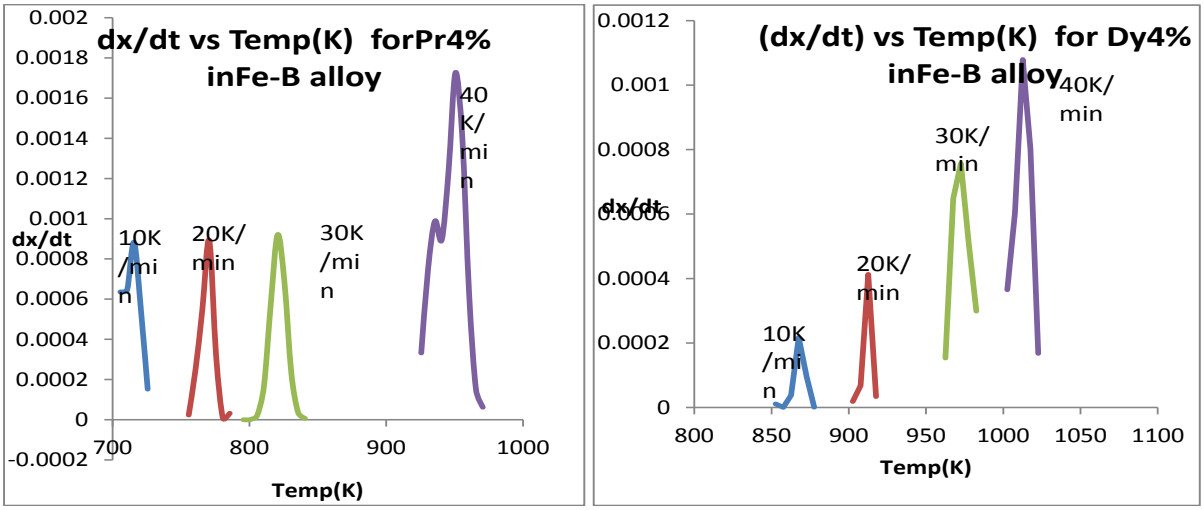

Figure 5. Crystallization rate, dx/dt, vs. temperature, T at different heating rates for $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys.

Table 2. Avrami (or) kinetics exponent (<n>) values calculated from (dx/dt) vs Temp(K) curves.

Composition	10 K/min	20 K/min	30 K/min	40 K/min	<n>
$Fe_{76}Pr_4B_{20}$	2.59	1.52	1.16	1.42	1.67≈2
$Fe_{76}Dy_4B_{20}$	0.6314	0.6644	0.92	1.11	0.831≈1

CONCLUSIONS

The average activation energy (E_a) for primary crystallization of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys using the a Kissinger's Method, Augis-Bennet's Method and Matusita-Sakka's Method is found to be 389.67 kJouls/mole and 578.59 kJouls/mole, respectively. The activation energy increases as the atomic number increases. The frequency factor (k_o) of amorphous

e-ISSN: 2321-6212
p-ISSN: 2347-2278

$Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys using Kissinger method is found to be 4.542 × 10^{19} $(sec)^{-1}$ and 8.5 × 10^{31} $(sec)^{-1}$, respectively. Also, the frequency factor(k_o) of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys using Augis-Bennet's method is found to be 2.37 × 10^{21} $(sec)^{-1}$ and 2.92 × 10^{33} $(sec)^{-1}$, respectively. The Avrami exponent of the kinetics exponent, <n> of amorphous $Fe_{76}Pr_4B_{20}$ and $Fe_{76}Dy_4B_{20}$ alloys is found to be 1.67 and 0.831, respectively. The Avrami exponent decreases as the atomic number increases.

ACKNOWLEDGEMENTS

The authors B. Bhanu Prasad and N. Rajya Lakshmi acknowledge the encouragement given by the management, the Principal, HOD of Sciences & Humanities and the staff of M.V.S.R. Engineering College, Nadergul, Hyderabad.

REFERENCES

1. Araújo EB and Idalgo E. Non-isothermal studies on crystallization kinetics of tellurite 20Li20-80Te02 glass. J Therm Analy Calorimetry 2009;95:37-42.
2. Araújo EB, et al. Crystallization kinetics and thermal properties of 20Li(2)0-80TeO(2) glass. J Mater Res Bull 2009;44:1596.
3. Kissinger HE. Reaction Kinetics in Differential Thermal Analysis. Anal Chem 1957;29:1702.
4. Matusita K and Sakka S. Kinetic Study on Non-Isothermal Crystallization of Glass by Thermal Anal. Bull Inst Chem Res 1981;59:159.
5. Augis AJ and Bennett JE. Calculation of the Avrami parameters for heterogeneous solid state reactions using a modification of the Kissinger method. J Thermal Analy Calorimetry 1978;13:283.
6. *Avrami M.* Kinetics of Phase Change. II Transformation-Time Relations for Random Distribution of Nuclei. *J Chem Phys 1940;8:212.*
7. Gao YQ and Wang W. On the activation energy of crystallization in metallic glasses. J Non-Cryst Solids 1986;81:129.