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Kinetics Studies of Cobalt Based Metallic Glass at High Heating Rates

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Abstract: **Onset temperature of crystallization, Tx and peak temperature of crystallization, Tp, were determined by Differential Scanning Calorimetric (DSC) measurements for cobalt based metallic glass 2714A($C0_{65}Si_{15}B_{14}Fe_4Ni_2$). The heating rates (β) employed are in the range $2 \leq \beta \leq 100$ K/min. Activation energy for peak crystallization (Ec) are determined using well known methods, Kissinger, Ozawa, Bosewell and Auguis and Bennett. The activation energy of crystallization Ec, is found to be 460.46 kJ/mol (Kissinger method) in the range $2 \leq \beta \leq 100$ K/min.**

Index Terms: **Metallic glass, Differential Scanning Calorimetry (DSC), Crystallization kinetics, Fragility. Activation Energy.**

I. INTRODUCTION

Cobalt based 2714A ($Co_{65}Si_{15}B_{14}Fe_4Ni_2$) amorphous alloys have increased soft magnetic properties when compared with the silicon steel materials (McHenry, M., et al.,1999; Varga, L.,2000). It is also evident from the literature the magnetic properties of the Cobalt based materials change when they are subjected to the thermal runs. Therefore, the study of crystallization kinetics in these materials paves the way to improve the magnetic properties for technological applications (Lim S., et al., 1994; Saitio A.,1994). The change and the control of number of crystalline phases are very important in the thermal history in these materials for industrial applications. The aim of the present research is to understand the variation of activation energy of crystallization with the effect of low heating rates ($2 \leq \beta \leq 10$) and high heating rates ($20 \leq \beta \leq 100$). Four methods are utilized to determine the activation energy of crystallization (E_c) and compared with the results of previously published paper (Rao T., et al.,2018).

II. EXPERIMENTAL METHODS

Specimens of amorphous 2714A ($Co_{65}Si_{15}B_{14}Fe_4Ni_2$) ribbons were procured from Metglas, USA. DSC measurements were performed for the as-quenched samples using Mettler Toledo instrument (Temperature precision: ±0.02 °C, energy sensitivity: better than 0.1 μW). Non-isothermal DSC curves were obtained with selected heating rates 20,40,60,80 and 100 $Kmin^{-1}$ from room temperature to 600 °C in air. The DSC thermograms are given in the figure1.

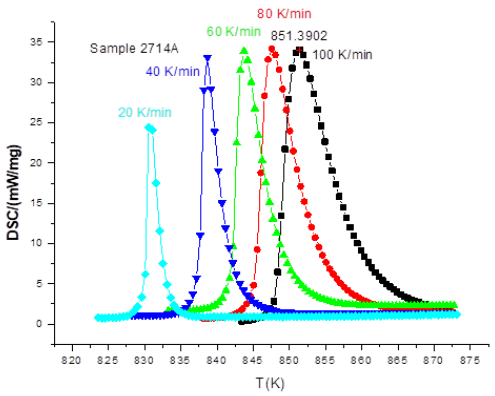

Fig. 1. DSC thermograms of 2714A

The DSC thermograms of 2714A ($Co_{65}Si_{15}B_{14}Fe_4Ni_2$) amorphous alloy at different heating rates have a single exothermic peak in the temperature scanned, and an extended supercooled liquid region before the onset of the crystallization. The onset and peak temperatures (T_x and T_p) for crystallization, are given in the Table 1. 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. Four different independent approaches are used to calculate the activation energy for crystallization.

Table 1. Onset and peak temperatures of crystallization at different heating rates (β)

Heating rate (β) K/min	20	40	60	80	100
T_x (K)	827.00	834.15	838.05	842.07	845.00
T_p(K)	830.79	838.68	843.73	847.56	851.39

A. Kissinger method

Using Kissinger's Equation (Kissinger H.,1957)

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

Where β is the heating rate and R the universal gas constant, the value of E_c can be obtained from the heating rate dependence of the peak temperature of crystallization. Figure 2 shows $\ln(\beta/T_p^2)$ vs $1000/T_p$ relationship. The value of E_c for crystallization is 460.46 kJ/mol.

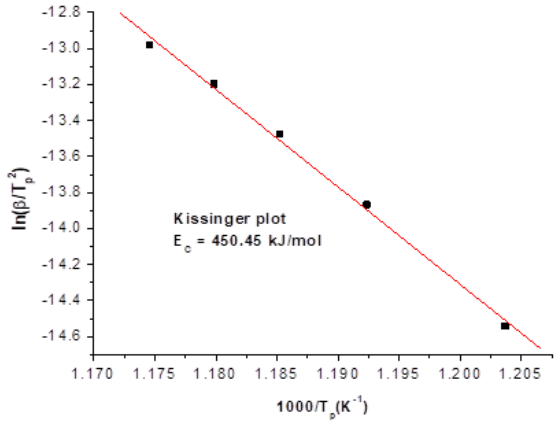

Fig. 2. ln (β/T_p^2) versus $1000/T_P$

B. Ozawa method

According to Ozawa (Ozawa T., 1965), the change of ln ($1/T_p^2$) with β is negligibly small compared to the change of ln(β) and therefore, the Kissinger's equation can be written as

$$\ln\beta = -1.0516\ E_c/RT_p + const \quad (2)$$

Plotting lnβ vs $1000/T_p$ (Figure.3), E_c is calculated and the value is 441.68 kJ/mol.

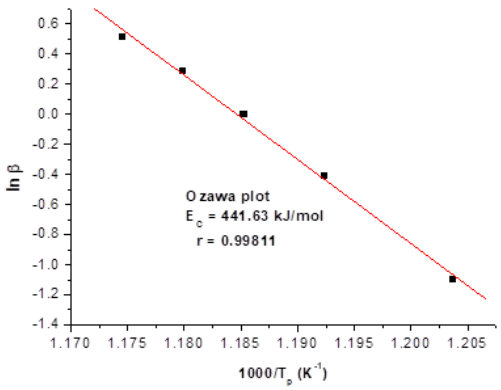

Fig. 3. ln β versus $1000/T_p$

C. Bosewell method

In order to determine the activation energy, Bosewell (Bosewell P.,1980) uses the following equation

$$\ln(\beta/T_p) = -E_c/RT_p + const \quad (3)$$

The slopes of the graph (Figure 4.) give the activation energy 467.46 kJ/mol.

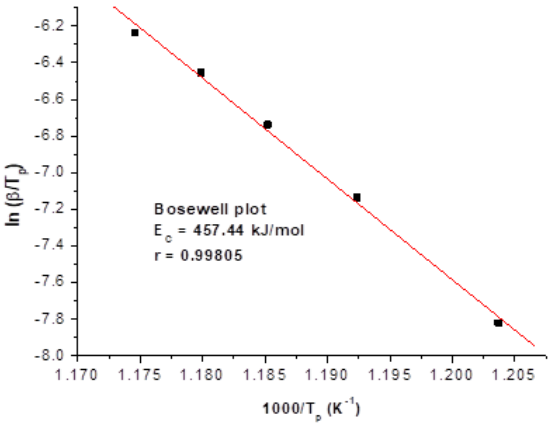

Fig. 4. Plot of ln(β/ T_p) versus 1000 / T_p

D. Augis and Bennett method

The equation given by Augis and Bennett (Augis, J.,et al.,1978)

$$\ln(\beta/(T_p - T_0)) = -E_c/RT_p + \ln A \quad (4)$$

Where T_p and T_o are the peak and the onset crystallization temperature respectively. Figure.5 shows the plot $\ln(\beta/(T_p\text{-}T_o))$ vs $1000/T_p$ and gives the E_c = 317.59 kJ/mol. The value is not consistent with the previous methods adopted, and may be due to the T_o value which is very difficult to ascertain from the thermogram.

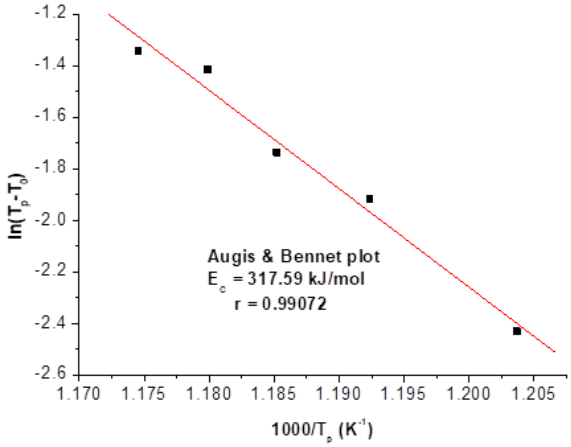

Fig. 5. Plot of ln [β/(T_g - T_0) versus 1000

CONCLUSION

The crystallization behavior of amorphous 2714A ($Co_{65}Si_{15}B_{14}Fe_4Ni_2$) ribbons was examined by DSC at high heating rates 20, 40, 60, 80 and 100 Kmin-1 from room temperature to 600 °C in air. The activation energy, Ec for the

crystallization is 460.46 kJ/mol (Kissinger method) at the higher heating rates (20-100 K/min) and 622.65 kJ/mol (Kissinger method) at lower heating rate (2-10 K/min).The activation energy Ec is composed of activation energy for nucleation E_N and activation energy for growth E_G . So, the probable reason for the decrease in the E_c value with heating rate is due to the reduced activation energies for growth and nucleation of the crystalline phase. The similar effect of heating rate on the activation energy E_c is also observed in amorphous Ge2Sb2Te5 thin film (Yunjung C., et al.,2009).

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