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INFLUENCE OF ANNEALING TEMPERATURE ON THE CRYSTALLIZATION KINETICS OF $Fe_{82}Si_8B_{10}$ AMORPHOUS RIBBON

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ABSTRACT

Amorphous soft magnetic materials have significant potential applications in specialist power transformers and in inductive devices. With the composition of $Fe_{82}Si_8B_{10,}$ 82% of the transition metals Fe and about 18% of metalloid or glass-former elements like B and Si are strongly magnetic at room temperature and offer dynamic opportunities for engineering applications. The crystallization kinetics has been studied by differential thermal analysis (DTA). The sample was annealed in a controlled way in the temperature range of 350-450°C at constant annealing time one hour. The kinetics of primary crystallization $\alpha - Fe(Si)$ phase and secondary crystallization Fe_2B phase was studied as affected due totemperature. The sample annealed at 350°C temperature is almost unchanged which is still lower than that of primary crystallization temperature but the same condition when sample annealed at 450°C completely shows that the primary crystallization $\alpha - Fe(Si)$ phase has vanished and crystallization event took place to a good extent.

Keywords: *Activation energy; Amorphous Ribbon; Annealing; Crystallization kinetics; DTA.*

1. INTRODUCTION

In recent decades, the effect of composition on the stability and magnetic properties of amorphous ribbon is of enormous interest both for application and magnetic devices. Research may originate from the improvements performed on the change of composition affects at ring ordering through nucleation and growth of crystallites. Recently, Fe-, Co- and Ni- based metallic glasses have received a great deal of attention owing to an attractive combination of electric and magnetic properties. Fe-, Co- and Ni- with metalloid such as B, Si, or C produce amorphous alloys with excellent soft magnetic properties (Luborsky, 1980; Petrakovski, 1981; Babilas *et al.,* 2011). The class of alloys containing about 80% of the transition metals, Fe, Co, and Ni, and about 20% of metalloid or glass-former elements such as B, C, P, and Si, are strongly magnetic at room temperature and offer important opportunities for engineering applications. The magnetic and structural stability have been evaluated at higher temperatures and are found to be adequate for most foreseeable applications (Graham *et al*., 1978). In magnetic glass, the macroscopic quantities which are the average kinetics of properties in the atomic scale are perturbed by structural disorder (Sikder *et al.,* 1999). Since the formation of an amorphous ribbon depends on the absence on long range order, changes of composition are expected to affectthe important crystallization parameters like glass transition (T_g) and crystallization (T_x) temperature controlled by thermal treatments like DTA measurements. First DTA peak T_g peak corresponds to the precipitation of an ordered bcc $\alpha - Fe(Si)$ solid solution embedded in an amorphous phase and second peak T_x corresponds to boride phase Fe_2B for effect on the apparent activation energy of crystallization process (Asgar *et al.,* 1999; Rao *et al.,* 2016; Tawhid *et al.,* 2018). The resultant amorphous solid generally has higher energy than the corresponding crystalline phase. The energy barriers to nucleation and growth of crystalline phase are so high compared with the thermal energy that metastable state can be studied for annealing time which is very long compared with period during which experiments are done. Yu *et al.* (2019) found the activation energy of crystallization, E =4.16 eV/K that indicates high thermal stability of the amorphous phase of the alloy. Till now researchers have not yet been able to formulate a stable set of rules for amorphous ribbons about a single property. The aim of this work is to study the crystallization kinetics of amorphous $Fe_{82}B_{10}Si_8$ ribbon on as cast and annealed conditions. Research in the development and application of amorphous ribbon could be profitable, especially at its new phase is only the effect of composition on the stability of amorphous state which is studied by keeping the heating rate constant with annealed affect.

2. MATERIAL AND METHODS

Amorphous ribbons with the nominal composition $Fe_{82}Si_8B_{10}$ were prepared by melt-spinning machine of the ribbon form in the amorphous state rapid solidification technique at the center of Materials Science, National University of Hanoi, Vietnam. With high purity of the constituent elements Fe (99.9%), Si (99.9%) and B (99.9%) were obtained from Johnson Matthey (Alfa Aesar, UK). Fe-Si-B ribbon is of special interest of magnetic elements (Fe) having different structure in their crystallite state tailoring the crystalline phase change of annealing effect as well as activation energy. Crystallization phase analysis was carried outby STA7200 (Thermal Analysis System, HITACHI, JAPAN) in the Solid-State Physics Laboratory of the Khulna University

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of Engineering & Technology, Khulna, Bangladesh. The activation energy for crystallization of glass transition $\alpha - Fe(Si)$ and secondary crystallization of Fe_2B phases has been calculated using Kissinger's equation (Kissinger *et al.,* 1957; Blaine *et al.,* 2012):

$$E = -kT_p ln\left(\frac{\beta}{T_p{}^2}\right)$$

Where β is the heating rate, T_p is the crystallization peak temperature, E is the activation energy and k is the Boltzmann's constant = 8.617×10^{-5} eV/K.

3. RESULTS AND DISCUSSION

3.1 DTA and Annealing

DTA observation of as cast sample from Figure 1 reveals that there are four exothermic peaks. The first peak is theprimary crystallization (T_{p1}) $[\alpha - Fe(Si)]$ peak and the second peak (T_{p2}) is the Secondary crystallization (Fe_2B) peak. The soft magnetic properties correspond to the primary crystallization phase and secondary crystallization causes magnetic hardening of the amorphous ribbon. Since the structure of the beneficial ferromagnetic amorphous phase is comprised of Fe-Si, as a result the study of primary and secondary crystallization temperature is important for the amorphous alloys (Mondal *et al.,* 2012). For this reason, another 3rd and 4th crystallization phase peaks which are interfacial B-rich phase like Fe_3B, higher order etc. corresponds to crystallization being suppressed by a barrier to redistribution on a long-range scale is not consider. From DTA scan of the primary crystallization peak temperature for as cast sample is incrementing in between 474ºC to 498ºC with the increment of heating rate from 10ºC/min to 60ºC/min and for secondary crystallization this incrimination is occurring in between the temperature 539ºC to 564ºC with theincrement of heating rate shown in Figure 1. The negligible peak shifting indicates that the sample is thermally active. It is also to be noted that primary glass transition temperature corresponding to structural relaxation i.e., release of stress initially formed by the rapid solidification technique and secondary crystallization peak is corresponding to re-crystallization that is reordering of the atom to for another crystalline phase. The calculative data for determining the activation energy has been presented in the Table 1 and with the Kissinger plot the activation energy has determined shown in Figure 4. The activation for Primary crystallization phase (α-Fe) is 3.76eV and for secondary crystallization peak is 3.69eV.

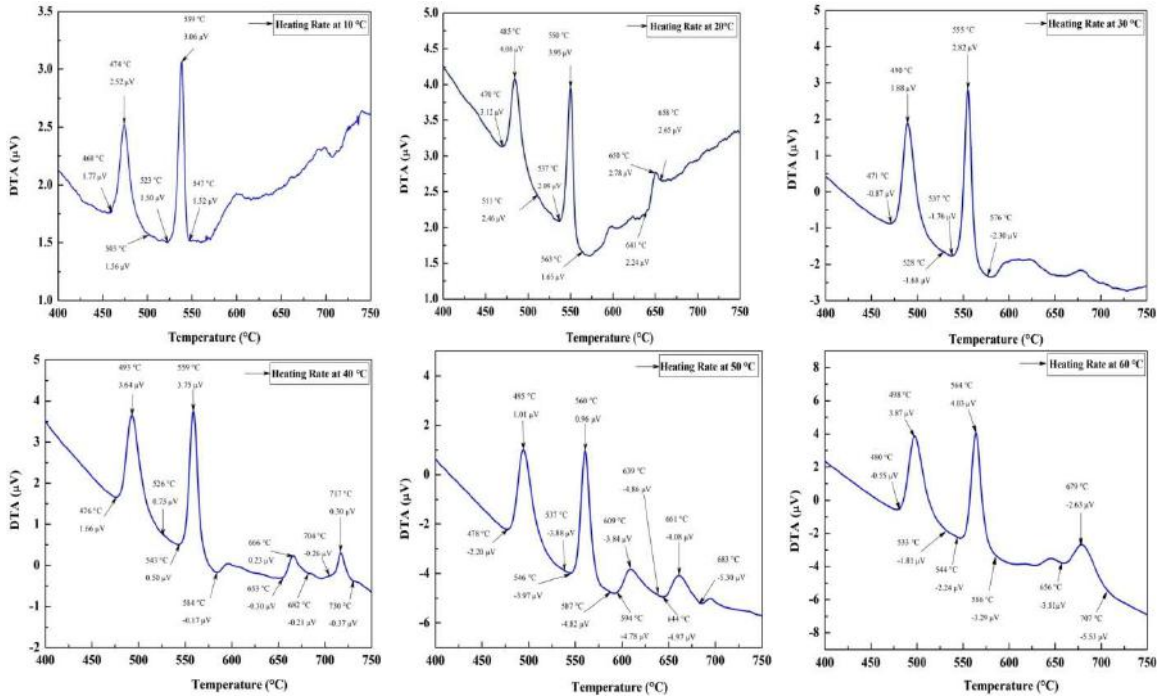

Figure 1: DTA trace of as-cast amorphous ribbon $Fe_{82}Si_8B_{10}$ at heating rate ranges 10°C/min to 60°C/min.

The primary crystallization temperature represents the upper limit of use for an amorphous material and the secondary crystallization temperature represents the upper limitof use for nanocrystalline materials (McHenry *et al.,* 1999). In present, the sample was annealed at two steps (350ºC and 450ºC). To check the crystallization behavior of the sample, it was annealed at 350ºC and DTA traces were carried out and shown in Figure 2. For

DTA scan of 350ºC annealed sample the peak is shifting towards the higher value though the sample holds its amorphousity. The negligible peak shifting indicates the sample is thermally active and it requires more heat energy for the formation of crystalline phases with cumulative heating rate. The peak is shifting for primary phase is in the range between 456°C to 526°C and for secondary phase this is in between 551°C to 591°C which is evident from Figure 2. The calculative data for determining activation energy of both the phases presented in Table 2 and with the Kissinger plot the activation energy for primary crystallization phase is 3.58eV and for secondary crystallization phase this is 3.68 eV was determined and shown in Figure 5. Drop in activation energy is interpreted as at this temperature annealing removes the stress though the sample is still amorphous.

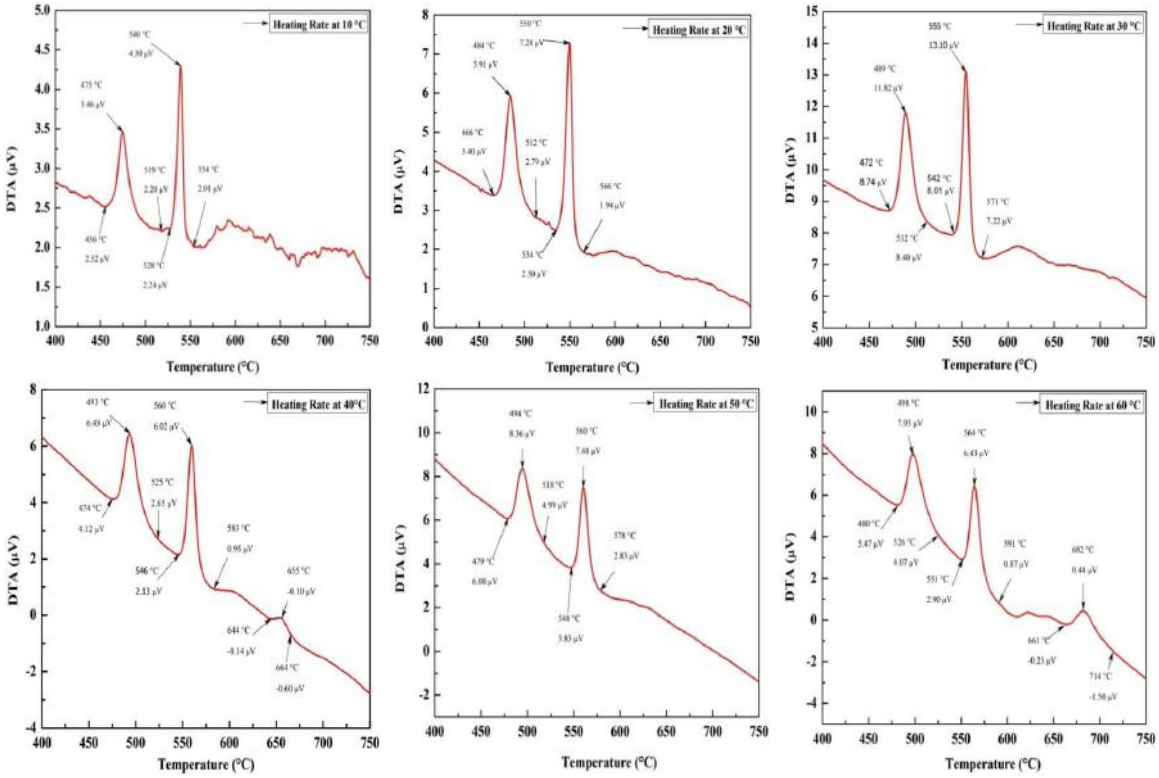

Figure 2: Effects on DTA trace of annealing temperature 350°C on the amorphous ribbon $Fe_{82}Si_8B_{10}$ at 10°C/min to 60°C/min at 1 hour.

Table 1: Effect of heating rate on 1st and 2nd crystallization of the as-cast amorphous ribbon with composition $Fe_{82}Si_8B_{10}$ state's calculative data for activation energy

Heating rate β°C/min	Heating rate β°K/min	1st Peak T_{p_1}	$1/T_{p_1}\times10^3$	$\ln\left(\frac{\beta}{T_{p_1}^2}\right)$	2nd Peak T_{p_2}	$1/T_{p_2}\times 10^3$	$\ln\left(\frac{\beta}{T_{p_2}^2}\right)$
10	13.41	747.16	1.33	-10.6366	812.16	1.23	-10.8034
20	26.89	758.16	1.31	-9.97003	823.16	1.21	-10.1345
30	40.24	763.16	1.31	-9.58007	828.16	1.20	-9.74355
40	53.66	766.16	1.30	-9.30011	832.16	1.20	-9.46538
60	80.46	771.16	1.29	-8.90803	837.16	1.19	-9.07227

As at 350ºC annealing the sample was still amorphous, an increment of annealing temperature to 450ºC was experimented through DTA traces. DTA scan was performed to see the annealing effect on its thermal kinetics. At 450ºC annealed sample DTA traces shows that the primary crystallization peak was vanished, and sample formed crystalline phases. The primary crystallization peak disappear before the crystallization onset temperature and this phenomenon is interpreted as this annealing temperature removes the internal stress which was initially formed by the rapid solidification process also accelerate the nucleation growth rate as a result the onset temperature reduces. The DTA-peak shift can be either positive or negative (as observed in our experiments) depending on the extent of growth of nucleation taking place during the pre-DTA heat treatment or annealing (Gupta *et al.*, 2002). The secondary crystallization peak temperature obtained from Figure 3 is between 540ºC to 563ºC with the heating rate of 10ºC/min to 60ºC/min. With Kissinger plot and From Table 3 the activation energy of secondary crystallization peak was determined as 3.31eV and shown in Figure 6.

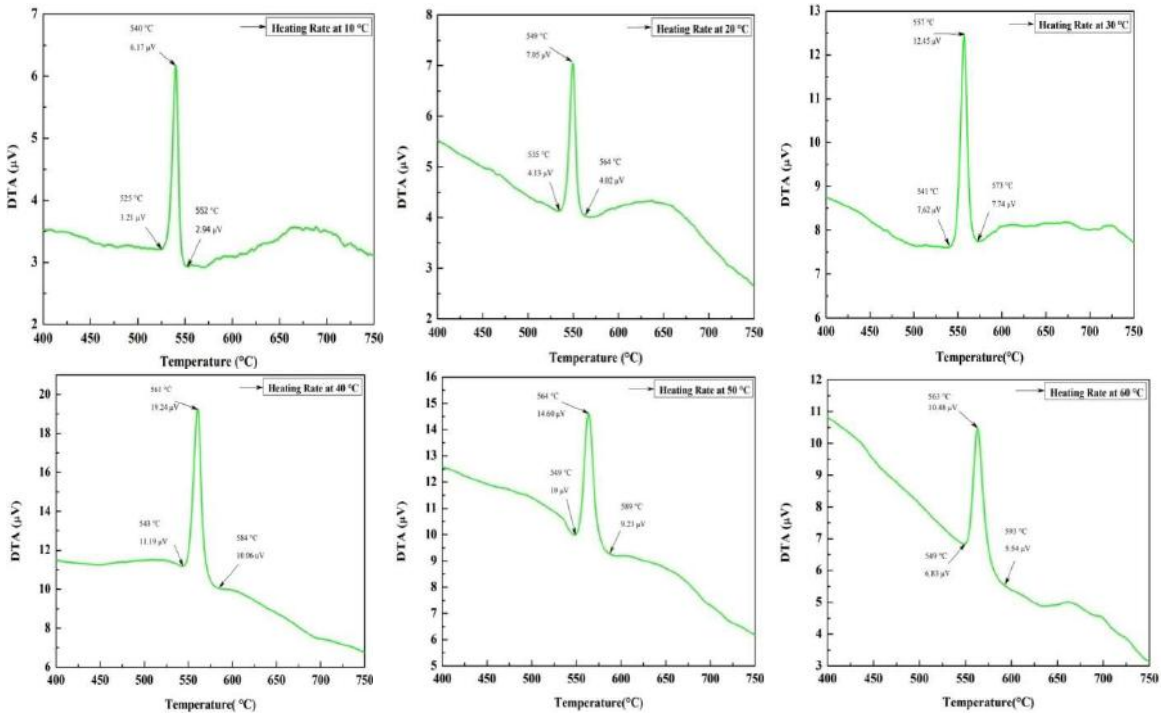

Figure 3: Effects on DTA trace of annealing temperature 450°C on the amorphous ribbon $Fe_{82}Si_8B_{10}$ at 10°C/min to 60°C/min at 1 hour

Table 2: Annealing effect of heating rate on 1st and 2nd crystallization of the amorphous ribbon with composition $Fe_{82}Si_8B_{10}$ state's annealed at 350°C for constant annealing time one hour

Heating rate β°C/min	Heating rate β°K/min	1st Peak T_{p_1}	$1/T_{p_1} \times 10^3$	$\ln\left(\frac{\beta}{T_{p_1}^{\,2}}\right)$	2nd Peak T_{p_2}	$1/T_{p_2} \times 10^3$	$\ln\left(\frac{\beta}{T_{p_2}^{\,2}}\right)$
10	13.41	748.16	1.33	-10.64	813.16	1.23	-10.80
20	26.89	757.16	1.32	-9.97	823.16	1.21	-10.13
30	40.24	762.16	1.31	-9.58	828.16	1.20	-9.74
40	53.66	766.16	1.30	-9.30	833.16	1.20	-9.46
60	80.46	771.16	1.29	-8.90	837.16	1.19	-9.07

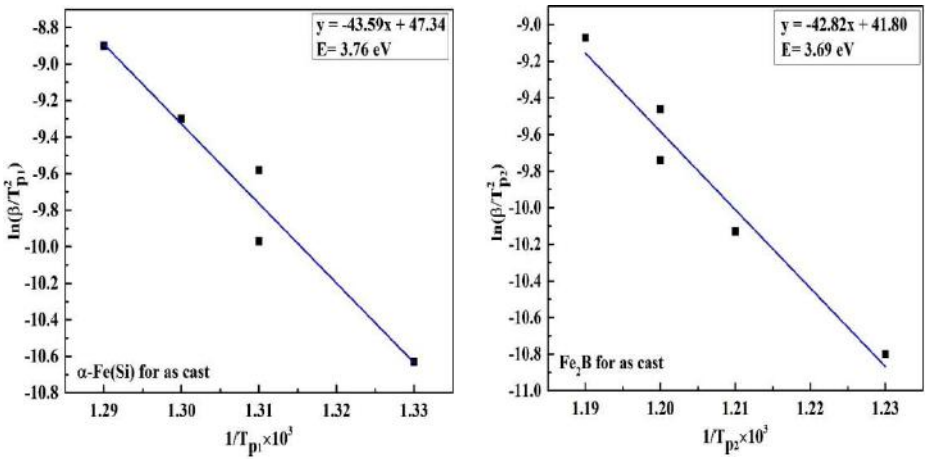

Figure 4: Kissinger's plot to determine the activation of (a) $\alpha - Fe(Si)$ phase and (b) Fe_2B phase for $Fe_{82}Si_8B_{10}$ for as-cast

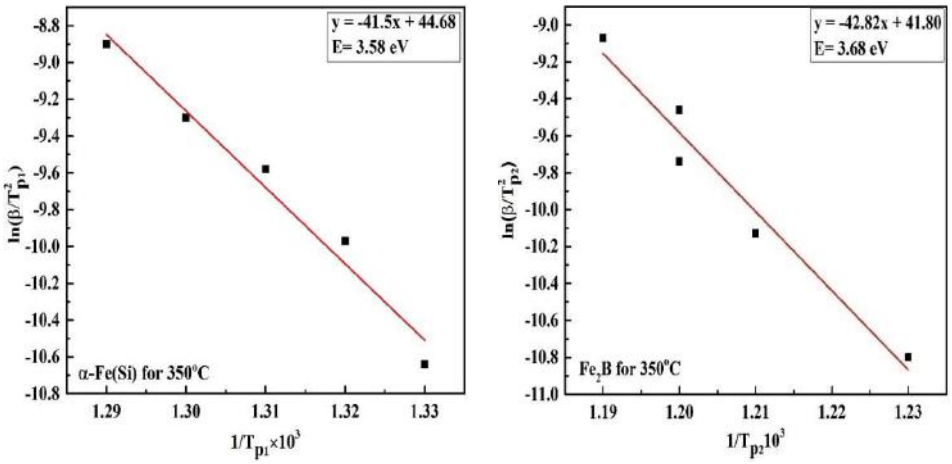

Figure 5: Kissinger's plot to determine the activation of (a) $\alpha - Fe(Si)$ phase and (b) Fe_2B phase for $Fe_{82}Si_8B_{10}$ annealed at 350°C for constant annealing time one hour.

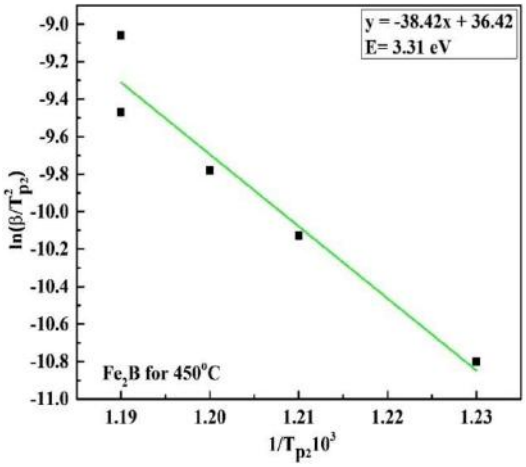

Figure 6: Kissinger's plot to determine the activation of Fe_2B phase for $Fe_{82}Si_8B_{10}$ annealed at 450°C for constant annealing time one hour

Table 3: Annealing effect of heating rate on 1st and 2nd crystallization of the amorphous ribbon with composition $Fe_{82}Si_8B_{10}$ state's annealed at 450°C for constant annealing time one hour

Heating rate β°C/min	Heating rate β°K/min	1st Peak T_{p_1}	$1/T_{p_1}\times10^3$	$\ln\left(\frac{\beta}{T_{p_1}^{\ 2}}\right)$	2nd Peak T_{p_2}	$1/T_{p_2}\times 10^3$	$\ln\left(\frac{\beta}{T_{p_2}^{\ 2}}\right)$
10	13.41	…	…	…	813.16	1.23	-10.80
20	26.89	…	…	…	822.16	1.21	-10.13
30	40.24	…	…	…	830.16	1.20	-9.75
40	53.66	…	…	…	834.16	1.19	-9.47
50	67.07	…	…	…	837.16	1.19	-9.25
60	80.46	…	…	…	836.16	1.19	-9.07

Table 4: The activation energy of $Fe_{82}Si_8B_{10}$ amorphous ribbon before and after annealing

Before annealing		After annealing			
As-cast		350°C		450°C	
α-Fe(Si)	Fe_2B	α-Fe(Si)	Fe_2B	α-Fe(Si)	Fe_2B
3.76	3.69	3.58	3.68	-----	3.31

4. CONCLUSION

DTA manifest two exothermic peaks for as cast $Fe_{82}Si_8B_{10}$ amorphous ribbon which are corresponds to primary crystallization event temperature $\alpha - Fe(Si)$ which indicates stability of amorphous state and magnetic softness.

The softest magnets corresponds to $\alpha - Fe(Si)$ phase to 474°C and magnetic hardening Fe_2B phase to 531°C for this ribbon with heating rate 10°C/min. Activation energy of $\alpha - Fe(Si)$ phase is 3.76eV and Fe_2B phase is 3.69eV. When the sample was annealed at 350ºC it holds its amorphousity though reduction in activation energy was found due to removal of internal stress and the sample said to be magnetically soft. Activation energy of $\alpha - Fe(Si)$ phase is 3.58eV and Fe_2B phase is 3.68eV. The sample annealed at 450ºC displays diffusive phenomenon and primary crystallization peak vanished which indicates that crystallization took place to a good extent. Activation energy of Fe_2B phase is 3.31eV. Heat treatment should be limited by 450ºC to obtain optimum soft magnetic behavior which corresponds well with the value obtained DTA and in significant influence of annealing effect on the crystallization phase and the activation energy.

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