The International Journal of Engineering and Science (IJES)
|| Volume || 9 || Issue || 08 || Series I || Pages || PP 08-14 || 2020 ||
ISSN (e): 2319-1813 ISSN (p): 20-24-1805

Crystallization Behavior and Effect of Annealed Temperature on Magnetic Properties of Nano Crystalline $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$Alloy

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----------*ABSTRACT*----------
The kinetics of crystallization of different crystalline phases of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ has been studied by differential thermal analysis (DTA). DTA diagrams of amorphous ribbons were taken in nitrogen atmosphere with continuous heating rate of 10 -50°C/min in step of 10°C. The primary exothermic peaks temperature for α-Fe (Si) was found 543^0C and the secondary exothermic peak temperature for Fe_2B phase was found 689^0C at the same heating rate 20^0C/min. Thermal analysis experiment and from the obtained data the activation energy is found 2.18eV for primary crystallization product,α-Fe(si) phase and for secondary crystallization Fe_2B phase was found 3.62eV.The ribbon in the form nanocrystalline state was evaluated by XRD. The alloy has been annealed in a controlled way in the temperature range of 450^0 C to 800^0C for 30 minutes. By XRD experiment crystallization onset temperature for α-Fe(si) phase was found around 650^0C.The lattice parameter, the Si content in bcc nanograins and the grain size of bcc grains can easily be calculated from the fundamental peaks of (110) reflection. In the optimized annealing condition the grain size has been obtained in the range 14-20 nm.The lattice parameter and Si at % shows an inverse relationship indicating that silicon diffuses out of α-Fe(si) grain for which the size α-Fe(si) lattice is regained. Thecurie temperature was found 692^OK.

KEYWORDS: *DTA, Activation energy, XRD, Lattice Parameter, Grain size,VSM and Curie temperature.*

Date of Submission: 30-09-2020 Date of Acceptance: 13-10-2020

I. INTRODUCTION

The enhancement of soft magnetic properties require reduction of crystalline grain sizes to a much smaller length scale that can overcome the anisotropy effects and result in an improved soft magnetic behavior. In this structure the particle diameter is less than 20 nm and the crystallization from the amorphous phase produces the fine structure of a bcc iron based solid solution. Amorphous alloys provide an extremely convenient-precursor material for preparation of nan crystals through the crystallization process controlled by thermal treatments [1, 2]. At Hitachi metals Ltd developed the first nan crystalline ultra soft magnetic alloy called FINEMET having composition $Fe_{73.5}$ Nb_3 Cu_1 $Si_{13.5}$ B_9 from the Fe-Si-B amorphous alloys to which addition of Cu and Nb were added [3]. The Cu and Nb additives play a key role in the formation of the nanocrystalline state Cu by multiplying the nucleation centres and Nb by inhibition the grain growth [4]. The annealing parameters (time, temperature and atmosphere) must be controlled and the nanocrystalline state can be obtained after conventional annealing under vacuum or atmosphere for typically 1h at $>550^0$C .The FINEMET consists of a two phase microstructure in its optimally annealed condition. The microstructure is made up of a ferromagnetic bcc α-Fe (Si) phase and /or Do_3 type of ordered Fe (Si) phase with grain size of 10-15nm embedded in this residual ferromagnetic amorphous matrix of about 1-2nm thickness.These represent a new family of excellent soft magnetic core materials and have stimulated an enormous research activity due to their potential applications[5, 6]. Effect of annealing temperature was studied in the influence of Cu/Nb content and annealing condition on the microstructure and the magnetic properties of FINEMET alloys [7]. Grain size, phase composition and transition temperature were observed to depend on the Cu/Nb content. This paper focuses on the experimental investigation of crystallization behaviour, nanocrystalline structure formation and magnetic properties of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloys in the amorphous and annealed states.

II. MATERIALS AND METHODS

The purity and origin of the amorphous ribbon were composed of the elements Fe (99.9%), Nb(99.9%), Cu (99.9%), Si (99.9%) and B (99.9%) as obtained from Johnson Mathey (Alfa Aesar Inc.).Before melting, the furnace chamber was evacuated (10^{-4}torr), and flashed with Ar gas. The process was repeated

several times to get rid of residual air and finally the furnace chamber were kept in an Ar atmosphere.Amorphous ribbon with the nominal composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ was prepared in an arc furnace on a water-cooled copper hearth under an atmosphere of pure Ar. The mother alloys, which are formed in the form of buttons in a furnace by sudden cooling and then cut into small pieces and is introduced in the quartz tube.

Melt spinning technique is a widely used production method for rapidly solidifying materials as well as preparing amorphous metallic ribbon [8]. In order to prepare amorphous of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloys, the melt spinning facilities was used at the Centre for Materials Science, National University of Hanoi, Vietnam. The resulting ribbon samples had thickness of about 20-25 μm and width ~6 mm. The Factors that is used to Control the thickness of ribbons when angular velocity ω = 2000rev/min and Surface velocity V = 20 m/s to 30 m/s. Gap between nozzle and rotating copper drum (h) = 200 to 30 μm. Oscillations of the rotating copper drum both static and dynamic has maximum displacement 1.5 to 5 μm. Pressure = 0.2 to 3.0 bar at argon atmosphere. Temperature of molten metals $T_m \approx 1500^0$C; the temperature did not exceed 1800^0 C otherwise quartz tube would be melted. A steady flow of the molten metals on the surface of the rotating drum needs to be ensured. Theactivation energy was calculatedFrom Kissinger's equation $E= -kT_p \boldsymbol{ln}\frac{\boldsymbol{\beta}}{\boldsymbol{T_x^2}}$, here E is the activation energy,β is heating rate and the respective crystallization temperature ($\boldsymbol{T_x^2}$). From the obtained data of XRD the lattice parameter has been calculated using equation, $2d\sin\theta = \lambda$ and, $a_0 = d\sqrt{2}$,where $\lambda = 1.54178$ Å for $Cu-K_\alpha$ radiation and a_0 is the determined lattice parameter within an error estimated to be ± 0.0001 Å. Grain size is determined using the following formula, $D_g = \frac{0.9\lambda}{\beta\cos\theta}$, β = FWHM (full width at half maximum) of the peak in radian. $X = \frac{(a_0 - 2.8812)}{0.0022}$ Where X is at. % Si in the nanograins. Temperature dependent magnetization were performed by VSM .

III. RESULT AND DISCUSSION

Differential Thermal Analysis

DTA traces of as-cast nanocrystalline amorphous ribbon $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$alloy taken in nitrogen atmosphere with the heating rates of $10^oC - 50^oC$/minute at the step of 10^oC with continuous heating from room temperature to 800^oC, are presented in figure 1(a) to figure 1(e) respectively. In each of the figure, two exothermic peaks are distinctly observed which corresponds to two different crystallization events at temperature Tx_1 of α-Fe(Si) and Tx_2 of Fe_2B takes place respectively. crystallization (Tx_1) of α-Fe(Si) takes place. Secondary crystallization (Tx_2) of Fe_2B caused magnetic hardening of the nanocrystalline alloy. From Figure 1(f) represents a combination of all DTA traces of amorphous $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ribbons.

It is observed that the crystallization of each phase has occurred over a wide range temperatures and that the peak temperatures shift to higher values with the increase of heating rate. That means, it is requires more heat energy for the formation of crystalline phases with increasing heating rates. From each of the DTA traces, it is obvious that the area under the first crystallization peak is larger than the area covered by the second crystallization peak. In the Table 1 crystallization peak temperatures of two phases ($Tp_1$and Tp_2) and crystallization onset temperatures of two phases ($Tx_1$and Tx_2) are given for different heating rates.

It has been observed that the crystallization temperature range of first phase occurred within 19^oC to 30.1^oC but this range for the second crystallization phase is 18^oC to 26^oC. So it is notable that the crystallization temperature range for first peak is always larger than the second peak.

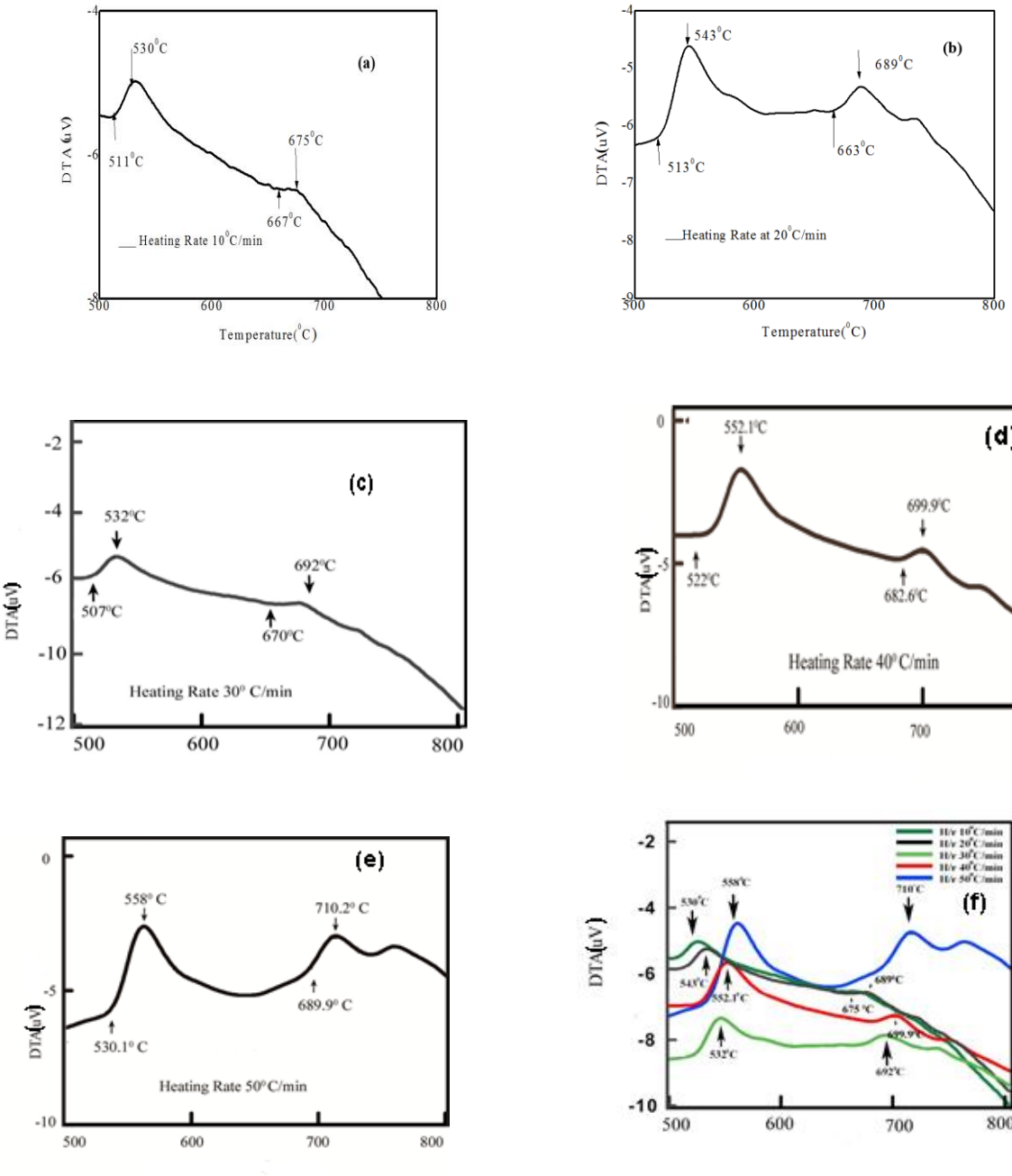

Figure 1. DTA trace of as cast amorphous ribbon $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ at the heating rate of (a) 10°C /min (b) 20°C /min(c) 30°C /min(d) 40°C /min(e) 50°C /min

Figure 1(f) Effects of heating rate on DTA traces of nanocrystalline amorphous ribbon with composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ at the heating rate of 10°C to 50°C /min

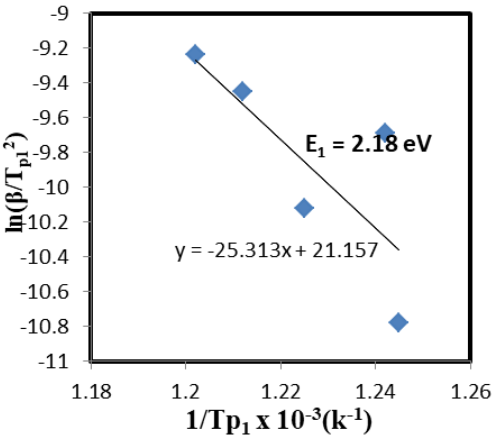

Figure 2(a)

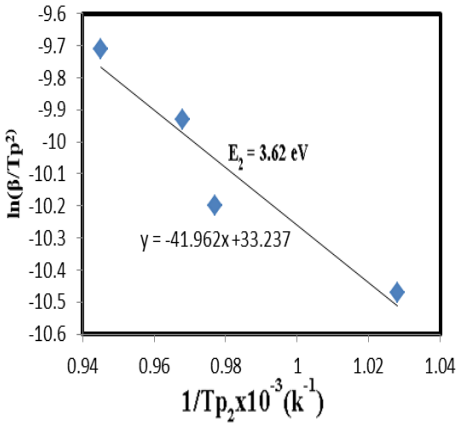

Figure 2(b)

Figure 2. Kissinger's plot to determine the activation energy of α-Fe(Si)) phase for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloy ***(a)*** before annealing ***(b)*** after annealing

It is also observed that the peak temperature shift to higher values and crystallization temperature range increase with the heating rates. From figure 1(f) it is seen that two crystallization phenomena have taken place with in a large temperature gap of around 145°C to 160°C.From table 1. and using Kissinger's plot shown in figure 2(a) and figure 2(b). It shows that first thermal crystallization activation energy of α-Fe (Si) phase E_1 is 2.18 eV and second Fe_2B phase E_2 is 3.62 eV.

Table 1. The values of crystallization onset temperature, peak temperature with respect to heating rate and activation energy of the nanocrystalline amorphous ribbon with composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$

Heating rate β°C/min	Onset temperature, T_{x_1}°C	1st Peak temperature, T_{p_1}°C	Temperature range of 1st state in °C	Activation energy of the peak before annealing (eV)	Activation energy of the peak after annealing (eV)
10	511	530	19	2.18	3.62
20	513	543	30		
30	507	532	25		
40	522	552.1	30.1		
50	530.1	558	27.9		

X-ray diffraction analysis

In the present work, structure of the $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$nanocrystalline ribbon alloys annealed at temperature (Ta) from 450°C to 800°C for annealing time 30 minutes are investigated by the XRD method are presented in figure 3. The figure indices of the reflecting planes are shown in the parenthesis XRD results indicate that no α-Fe(Si) phases are present in the alloys annealed below 600°C for 30 minutes.

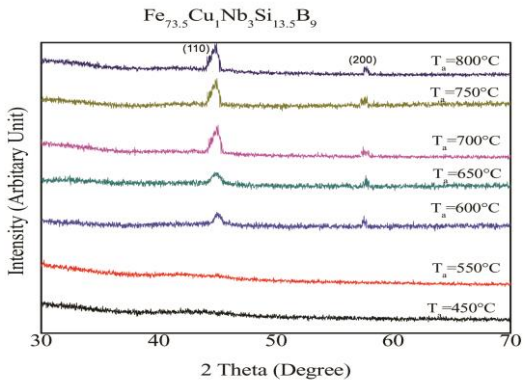

Figure3.XRD spectra of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ alloys of annealed at different temperatures at constant annealing time 30 minutes

When the alloys were annealed at or above 600°C, crystalline phase is developed on the amorphous ribbon. Patterns of Ta = 600°C indicates a clear α-Fe(Si) phase of said composition after heat treatment for 30 minutes. The same pattern observed for all the samples at different annealing temperature indicating the α-Fe(Si) phase. The intensity of the diffracted peak of α-Fe(Si) phase in the alloy is increased with the increase of annealing temperature. For an annealing at higher temperature i.e 600°C, 650°C, 700°C, 750°C and 800°C, α-Fe(Si) phase were found at lower values of 2θ at.% 44.96°, 44.76°, 45.75°, 45.5oand 44.84° respectively with 100% peak intensity on (110) line. All the results of θ, d-values, FWHM from XRD analysis are listed inTable 2.

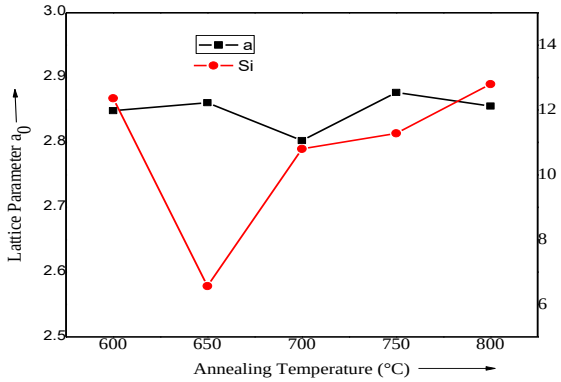

Figure-4

Figure 4. Change of Si (at. %) contentand Lattice Parameter with different annealing temperature for the sample with composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$

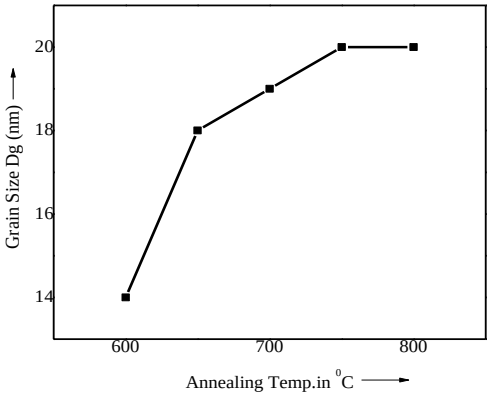

Figure-5

Figure 5. Change of Grain Size with different annealing temperature for the sample with composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$

Figure 4.Shows the variation of lattice parameter and Si-content α-Fe(Si) phase with respect to the annealing temperature of the samples. For the annealing temperature 600°C an increase of lattice parameter and attains the minimum value at 700°C. The lattice parameter of α-Fe(Si) phase is always smaller than that of pure Fe, the value of which is 2.8664Å [9, 10]. The systematic but negligible shift of the peak forwards the larger angles with increasing temperature indicates that lattice parameter of the phase gradually decreases due to the increase of Si-content of the α-Fe(Si) phase. Both the decrease in lattice parameter and increase in intensity of the fundamental peak with increasing annealing temperature suggest that Si-atom diffuse most intensity into the bcc α-Fe with increase of annealing temperature. The diffusion of Si increases in bcc α-Fe with annealing temperature. Percentage of Si is the controlling parameter of structural change for nanocrystalline alloy. Percentage of Si in the α-Fe(Si) phase is the point of saturation i.e. maximum value. For this sample it is about 12.36% and obtained at 600°C. Above or below this critical annealing temperature %Si decreases i.e. lattice parameter increases So, Si-content and lattice parameter is closely related which is expressed in [11].

Table 2. Experimental XRD data of nanocrystalline $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous ribbon at different annealing temperatures

Annealing Temp. in °C	θ (deg.)	d (Å)	FWHM (deg.)	a_0 (Å)	D_g (nm)	Si (at. %)
450	--	--	--	--	--	--
550	--	--	--	--	--	--
600	22.48	2.014	0.6	2.8489	14	12.36
650	22.38	2.0232	0.48	2.8673	18	6.57
700	22.87	1.9819	0.43	2.8028	19	10.80
750	22.25	2.0342	0.40	2.8770	20	11.28
800	22.42	2.0196	0.39	2.8561	20	12.4

Temperature Dependence of specific Magnetization

The variation of saturation magnetization (Ms) as a function of temperature in the range 300 k to 800 k measured with an applied field of 10kOe in the amorphous state for the nanocrystalline amorphous samples with composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$are shown in figure 7. From these curve Tc has been determined as the temperature corresponding to the infixion point where the rate change of magnetization with respect to temperature is maximum shown in figure 7(a), 7(b) .As the temperature approaches to the Tc, magnetization falls more rapidly near to zero as the thermal energy exceeds the magnetic ordering or the exchange energy. The accurate determination of Tc of amorphous material is really difficult due to irreversible components of the structural relaxation like long range internal stress, topological and chemical short range order.

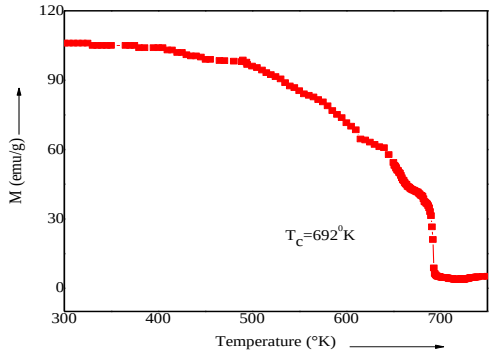

Figure 7 (a) Temperature dependence of specific magnetization of amorphous nanocrystalline ribbons with composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$alloy.

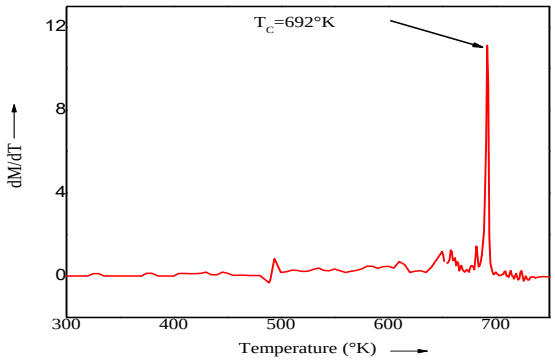

Figure 7(b)$\frac{dM}{dT}$ versus temperature curve of amorphous Nanocrystalline ribbons with composition $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$alloy.

IV. CONCLUSIONS

The crystallization behavior of the sample was investigated by the experiments of DTA and XRD and VSM as a result the following outlined can be concluded:

- DTA experiment was performed for five different rates 10 to 50°C/min in steps of 10°C/min up to a temperature of 800°C. DTA reveals the primary and secondary crystallization onset temperature with the manifestation of two well defined exothermic peaks corresponding to nanocrystallization α-Fe(Si) (Tx_1) and Fe_2B(Tx_2) phases respectively. First crystallization phase Tx_1indicates stability of amorphous state of structural stability and magnetic ordering values of Tx_1 are observed 513°C for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$with heating rate 20°C/min.
- The activation energy of the first crystallization phase α-Fe(Si) and second crystallization phase Fe_2B phase before and after annealingis found 2.18eVand 3.62eV respectively.
- The amorphous stage of the as- cast ribbon has been confirmed by XRD. The evolution of the primary phase on annealed samples has been confirmed as α-Fe(Si) phase with average grain grown in the amorphous matrix 14 - 20 nm for $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$. This is quite reasonable since the crystallization onset temperature is 650°C and higher. The lattice parameter and Si at% shows an inverse relationship indicating that Si diffuses out of α-Fe(Si) grain for which the size of α-Fe lattice is regained.
- The curie temperature of the sample has been determined by temperature dependence saturation magnetization that is 419°C. The sharp fall of M_s at $T_c$indicates that the material is quite homogeneous.

ACKNOWLEDGEMENTS

We are grateful to Bangladesh Council for Scientific and Industrial Research(BCSIR) for giving experimental facilities and cordial co-operations.

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A.K.M. Asaduzzaman, et. al. "Crystallization Behavior and Effect of Annealed Temperature on Magnetic Properties of Nano Crystalline Fe73.5Cu1Nb3Si13.5B9Alloy." *The International Journal of Engineering and Science (IJES)*, 9(8), (2020): pp. 08-14.