American Journal of Chemistry and Materials Science
2018; 5(4): 72-77
http://www.openscienceonline.com/journal/ajcms

Enhancement of Coercivity and Maximum Energy Product of Annealed Nd-Fe-B Nanocomposite Alloys

Palash Chandra Karmaker[1, 2, 3, *], Mohammad Obaidur Rahman[1], Nguyen Huy Dan[4], Samia Islam Liba[2], Per Nordblad[5], Sheikh Manjura Hoque[2]

[1]Department of Physics, Jahangirnagar University, Savar, Dhaka, Bangladesh

[2]Materials Science Division, Atomic Energy Center, Dhaka, Bangladesh

[3]Department of EEE, University of Information Technology & Sciences, Dhaka, Bangladesh

[4]Institute of Materials Science, Vietnam Academy of Science and Technology, Hanoi, Vietnam

[5]Solid State Physics, Department of Engineering Science, Uppsala University, Uppsala, Sweden

Email address

pckarmakerpu@gmail.com (P. C. Karmaker)

[*]Corresponding author

To cite this article

Palash Chandra Karmaker, Mohammad Obaidur Rahman, Nguyen Huy Dan, Samia Islam Liba, Per Nordblad, Sheikh Manjura Hoque. Enhancement of Coercivity and Maximum Energy Product of Annealed Nd-Fe-B Nanocomposite Alloys. *American Journal of Chemistry and Materials Science.* Vol. 5, No. 4, 2018, pp. 72-77.

Received: June 19, 2018; **Accepted**: July 3, 2018; **Published**: September 1, 2018

Abstract

Nanocomposite $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0 and 1) ribbons were prepared by melt spinning technique with constant wheel speed of 40 m/s. The samples have been annealed in an evacuated quartz tube using a pressure of around 10^{-5} mbar for 10 minutes at different crystallization temperatures like 675°C, 687°C, 700°C, 712°C and 725°C which are found by differential scanning calorimetry (DSC). Crystallization behavior was studied by X-ray diffraction (XRD) using CuK_α radiation (1.5418Å). The ribbon samples were also characterized by vibrating sample magnetometer (VSM). Highest value of H_c has been obtained as 1.06 kOe for the sample of composition $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0) annealed at 700°C for 10 min. At 700°C maximum energy product $(BH)_{max}$ and remanent ratio (M_r/M_s) have been found to be 2.55 MGOe and 0.61 respectively. Higher Tb substitution has significantly reduced the value of coercivity (H_c) and maximum energy product $(BH)_{max}$. The M-H hysteresis loops show extremely soft natures which do not possess any area. However, with the annealing of the samples in the above mentioned temperature evolution of large coercivity was observed due to the formation of exchange couple hard and soft nanocrystal composites.

Keywords

Nanocomposite, Soft and Hard Phase, Coercivity, Maximum Energy Product, Remanent Ratio, Crystallization Temperature

1. Introduction

$Nd_2Fe_{14}B/Fe_3B$ nanocomposites consisting of coupled hard and soft phases exhibits higher maximum energy product $(BH)_{max}$ than single phase $Nd_2Fe_{14}B$ magnets. Since magnetic properties of nanocomposite strongly depend on its microstructure, investigations on some characteristics, such as grain size, distribution of magnetic phase and formation of magnetic anisotropy are still of interest worldwide. Therefore, the nanocomposite magnet alloy has been widely noticed as a hard magnetic material of the next generation [1]. High reduced remanence characteristic to these materials arises from exchange coupling of magnetic moments across the interface between two phases. This causes the magnetic moments of both the phases to remain in the same direction. It has been demonstrated earlier by Kneller and Hawig [2] that the enhancement of the remanence and coercivity by this mechanism is mainly governed by the crystallite sizes of both phases, in particular the soft phase, which can be controlled by dopants and/or additives and also by controlling heat treatment. Compared to single phase $Nd_2Fe_{14}B$, nanocomposite $Nd_2Fe_{14}B/Fe_3B$ based alloys are economic and corrosion resistant. Various dopants and substituents have been used to enhance the value of coercivity. A partial substitution of Nd by heavy rare earth elements like Tb increases the anisotropy field, which enhances the coercive field, but decreases strongly the remanence due to its antiferromagnetic coupling between rare earth and the transition metal [3]. In the present investigation, samples of composition $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0 and 1) have been annealed at different temperatures and times to observe the effect of annealing upon hysteresis loop parameters. This specific composition has been chosen since a mixture of rare earth elements Nd and Tb reduces the cost of the material compared with using pure Nd. In this study, equiatomic values of Nd and Tb with other additives such as Cu, Nb have been chosen. The formation of the both phases in the nanocomposite magnets should be crucially influenced by the heat-treating processes [4-6]. As the annealed temperature is increased, Fe_3B (soft phase) is crystallized at first and at higher temperature Fe_3B is finally decomposed to convert $Nd_2Fe_{14}B$ (hard phase). In these cases, the magnetic exchange coupling between the soft and hard phases should interacts through the ferromagnetic phase, which is supposed to be amorphous and annealed samples from the observation with X-ray diffraction methods [7-8].

2. Experimental Procedure

2.1. Materials and Method

An ingot of composition $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0 and 1) were prepared by arc melting the constituent elements in an Ar atmosphere. The purity and origin of the materials were Fe (99.98%), Cu (99%), Nb (99.8%), B (99.5%), Nd (99.9%) and Tb (99.9%) from Johnson Matthey (Alfa Aesar) and Co (99.8%) from Chempur Feinchemikalien. Amorphous ribbons were prepared from the ingot using a melt spin machine with a wheel speed of 40 ms^{-1} in an Ar atmosphere.

2.2. Characterization

The resulting ribbons were heat treated in an evacuated quartz tube of 10^{-5} mbar pressure at different temperatures in the liquid nitrogen atmosphere and holding time to observe the effect of annealing condition on the magnetic properties [9]. Differential Scanning Calorimetry (DSC) was used to determine the crystallization temperature. X-ray diffraction (CuK_α) was used to identify the structures and phases present in the samples at different stages of the crystallization process. Magnetization measurements and temperature dependence of magnetization (Curie temperature) were performed by vibrating sample magneto meter (VSM) [10].

3. Results and Discussion

3.1. Crystallization Temperature

The crystallization temperature of $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0 and 1) was identified differential scanning calorimetry (DSC). The DSC trace shown in Figure 1 has been measured on a sample in the as-cast condition by carrying out measurement in a nitrogen atmosphere with a continuous heating rate of 10°C/min. The curves show exothermic peaks which represent the formation of metastable, hard and soft phases [11].

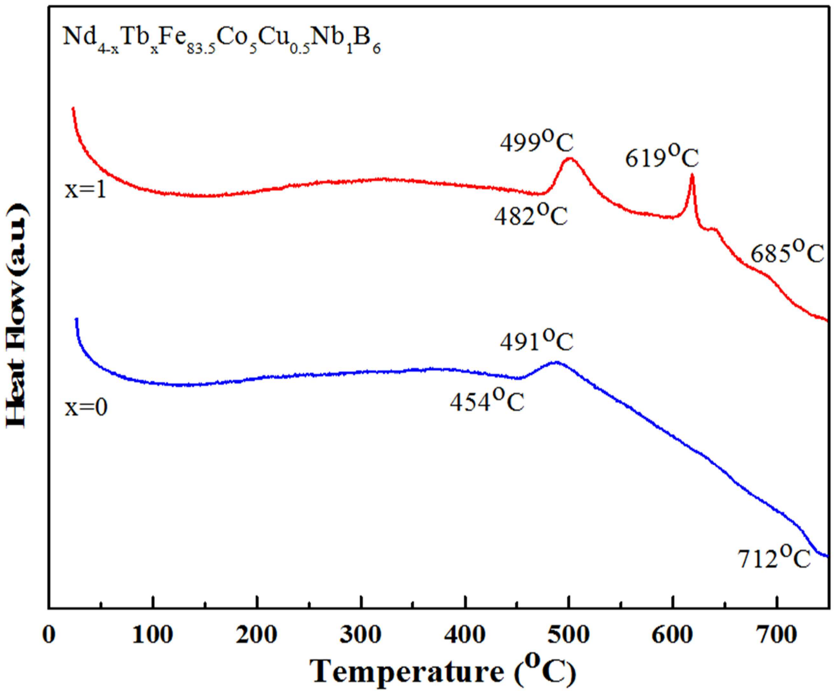

Figure 1. *DSC trace of $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x= 0 and 1) in the as-cast condition with a heating rate of 10°C/min.*

Onset of crystallization of the first exothermic peak is at 454°C for x=0 while the peak temperature is at 491°C and which at 520°C fall in crystallization. For the second exothermic peak, initiation temperature of crystallization is 690°C where the peak temperature is 712°C. The second exothermic peak for x=0 fall in crystallization at 720°C, where the crystallization process is completed around 725°C [12]. For x=1, the peak temperatures of the first, second, third and forth exothermic peaks are at 499°C, 619°C, 640°C and 685°C, where initiation temperatures are 492°C, 598°C, 630°C and 670°C respectively. Fall in crystallization temperature for these three exothermic peaks are at 520°C, 625°C, 645°C and 715°C. Around at 725°C, the crystallization process is fully completed for this composition. The exothermic peaks are gradually increased and sharpen for higher Tb concentration has been observed. Finally the overall crystallization process is completed within the range of 454°C to 725°C have been identified [13].

3.2. Identification of Phases

In order to determine crystallization products at different stages of crystallization X-ray diffraction studies have been performed. Diffraction patterns of the ribbon samples in the as-cast condition and annealed at 700°C and 725°C for 10 min as shown in Figure 2.

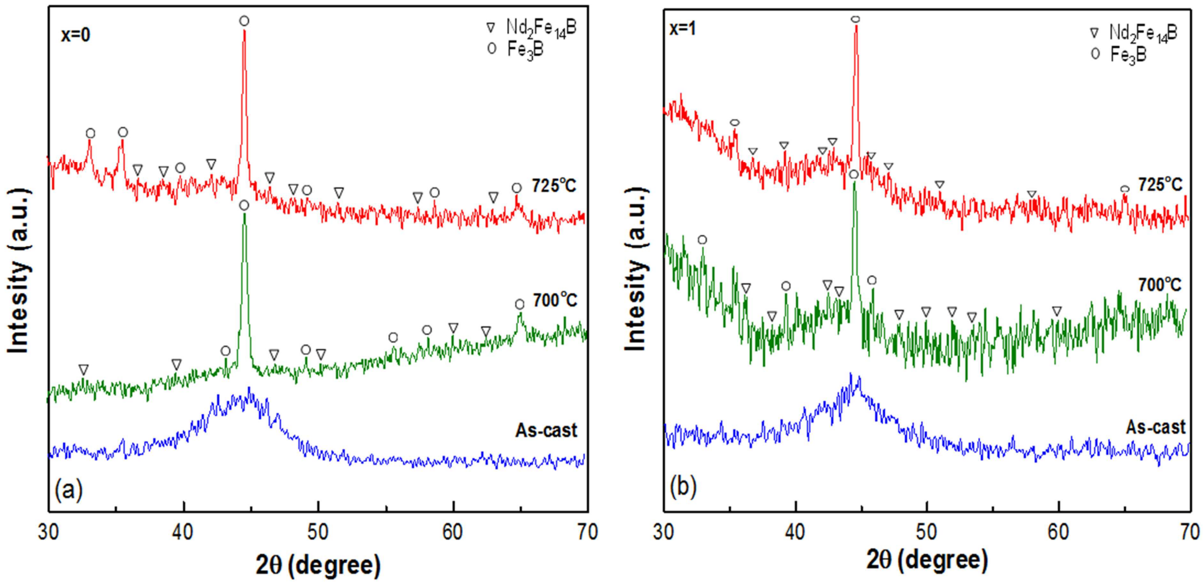

Figure 2. *X-ray diffraction patterns of $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ for (a) x=0 and (b) x=1 samples in the as-cast and annealed at various temperatures for 10 min.*

In the as-cast condition, all the ribbons were in fully amorphous state. Hard magnetic phase ($Nd_2Fe_{14}B$) has formed in small amount in association with the soft phase (Fe_3B) for the annealing temperature of 700°C. At higher annealing temperature of 725°C, the diffraction patterns for the mixture of soft and hard phases are more clear [8]. The diffraction peaks around 33° and 65° due to Fe_3B and $Nd_2Fe_{14}B$ start to appear from 700°C. The intensity of the diffraction peaks around 45° due to Fe_3B increases significantly at 700°C and 725°C. For the composition of $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0), the peaks around 36-43° and at 48-65° due to $Nd_2Fe_{14}B$ also grow up in the ribbon at 700°C are shown in Figure 2(a). From the above results, it can be said that soft phase and hard phase both exist collectively at 700°C [14].

The diffraction patterns are shown in Figure 2(b) for the composition of x=1. Around 34-65°, the diffraction peaks due to Fe_3B and $Nd_2Fe_{14}B$ start to appear from 700°C [9]. The peak due to Fe_3B at 35° is well formed and clearer at 700°C and some peaks for soft phase are well formed around 33-35° at 725°C. The diffraction peaks around 36-43° and at 47-65° due to $Nd_2Fe_{14}B$ also grown up in the ribbon with the increase in temperature. From the above results, it can be said that Fe_3B and $Nd_2Fe_{14}B$ start to be crystallized collectively at 700°C. At higher annealing temperature of 725°C characteristic patterns of the mixture of soft and hard phases have also been observed. The maximum intensity of the diffraction peak has been found at 700°C [15].

3.3. Hysteresis Parameters

For the nanocomposite melt spun ribbon samples of composition $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0 and 1), hysteresis parameters have been determined in as-cast condition and annealed at different crystallization temperatures by hysteresis loop analysis are shown in Figure 3. Saturation magnetization, coercivity, remanent ratio and maximum energy product were obtained from the hysteresis loops as shown in Table 1. The coercivity increase with the increase of annealing temperature, remain almost higher at 700°C and then decrease while varying the higher annealing temperature have been observed. For the composition of x=0, the highest value of coercivity (H_c) has been obtained at optimal annealing temperature 700°C [16].

Table 1. *Hysteresis loop parameters for the samples of composition $Nd_{4+x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0 and 1) annealed at various temperatures and for annealing time 10 min [4].*

Composition	Annealing temperature (°C)	Ms (emu/g)	Hc (KOe)	Mr/Ms	(BH)max (MGOe)
	675	141.3	0.99	0.42	0.82
	687	149.5	1.05	0.48	1.13
x=0	700	190.8	1.06	0.61	2.55
	712	136.1	0.58	0.33	0.00
	725	173.3	0.18	0.25	0.00
	600	166.3	0.63	0.49	1.12
	625	142.4	0.57	0.47	0.08
x=1	650	204.4	0.77	0.53	1.49
	675	179.5	0.51	0.38	0.61
	700	165.8	0.40	0.36	0.17

For all the compositions, the maximum energy product $(BH)_{max}$ increase with the increase of annealing temperature, remain almost higher at optimal annealing temperature 700°C and then decrease while varying the annealing temperature. The highest value of maximum energy product has been achieved for the composition of x=0 at 700°C. As shown in Table 1 and Figure 3, saturation magnetization (M_s) increases initially with the increase of annealing temperature, shows highest value at 700°C and then decreases drastically with the increase of annealing temperature. The highest value of M_s has been achieved for the composition of x=1. Due to the addition of Tb and there is some fluctuation in the variation of magnetization with the increase of annealing temperature. This is probably because the optimum crystallization temperature was in between the annealing temperatures presented in this study. However, M_r/M_s ratio remains almost constant for most of the annealing temperature other than 725°C which is over-annealed temperature for most of the samples. According to the previous results reported [12], the effect of annealing process for this kind of material is important to enhance H_c and $(BH)_{max}$.

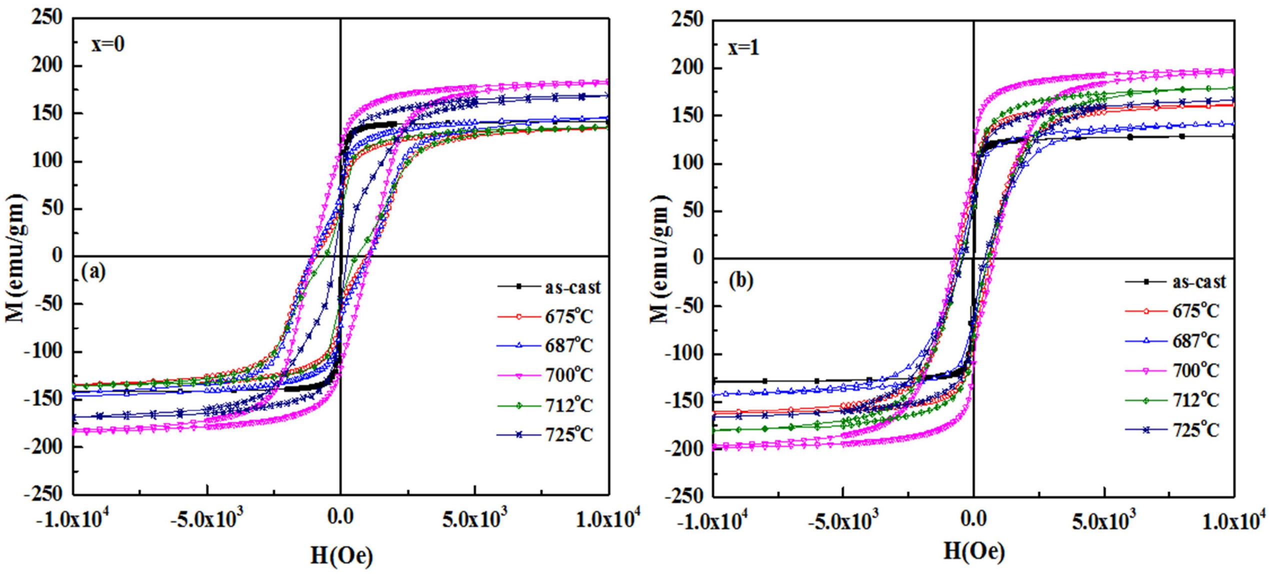

Figure 3. *Hysteresis loops of $Nd_{4+x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0 and 1) samples in the as-cast and annealed at different temperatures for 10 min.*

In order to enhance the hard magnetic property, the nanocomposite ribbons were annealed at various temperatures 675°C, 687°C, 700°C, 712°C and 725°C for 10 min. The variation of the H_c, M_r/M_s and $(BH)_{max}$ with the annealing temperatures are shown in Figure 4.

Since the magnetic properties of various compositions are sensitive to the annealing temperature, it is therefore essential that individual annealing conditions should be adopted for the particular alloy composition [13]. Due to the effect of annealing, shape of the hysteresis loops is strongly changed with annealing temperature and concentration of Tb. The hysteresis loops of all the ribbons are greatly expanded at most of the selected annealing temperatures. That means the hard magnetic phases were formed in the annealed alloys resulting in an increase in coercivity of the materials [17]. The coercivity decreases with the increase of Tb concentration.

3.4. Curie Temperature

The temperature dependence of magnetization results for the ribbon samples were presented in Figure 4, where the applied magnetic field was 10 kG have been investigated. Two magnetic phases which are the hard phase and soft phase for all the ribbon samples have been identified. For the composition of x=0, two magnetic transitions (Curie point) for as-cast and annealed samples have been found. For the as-cast sample, the Curie temperature (Tc_1) due to first transition is 340°C and it corresponds to the $Nd_2Fe_{14}B$ phase while for the annealing temperatures of 675°C, 712°C, and 725°C, the Curie temperatures are 350°C, 360°C and 380°C corresponding to the $Nd_2Fe_{14}B$ phase respectively [18].

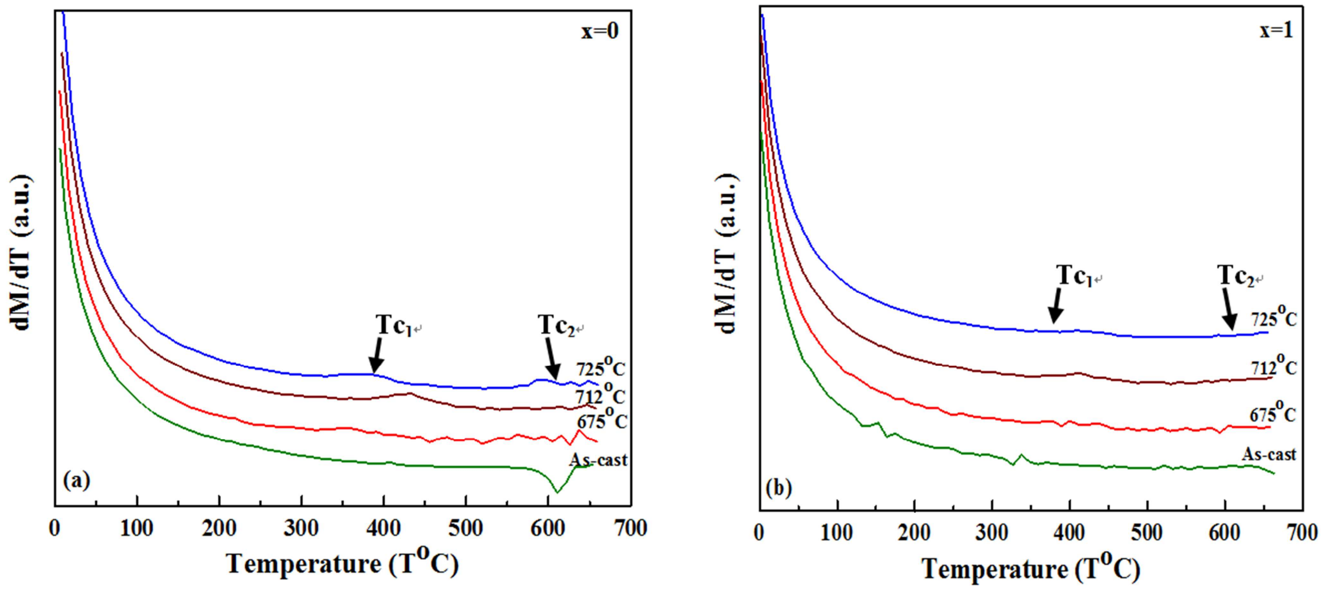

Figure 4. *Temperature dependence of the magnetization for $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0 and 1) samples in the as-cast and annealed condition.*

The Curie temperature (Tc_2) due to second transition is 590°C for as-cast sample and it corresponds to the Fe_3B phase while for the annealed samples, Curie temperatures for second transitions are 620°C, 630°C and 630°C corresponding to the Fe_3B phase as shown in Figure 4(a). Similarly Curie temperatures for other composition x=1 have been determined and it can be stated that the Curie temperature increases with the increase of annealing temperature which are shown in Table 2 [19].

Table 2. *Curie temperature for the samples of $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0 and 1) in the as-cast and annealed at various temperatures with annealing time 10 min.*

Tb_x	Annealing condition	Tc_1 (°C)	Tc_2 (°C)
x=0	As-cast	340	590
	675°C	350	620
	712°C	360	630
	725°C	380	630
x=1	As-cast	340	600
	675°C	370	620
	712°C	410	620
	725°C	410	620

Though anenhancement of coercivity takes place due to the higher anisotropy field when Nd is partially substituted by Tb, remanent ratio is decreased due to antiferromagnetic coupling between rare earth and transition metal [3]. The magnetization of light rare earth (LRE) sublattice couples ferromagnetically to the magnetization of the transition metal sublattice. Combined effect of antiferromagnetic coupling between Fe and Tb and higher anisotropy field of $Tb_2Fe_{14}B$ led to the enhancement of coercivity and reduction of remanent ratio, which in turn has resulted in lower value of energy product [20].

4. Conclusion

Magnetic properties of $Nd_{4-x}Tb_xFe_{83.5}Co_5Cu_{0.5}Nb_1B_6$ (x=0 and 1) nanocomposite magnets with low rare-earth contents have been investigated and are found to depend on annealed condition. A small amount of Tb substitution for Nd leads to an enhancement of coercivity and maximum energy product for the sample annealed at 675°C to 725°C for 10 min. The soft and hard phases are well formed due to the samples annealed at different crystallization temperatures. For the sample of composition x=0 annealed at 700°C, the highest values of coercivity (H_c) have been achieved to be 1.06 kOe. The highest value of maximum energy product $(BH)_{max}$ 2.55 MGOe for x=0 annealed at 700°C. At the optimal annealing condition, enhancement of exchange coupling between soft and hard phases causes a highly reduced remanent ratio (M_r/M_s) up to 0.36. The optimum annealing conditions for the best hard magnetic performance of the ribbons were obtained. The composition dependence of the structure and magnetic properties of the alloys have been discussed.

Acknowledgements

Financial support provided by the International Program for Physical Sciences [IPPS, BAN: 02], Uppsala University, Uppsala, Sweden is acknowledged. The authors acknowledge kind help provided by Prof. N. Q. Liem, Director, Institute of Materials Science, Vietnam Academy of Science and Technology, Hanoi, Vietnam. The authors acknowledge respectfully to Ministry of Science and Technology, Government of the People's Republic of Bangladesh. The authors highly acknowledge the support provided by Materials

Science Division, Atomic Energy Centre, Dhaka and department of Physics, Jahangirnagar University, Savar, Dhaka, Bangladesh.

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