Crystalline Evolution and Large Coercivity in Exchange-Biased Nd$_2$Fe$_{14}$B/Fe$_3$B Nanocomposite Magnets

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Abstract

Tb substituted amorphous ribbons of composition Nd$_{4-x}$Tb$_x$Fe$_{71+y}$Co$_5$Cu$_{0.5}$Nb$_1$B$_{18.5-y}$ (x=0.4; y=12.5 and 0) prepared by a melt spinning technique in an Ar atmosphere has been studied to observe the exchange coupled soft and hard magnetic phases in the nanocrystalline state. For thermal analysis of the ribbon samples differential scanning calorimeter (DSC) was used in order to determine the crystallization temperatures. Significant changes in the crystallization temperatures are observed in the DSC traces due to the difference in B (Boron) content of two batches of composition. The samples were characterized by X-ray diffractometer (XRD) with CuK$_\alpha$ radiation and vibrating sample magnetometer (VSM) of as-quenched and annealed condition during 10 minutes. Structure and magnetic properties of the ribbons clearly depend on their composition. Glass forming ability (GFA) of the alloys is decreased with decreasing B-concentration. Coercivity ($H_c$) and maximum energy product ($BH_{max}$) of the alloys is significantly enhanced by increasing B-concentration. The optimal 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 was discussed.

Keywords

Exchange-Spring Magnets, Soft and Hard Phase, Coercivity, Maximum Energy Product, Crystallization Temperature

1. Introduction

A so-called nanocomposite magnet alloy is composed of soft and hard magnetic grains on a nanometer scale. This alloy has a high coercivity as well as a comparatively high maximum energy product due to the magnetic exchange coupling between the soft and hard magnetic grains. 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

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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$_2$Fe$_{14}$B, nanocomposite Nd$_2$Fe$_{14}$B/Fe$_3$B 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$_x$Fe$_{71+y}$Co$_5$Cu$_{0.5}$Nb$_1$B$_{18.5-y}$ (x=0.4; y=12.5, 0) 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, we have chosen equiatomic values of Nd and Tb with other additives such as Cu, Nb. 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$_3$B (soft phase) is crystallized at first and at higher temperature Fe$_3$B is finally decomposed to convert Nd$_2$Fe$_{14}$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
2.1. Materials and Methods
An ingot of composition Nd$_{4-x}$Tb$_x$Fe$_{71+y}$Co$_5$Cu$_{0.5}$Nb$_1$B$_{18.5-y}$ (x=0.4; y=12.5, 0) were prepared by arc melting the constituent elements in an argon 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 40ms$^{-1}$ in an Ar atmosphere. 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].

2.2. Characterization of Ribbon Samples
Differential Scanning Calorimetry (DSC) was used to determine the crystallization temperature and these measurements were performed in the institute of materials science, Vietnam Academy of Science and Technology, Hanoi, Vietnam. X-ray diffraction (CuK$_\alpha$) was used to identify the structures and phases present in the samples at different stages of the crystallization process. Magnetization measurements were performed by vibrating sample magnetometer (VSM). X-ray diffraction experiment and magnetization measurements were performed in the materials science division, Atomic Energy Centre, Dhaka, Bangladesh [10].

3. Results and Discussion
3.1. DSC
The crystallization temperature of Nd$_{4-x}$Tb$_x$Fe$_{71+y}$Co$_5$Cu$_{0.5}$Nb$_1$B$_{18.5-y}$ (x=0.4; y=12.5, 0) 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 curve shows exothermic peaks which represents the formation of both soft and hard phases [11].
On set of crystallization of the first exothermic peak is at 465°C for B₆, while peak temperature is at 494°C. For the second, third and forth exothermic peaks, the peak temperatures are 548°C, 590°C and 634°C respectively and the crystallization process is completed around 700°C [12]. For the sample B₁₈.₅ the first exothermic peak is at 610°C and the peak temperatures are 620°C, 630°C and 650°C for the second, third and forth exothermic peaks respectively. The crystallization process is also completed around 700°C for B₁₈.₅. For these two compositions the crystallization process is also completed around 700°C. Finally we can see that the overall crystallization process is completed around 460°C to 700°C for both the composition [13].

3.2. XRD

In order to determine crystallization products at different stages of crystallization X-ray diffraction studies have been performed.

![X-ray diffraction patterns](image)

We have observed that all the ribbons are in fully amorphous state before annealed. For the composition of NdₓTbxFe₇₁₋ₓCo₅Cu₀.₅Nb₁B₁₈.₅ the diffraction patterns are shown in Figure 2(a). The diffraction peaks around 35° and 55° due to Fe₃B and Nd₂Fe₁₄B start to appear from 700°C. The intensity of the diffraction peaks around 45° due to Fe₃B increased significantly with the increase of temperature. At 725°C the intensity of the diffraction peak has been found maximum. The peaks around 36°-42° and at 48°-55° due to Nd₂Fe₁₄B also grown up in the ribbon with the increase in temperature [14].

The pattern for the ribbon of composition NdₓTbxFe₇₁₋ₓCo₅Cu₀.₅Nb₁B₁₈.₅ annealed at 600°C is quite similar to that of the as-cast ribbon and both patterns have broad banks probably due to the phase structure being at an almost amorphous state as shown in Figure 2(b). The diffraction peaks around 35° and 55° due to Fe₃B and Nd₂Fe₁₄B start to appear from 650°C. The intensity of the diffraction peak around 45° due to Fe₃B increases significantly at 650°C and 700°C. The peaks around 36°-42° and at 48°-55° due to Nd₂Fe₁₄B also grown up in the ribbon at 650°C. From the above results, it can be said that Fe₃B and Nd₂Fe₁₄B start to be crystallized collectively at 650°C. The diffraction peaks around 45° due to Fe₃B and besides these peaks due to Nd₂Fe₁₄B some peaks are well formed at 700°C for the composition of NdₓTbxFe₇₁₋ₓCo₅Cu₀.₅Nb₁B₁₈.₅ [1]. From the above results, it can be said that Fe₃B and Nd₂Fe₁₄B start to be crystallized collectively for both the compositions. We have also found that at higher annealing temperature of 700°C and 725°C characteristic patterns of the mixture of soft (Fe₃B) and hard (Nd₂Fe₁₄B) phases [6].

3.3. VSM

Hysteresis loops of the samples of composition Nd₄₋ₓTbxFe₇₁₋ₓCo₅Cu₀.₅Nb₁B₁₈.₅ (x=0.4, y=12.5 and 0) ribbons have been measured by vibrating sample magnetometer at room temperature for the ribbons annealed at different temperatures and also for the as-cast condition to observe the variation of magnetic properties with annealing condition which are shown in Figure 3 [15]. Values of saturation magnetization, coercivity, remanent ratio and maximum energy product derived from the hysteresis loops as shown in Table 1.
Table 1. Hysteresis loop parameters for the samples of composition Nd\(_{4-x}\)Tb\(_x\)Fe\(_{71+y}\)Co\(_5\)Cu\(_{0.5}\)Nb\(_1\)B\(_{18.5-y}\) (x=0.4, y=12.5 and 0) annealed at various temperatures and for annealing time 10 min [4].

<table>
<thead>
<tr>
<th>Composition</th>
<th>Annealing temperature (°C)</th>
<th>(M_s) (emu/g)</th>
<th>(H_c) (KOe)</th>
<th>(M_r/M_s)</th>
<th>((BH)_{max}) (MGOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.4, y=12.5</td>
<td>675</td>
<td>129.40</td>
<td>1.06</td>
<td>0.42</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>687</td>
<td>140.60</td>
<td>1.54</td>
<td>0.57</td>
<td>2.18</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>211.40</td>
<td>1.34</td>
<td>0.49</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td>712</td>
<td>124.70</td>
<td>1.09</td>
<td>0.47</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>725</td>
<td>151.50</td>
<td>0.56</td>
<td>0.37</td>
<td>0.41</td>
</tr>
<tr>
<td>x=0.4, y=0</td>
<td>600</td>
<td>138.00</td>
<td>3.10</td>
<td>0.71</td>
<td>8.08</td>
</tr>
<tr>
<td></td>
<td>625</td>
<td>142.00</td>
<td>3.43</td>
<td>0.74</td>
<td>9.37</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>137.00</td>
<td>3.55</td>
<td>0.75</td>
<td>8.20</td>
</tr>
<tr>
<td></td>
<td>675</td>
<td>123.00</td>
<td>3.66</td>
<td>0.77</td>
<td>7.87</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>163.00</td>
<td>1.81</td>
<td>0.78</td>
<td>7.02</td>
</tr>
</tbody>
</table>

From Figure 3, we can see all as-cast samples reveal soft magnetic behaviour with less coercivity and higher saturation magnetization. According to the previous results [5-7], the choice of annealing process for this kind of the material is important to enhance maximum energy product \((BH)_{max}\) for the material.

We can see that after annealing, shape of the hysteresis loops is strongly changed with annealing temperature and concentration of B (Boron). The hysteresis loop of all the ribbons is greatly expanded at most of the selected temperatures. That means the hard magnetic phase was formed in the annealed alloys resulting in an increase in coercivity of the material [16]. From Figure 3 we can see the coercivity strongly increases with increasing concentration of B. In detail, when B concentration is low, the highest coercivity of the alloy is only 1.54 kOe at 687°C. When B concentration is increased by B\(_{18.5}\), the coercivity is enhanced by 3.66 kOe at that temperature 675°C. At 700°C for the composition of B\(_6\) the value of maximum energy product is 2.43 MGOe and at 625°C for the composition of B\(_{18.5}\) the maximum energy product is 9.37 MGOe respectively and we have seen remanent ratio increased [17].

Figure 3. Hysteresis loops of Nd\(_{4-x}\)Tb\(_x\)Fe\(_{71+y}\)Co\(_5\)Cu\(_{0.5}\)Nb\(_1\)B\(_{18.5-y}\) (x=0.4, y=12.5 and 0) samples in the as-cast and annealed at different temperatures for 10 min.

At the optimal annealing temperature 675°C a comparison of magnetic parameters between B\(_6\) and B\(_{18.5}\) have been investigated. We have seen for the composition of B\(_6\) the coercivity and maximum energy product are 1.06 kOe and 0.88 MGOe respectively, but for the composition of B\(_{18.5}\), the coercivity and maximum energy product are 3.66 kOe and 7.87 MGOe. We can see that for B substitution the coercivity and maximum energy product increased 245% and 794% respectively [18-19].

Though an enhancement 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 with higher anisotropy field of Tb\(_{18.5}\)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$_{x}$Tb$_{0.4}$Fe$_{71}$Co$_{6}$Cu$_{6}$Nb$_{18.5}$ (x=0.4, y=12.5 and 0) nanocomposite ribbons have been discussed. A small amount of Tb substitution for Nd leads to an enhancement of coercivity and maximum energy product for the sample annealed at 600°C to 700°C for 10 min. By X-diffraction analysis we have seen that the soft and hard phases are formed due to the samples annealed at different crystallization temperatures. For the sample of composition Nd$_{1.6}$Tb$_{0.4}$Fe$_{71}$Co$_{6}$Cu$_{6}$Nb$_{18.5}$ annealed at 675°C, the highest values of coercivity (Hc) have been achieved to be 3.66 kOe. The highest value of maximum energy product (BH)$_{max}$ 9.37 MGOe for Nd$_{1.6}$Tb$_{0.4}$Fe$_{71}$Co$_{6}$Cu$_{6}$Nb$_{18.5}$ annealed at 625°C. At the optimal annealing condition, enhancement of exchange coupling between soft and hard phases causes a highly reduced remanent ratio (Mr/Mr) up to 0.77. 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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