INFLUENCE OF HEAT TREATMENT ON MAGNETIC PROPERTIES OF NANOCRYSTALLINE Nd$_{9}$Fe$_{84}$Zr$_{1}$B$_{6}$ RIBBONS RECEIVED BY RAPID SOLIDIFICATION METHOD

The effect of the annealing on the phase composition and magnetic properties of nanocomposite melt-spun Nd$_{9}$Fe$_{84}$Zr$_{1}$B$_{6}$ ribbons has been investigated. From the X-ray diffraction studies confirmed by thermomagnetic curves measurements results that the microstructure of the material investigated is composed of a mixture of magnetically hard Nd$_{2}$Fe$_{14}$B and soft $\alpha$-Fe, Fe$_{3}$B nanosized grains. The small amount of undesirable Nd$_{2}$Fe$_{23}$B$_{3}$ metastable phase has been found which do not decompose at the highest annealing temperature. The hysteresis loop measurements certify that the ribbon annealed at 863K show the best coupling between the hard and soft magnetic phases and thus the highest coercivity of 0.38T. The grain sizes increase with increasing annealing temperature causing the coercivity to be decrease.

Keywords: nanocomposites, rapid solidification method, Nd-Fe-B alloys, hard magnetic materials, nanocrystalline magnets

1. Introduction

Nanocomposite magnets belong to the latest generation of neodymium magnets made from Nd-Fe-B alloys. These magnets are produced from alloys with lower Nd concentration compared to those of magnetically hard Nd$_{2}$Fe$_{14}$B phase (Nd$_{11.8}$Fe$_{82.4}$B$_{5.9}$%at.) responsible for high magnetic properties of such magnets. The nanocomposite magnets consist of uniformly distributed hard magnetic Nd$_{2}$Fe$_{14}$B (high magnetocrystalline anisotropy energy) and soft $\alpha$-Fe or Fe$_{3}$B (high saturation magnetization) fine exchange coupled grains. If the grain diameters of both the hard and the soft phase are less than 50 nm the exchange interactions occurring between grains prevents the soft $\alpha$-Fe reversal leading to the remanence $\mu_0M_{R}$ and maximum energy product (BH)$_{max}$ enhancement [1-4].

In spite of considerably lower amount of Nd$_{2}$Fe$_{14}$B phase in nanocomposite magnets compared to these based on Nd-Fe-B alloys (e.g. neodymium sintered magnets have 85% by volume of Nd$_{2}$Fe$_{14}$B phase) magnetic properties are comparable to ones of other magnets and manufacturing costs are lower. The starting material for nanocomposite magnets production is the powder obtained from ribbons prepared by rapid quenching of the liquid alloy on a rotating copper wheel (melt-spinning process). Depending on the wheel speed the nanocomposites may be obtained either directly from the melt during the melt-spinning process (lower wheel speed) or by the annealing the precursor amorphous alloy (higher wheel speed) at appropriate temperature in order to obtain optimum microstructure and magnetic properties. With the aim of preventing the unwanted grain growth
during crystallization a small amount (1% at.) of other constituents, usually zirconium or niobium is added [5].

If the content of Nd is below the stoichiometric one the magnetically soft Nd$_2$Fe$_{23}$B$_3$ metastable phase crystallizes as intermediary phase which undesirably influences the magnetic properties. However, only a few papers mention about the existence of this phase [6-10].

If the temperature of annealing is high enough the metastable phase decomposes into $\alpha$-Fe and Nd$_2$Fe$_{14}$B phases and if the time of annealing is short as possible the increase in grain size of the phases forming the nanocomposite is minimized and does not considerably influences the ribbon magnetic properties especially the coercivity $\mu_0H_C$.

In spite of a lot of works published so far on the nanocomposites they are still the subject of intense study.

The aim of this work was to examine the phase composition and magnetic properties of Nd$_8$Fe$_{84}$Zr$_1$B$_6$ nanocrystalline ribbons annealed at different temperatures.

2. Experimental details; material studied

Alloy ingots with composition of Nd$_8$Fe$_{84}$Zr$_1$B$_6$ were obtained from high purity elements using the arc melting in the protective argon atmosphere. In order to homogenize the samples they were melted several times. By rapid cooling the liquid alloy on a rotating wheel at the linear velocity of 35m/s the amorphous ribbons were obtained which then were annealed at temperatures between 823K and 983K for 5 minutes.

The phase composition was analysed using a Bruker D8 Advance X-ray diffractometer with CuK$_\alpha$ radiation. The hysteresis loops were measured using the LakeShore vibration sample magnetometer at a magnetic field up to 2T.

Thermomagnetic curves $\mu_0M(T)$ were measured using the Faraday’s force magnetometer operating at a field of 0.87 T in the temperature range of 300K-850K with the heating rate of 10K/min. The Curie temperatures were estimated from the minima of the $d(\mu_0M(T))/dT$ curves.

3. Results and discussion

Fig. 1 shows the X-ray diffractograms for the as-spun sample and those annealed at temperatures between 823K and 923K. The diffractogram for the as-spun ribbon has a wide diffraction halo which is characteristic of the amorphous alloy. Diffractograms for the sample annealed at 823K and 863K have diffraction peaks corresponding to $\alpha$-Fe and Nd$_2$Fe$_{14}$B phases with visible amorphous halo. As the annealing temperature increases to 923K the amorphous halo decreases and peaks from Fe$_3$B and Nd$_2$Fe$_{23}$B$_3$ phases are observed. The relative intensity of diffraction peaks corresponding to the Nd$_2$Fe$_{14}$B phase increases with increasing the annealing temperature which means that the amount of Nd$_2$Fe$_{14}$B increases. At the same time, the intensity of peak at $2\theta = 44.69$ corresponding to the $\alpha$-Fe decreases with the increase in the annealing temperature At the highest annealing temperature the peaks from metastable Nd$_2$Fe$_{23}$B$_3$ phase are still seen which means that this phase does not completely decompose.

From the diffraction lines broadening using the Scherrer’s formula the average grain size of Nd$_2$Fe$_{14}$B and $\alpha$-Fe phases were estimated and listed in Tab.1. The smallest grain size of Nd$_2$Fe$_{14}$B and $\alpha$-Fe phases are equal to 50 nm and 28 nm, respectively for the ribbon annealed at 863K.

Crystallization of different phases influences the shape of the hysteresis loops as it is seen in Fig. 2 and 3.

From these loops the values of coercivity $\mu_0H_C$, remanence $\mu_0M_R$ and $(BH)_{max}$ were calculated. Hysteresis loops (for clarity reason the loops are presented in separated figures) in the second quadrant of coordinate system for the samples annealed at temperatures 883K (Fig. 2), 903K, 923K (Fig. 3) show a kink which is characteristic for the multi-phase samples. This is due to the lack of exchange interactions between the soft and hard phases which demagnetize independently showing the kink in the demagnetization curves [6]. Only for the sample annealed at 863K the demagnetization curve is smooth and shows no kink (Fig.2). Although there are some different phases the demagnetization curve for this sample shows a single-phase behaviour suggesting the
existence of the exchange interactions between the $\alpha$-Fe, Fe$_3$B and Nd$_2$Fe$_{14}$B grains [1-3].

Fig. 2. Hysteresis loops of ribbons annealed at temperatures of 823K, 863K and 883K

The sample annealed at 863K has the largest value of coercivity, and the lowest remanence in spite of the existence of exchange interactions. This is likely due to the presence of certain amount of amorphous phase which lower the remanence. The decrease in the coercivity for higher annealing temperature is due to the increase in grain size (Table 1) whereas the increase the remanence as the annealing temperature increases is caused by the increasing amount of Nd$_2$Fe$_{14}$B phase.

Fig. 4 presents the thermomagnetic curves M(T) for the samples annealed at 863K and 923K.

Fig. 3. Hysteresis loops for the amorphous as-spun ribbon and those annealed of 903K and 923K

The figure shows sudden falls in the magnetization curves caused by the phase transition from the ferromagnetic to paramagnetic states confirming the multi-phase structure of samples. The curves allow estimating the Curie temperature of phases present in the alloy. The values of the Curie temperature are presented in Ta.2 along with the data found in the literature [9, 11, 12]. The shape of the thermomagnetic curves shows that the metastable phase Nd$_2$Fe$_{23}$B$_3$ starts to decompose into the Fe$_3$B and $\alpha$-Fe phases above 700K increasing the magnetization. Unfortunately, the highest possible temperature achieved in this experiment is too low to calculate the Curie temperature for $\alpha$-Fe.

<table>
<thead>
<tr>
<th>Annealing temperature [K]</th>
<th>$\mu_0H_C$ [T]</th>
<th>$\mu_0M_R$ [T]</th>
<th>The grain size of Nd$<em>2$Fe$</em>{14}$B phase [nm]</th>
<th>The grain size of $\alpha$-Fe phase [nm]</th>
<th>(BH)$_{max}$ [kJ/m$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>823</td>
<td>0.24</td>
<td>0.69</td>
<td>-</td>
<td>36</td>
<td>2.2</td>
</tr>
<tr>
<td>863</td>
<td>0.38</td>
<td>0.61</td>
<td>50</td>
<td>38</td>
<td>34.1</td>
</tr>
<tr>
<td>883</td>
<td>0.23</td>
<td>0.71</td>
<td>121</td>
<td>64</td>
<td>36.7</td>
</tr>
<tr>
<td>903</td>
<td>0.25</td>
<td>0.75</td>
<td>131</td>
<td>70</td>
<td>35.7</td>
</tr>
<tr>
<td>923</td>
<td>0.26</td>
<td>0.82</td>
<td>222</td>
<td>73</td>
<td>45.4</td>
</tr>
</tbody>
</table>

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TABLE 2

The Curie temperature of the phases present in the alloy and found in the literature [9,11,12]

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>466</td>
<td>–</td>
<td>463</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
<td>576</td>
<td>583</td>
<td>585</td>
</tr>
<tr>
<td>Nd$<em>2$Fe$</em>{23}$B$_3$</td>
<td>–</td>
<td>658</td>
<td>655</td>
</tr>
<tr>
<td>Fe$_3$B</td>
<td>779</td>
<td>791</td>
<td>783</td>
</tr>
</tbody>
</table>

4. Conclusions

The method of obtaining samples allowed preparing nanocrystalline ribbons based on the Nd$_2$Fe$_{14}$B phase doped with zirconium (1% at.).

Based on the research the following conclusions can be drawn:

- ribbons examined are multiphase, consisting of the magnetically hard phase Nd$_2$Fe$_{14}$B and soft Fe$_3$B, α-Fe and Nd$_2$Fe$_{23}$B$_3$ phases
- the demagnetization curve is smooth for the ribbon annealed at the temperature of 863K, which signifies the existence of the exchange interactions between grains of α-Fe and Nd$_2$Fe$_{14}$B
- the grains size of α-Fe and Nd$_2$Fe$_{14}$B increases with the increasing temperature causing the lower coercivity
- demagnetization curves of the ribbons annealed at higher temperature are characteristic for the multi-phase material.

REFERENCES


Received: 10 January 2011.