Low Field Magnetic Properties of Nd$_{50}$Fe$_{40}$Si$_{10-x}$Al$_x$ Melt-Spun and Bulk Amorphous Alloys

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Glass-forming ability and low field magnetic properties of Nd$_{50}$Fe$_{40}$Si$_{10-x}$Al$_x$ ($x = 0$–10) melt-spun ribbons and cast rods are investigated in the temperature range 5–600 K. The dependence of the coercive field on the thickness and preparation method is ascribed to the existence in the amorphous matrix of very small Fe–Nd-based ferromagnetic clusters, which can not be detected by XRD measurements, the size of which approaches to a single magnetic domain. Coercivity increases substantially at reduced temperatures even in low fields. The development in Nd–Fe-based bulk amorphous alloys of two different types of magnetic order, i.e. short-range spin-glass-like order and long-range ferromagnetic order is revealed by zero-field-cooled and field-cooled magnetization measurements.

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1. Introduction

Magnetic properties of binary amorphous rare earth—transition metal alloys have predicted the greatest stimulus for research into their preparation and behavior. These materials form a large variety of magnetic structures ranging from ferromagnetic to sperrimagnetic or sperimagnetic one due to the competition between the development of the RE large single ion anisotropy and exchange interaction. It is worth to note that the high coercivity observed by Croaf in RE–Fe (RE=Nd, Pr) melt spun ribbons is perhaps the first evidence of the existence of an unknown metastable hard magnetic phase in these binary systems. The main stimulus for these studies isthe high coercivity observed for these alloys which could be explained as being due to the existence of a new phase with a high anisotropy field. Recently, it has been reported that Nd–Fe–Al and Nd–Fe–Si ternary amorphous alloys are formed in a wide range of compositions and exhibit also large coercivities at room temperature. Coercive field is believed to result from the development of a mixture of different local atomic structures.

In this paper we present some new magnetic and structural data on Nd$_{50}$Fe$_{40}$Si$_{10-x}$Al$_x$ amorphous melt spun ribbons and cast rods in the temperature range 5–600 K. Comparative studies as a function of composition and the shape of the amorphous samples are presented.

2. Experimental Procedure

Nd$_{50}$Fe$_{40}$Si$_{10-x}$Al$_x$ ($x = 0$ to 10 at%) master alloys were prepared by arc melting high purity Nd (99.9%), Fe (99.99%), Si (99.99%) and Al (99.99%). Amorphous samples were obtained by melt-spinning or suction casting under an atmosphere of argon, at National Institute of Research and Development for Technical Physics in Iasi, Romania. Changing the surface velocity of the Cu wheel and maintaining the orifice size and the ejection pressure to be constant were obtained ribbons with thicknesses ranging from 25 to 145 μm. Rods with diameters between 0.5 and 2 mm were prepared by suction casting technique using different Cu mold cavities. The master alloy was melted in a water-cooled Cu crucible in arc melting chamber and sucked thereafter in the water-cooled Cu mould. The structure of the samples was checked by X-ray diffraction (XRD) method using Mo-Kα radiation. Data on the glass-forming ability were obtained from differential scanning calorimetric (DSC) measurements at a heating rate of 0.67 K/s. DC-magnetic measurements in the temperature range 5–300 K and in fields up to 800 kA/m were performed by using a MPMS$^\text{2}$ SQUID Magnetometer at Royal Institute of Technology in Stockholm. Each sample was thermally demagnetized prior to each measurement. AC-susceptibility was measured by using a very sensitive susceptometer in AC-magnetic fields between 160 and 1600 A/m, frequencies ranging from 29.1 to 291 Hz, in the temperature range 4.2–300 K. Zero field cooled (M$_{ZFC}$) and field cooled (M$_{FC}$) magnetization measurements were carried out using a vibrating sample magnetometer (VSM).

3. Results and Discussion

Table 1 summarizes the results of XRD and DSC studies performed on Nd$_{50}$Fe$_{40}$Al$_{10}$ and Nd$_{50}$Fe$_{40}$Si$_{10}$ melt spun ribbons and cast rods. The replacement of Si by Al results in an increase of the glass forming ability by reducing the region between the crystallization temperature and melting temperature. The higher the reduced crystallization temperature ($T_c/T_m$), the higher the probability to suppress the nucleation process. The increase of the glass forming ability makes possible the fabrication of bulk amorphous samples by casting techniques. DSC curves show only one endothermic peak corresponding to the melting process and no exothermic peaks for crystallization for Nd$_{50}$Fe$_{40}$Si$_{10}$ melt spun ribbons thicker than 100 μm and cast rods indicating that the samples are crystalline. Our previous XRD studies indicate for the as-cast fully crystalline samples the coexistence of three crystalline phases: α-Nd, Nd$_3$Fe$_{17}$ and one unknown phase.
Table 1 Composition of Nd–Fe-based melt spun ribbons and cast rods with different thicknesses, corresponding X-ray diffraction results and data about thermal stability ($T_s$-crystallization temperature; $T_m$-eutectic melting temperature; $T_s/T_m$-reduced crystallization temperature).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sample</th>
<th>Thickness (mm)</th>
<th>Structure</th>
<th>$T_s$ (K)</th>
<th>$T_m$ (K)</th>
<th>$T_s/T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$<em>{50}$Fe$</em>{40}$Si$_{10}$</td>
<td>Ribbon</td>
<td>0.030</td>
<td>amorphous</td>
<td>737</td>
<td>946</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>Ribbon</td>
<td>0.050</td>
<td>amorphous</td>
<td>780</td>
<td>943</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>Ribbon</td>
<td>0.085</td>
<td>amorphous</td>
<td>753</td>
<td>946</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>Ribbon</td>
<td>0.105</td>
<td>crystalline</td>
<td>—</td>
<td>947</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Ribbon</td>
<td>0.142</td>
<td>crystalline</td>
<td>—</td>
<td>947</td>
<td>—</td>
</tr>
<tr>
<td>Cast rod</td>
<td>1.8</td>
<td></td>
<td>crystalline</td>
<td>—</td>
<td>947</td>
<td>—</td>
</tr>
</tbody>
</table>

Nd$_{50}$Fe$_{40}$Al$_{10}$

| Ribbon | 0.030 | amorphous   | 812 | 931 | 0.87 |
| Ribbon | 0.050 | amorphous   | 804 | 928 | 0.87 |
| Ribbon | 0.085 | amorphous   | 806 | 927 | 0.87 |
| Ribbon | 0.105 | amorphous   | 818 | 929 | 0.88 |
| Ribbon | 0.142 | amorphous   | 803 | 926 | 0.87 |
| Cast rod | 1.8 | amorphous   | 826 | 925 | 0.89 |

and no amorphous phase. It is worth to note that the highest value for the reduced crystallization temperature of about 0.83 was obtained for Nd$_{50}$Fe$_{40}$Si$_{10}$ melt spun amorphous ribbon 50 μm thickness which exhibits also the largest amount of heat during crystallization indicating the highest degree of structural disorder. In the case of Nd$_{50}$Fe$_{40}$Al$_{10}$ amorphous alloys the highest degree of structural disorder is attained for cast rods.

Replacing Si with Al affects both glass forming ability (Table 1) and magnetic properties at room temperature, as it can be seen in Fig. 1. The magnetization slightly increases for melt-spun ribbons and exhibit a huge increase for cast rods by substituting Si with Al. The coercive field measured for melt-spun ribbons slightly decreases, regarding of their thickness, and increases about 5 times for cast rods by replacing Si with Al. It is very important to note that the disappearance of the amorphous phase results in the disappearance of the ferromagnetic properties. Thus, the high coercivity of Nd–Fe-based bulk amorphous alloys is related only to the existence of the amorphous phase, contrary with the previous results on the Nd–Fe binary crystalline alloys. The different behavior of magnetic characteristics of Nd$_{50}$Fe$_{40}$Si$_{10}$–xAl$_{x}$ amorphous alloys depends on the thickness of the amorphous samples, namely on the cooling rate as well as the preparation method, therefore on the microstructure involved in the amorphous matrix. The large values of the coercive field can be explained by assuming the existence of some very small magnetic clusters dispersed in the amorphous matrix. These clusters are coupled between them by magnetic exchange interactions through the amorphous matrix. The presence of these magnetic clusters cannot be revealed by XRD measurements. The shape, the composition and the size of these clusters are determined mainly by the value of the cooling rate.

In order to obtain information on magnetic coupling of the hard magnetic phase detected in Nd–Fe–(Si, Al) amorphous alloys, the low temperature dependence of the magnetization measured in a maximum applied field of 800 kA/m and coercive field are plotted in Fig. 2 for Nd$_{50}$Fe$_{40}$Al$_{10}$ melt spun amorphous ribbons and amorphous cast rods. It can be seen that the magnetization tends to show a magnetic anomaly in the vicinity of 200–230 K, reaches a maximum and decreases thereafter. This anomaly can be explained by assuming a change in the direction of the easy axis of the magnetic clusters. Subsequent increase of the temperature above room temperature leads to the appearance of another marked cusp on the magnetization curves (see $M_{ZFC}$ curves shape in Fig. 5), indicating the spin reorientation.

The humps appearing in the coercivity curves over a narrow range (150–200 K) suggest the existence of one pronounced
Fig. 2. Temperature dependence of magnetization and coercive field of amorphous melt spun ribbons and cast rods with nominal composition Nd$_{0.4}$Fe$_{60}$Al$_{10}$.

Fig. 3. Temperature dependence of the magnetization at 800 kA/m (solid lines and solid symbols) and coercive field (dashed lines and open symbols) of Nd$_{0.4}$Fe$_{60}$Si$_{10}$ and Nd$_{0.4}$Fe$_{60}$Al$_{10}$ amorphous ribbons 30 μm thickness.

Fig. 4. Real part ($\chi''$) and imaginary part ($\chi'$) (inset) of AC-susceptibility at 800 A/m and 182 Hz for Nd$_{0.4}$Fe$_{60}$Si$_{10}$ (x = 0, 10) melt-spun ribbons and cast rods.

The decrease in $H_c$ at very reduced temperatures is similar to that found in crystalline binary and ternary neodymium-transition metal compounds$^{10,11}$ and is believed due to a change in the magnetocrystalline anisotropy of the magnetic clusters phase as a function of temperature. The difference in the absolute values of the coercivity as a function of the samples thickness may result from the extrinsic factors, such as cooling rate of the samples, the amount of the magnetic clusters phase in the amorphous residual matrix, and the strength of the applied field. The similar behaviour of the magnetization and coercive field at reduced temperatures is obtained for Nd$_{0.4}$Fe$_{60}$Si$_{10}$ amorphous ribbons (Fig. 3).

From the specific behaviour of the magnetization and coercive field at low temperatures, one can conclude that, in the temperature range 5–250 K, three magnetic phase transitions take place, as it can be observed from AC-susceptibility measurements presented in Fig. 4. At very low temperatures, the large anisotropy energy of Nd ions plays an important role in freezing randomly the spins of Fe and Nd. The anisotropy axes of the Fe–Nd based clusters are oriented randomly and low applied fields are not enough to align them. Therefore, the magnetization and coercive field are small at temperatures below 100 K. The first maximum observed in real part of the AC-susceptibility curve at around 10 K could be ascribed to a spin-glass like transition and can be related to the Néel temperature of the Nd antiferromagnetic double hexagonal compact phase. The second maximum observed around 70 K, which is very pronounced for Nd$_{0.4}$Fe$_{60}$Si$_{10}$ crystalline samples, can be associated with a magnetic transition from a completely disordered magnetic state to sperromagnetic or sperromagnetic one, depending on the value of the exchange energy comparatively with the anisotropy energy.$^{11}$ The largest values of about 580 kA/m and respectively 480 kA/m amounting for coercive field in the range 150–200 K for the Nd$_{0.4}$Fe$_{60}$Al$_{10}$ and Nd$_{0.4}$Fe$_{60}$Si$_{10}$ amorphous samples, respectively, are in agreement with the
increases obtained for both the real and imaginary part of the AC-susceptibility. This behaviour proves that, in this range of temperatures, the thermal activation effects and the anisotropy energy are small enough and the exchange anisotropy plays the dominant role in determining the coercivity mechanism.

The coexistence of two types of magnetic order, short-range spin-glass-like order and long-range ferromagnetic order even in amorphous rods, is evidenced by zero-field and field cooled thermomagnetic measurements in Fig. 5. The presence of the maximum on the $M_{ZFC}$ curves and the bifurcation between $M_{ZFC}$ and $M_{FC}$ curves prove the coexistence of two magnetic phases. The displacement of the $M_{ZFC}$ maximum towards high temperatures with the increase of the thickness of the amorphous samples is determined by the fact that as thinner the ribbons the higher glassy disorder and the higher the thermal energy required to destroy it. The coexistence of two types of Fe-based magnetic phases in a ratio of 9:1 was evidenced by our recent Mössbauer spectrometry measurements. The results of these studies will be done elsewhere.12}

4. Summary

It was found that Nd$_{90}$Fe$_{40}$Al$_{10}$ melt-spun amorphous ribbons and cast amorphous rods as well as Nd$_{90}$Fe$_{40}$Si$_{10}$ melt-spin ribbons exhibit coercivities up to 300 kA/m at room temperature. The coercive field increases up to 580 kA/m with decreasing the temperature down to 200 K. The dependence of the coercive field on the thickness, namely on the cooling rate and preparation method, is ascribed to the formation in the amorphous matrix of very small magnetic clusters. These clusters have different compositions and sizes, possess large random anisotropies and are coupled between them by ferromagnetic exchange interactions through the amorphous matrix. AC-susceptibility measurements at reduced temperatures show three magnetic phase transitions that take place with the increase of the temperature. The shape of the thermomagnetic curves evidences the existence of short-range order existing inside the clusters and ferromagnetic long-range order resulted from the exchange interactions between clusters. The possibility to tailor the magnetic properties of Nd$_{90}$Fe$_{40}$Si$_{10-15}$Al$_{x}$ amorphous alloys as a function of the cooling rate makes these alloys interesting for glass formation phenomenon studies, spin dynamics research and also for different applications as recording media, magnetoresistive alloys or magnets.

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REFERENCES