Temperature-Dependent Magnetic Properties of SiO2-Coated Ni75Fe25 Nanoparticles

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ABSTRACT

SiO2-coated Ni75Fe25 nanoparticles were prepared using a wet chemical method and their structure and magnetic properties were investigated using x-ray diffraction, high-resolution transmission electron microscopy, and a superconducting quantum interference device magnetometer. The SiO2 material was in an amorphous state. The Ni75Fe25 nanoparticles were in a simple cubic state and contained inner oxide (Ni-oxide and Fe-oxide) cores whose size decreased with increasing calcination temperature. The nanoparticles were basically in the ferromagnetic state. Their saturation magnetization increased with increasing calcination temperature, whereas their coercivity decreased with increasing calcination temperature. The nanoparticles exhibited strong temperature-dependent magnetic behaviors. The Bloch exponent fell from 1.5 for the bulk to smaller values and decreased with increasing oxide content, while the Bloch constant was much bigger than that for bulk and increased significantly with oxide content. The value of coercivity decreased with increasing temperature, and this decrease was more pronounced for the nanoparticles containing high oxide content. The exchange anisotropy arising from the exchange coupling across the Ni75Fe25/oxide interfaces was examined and was used to interpret the observed temperature-dependent behaviors.

INTRODUCTION

Studies on insulator-coated ferromagnetic nanoparticles have been and continue to be an area of great interest. From a fundamental perspective, the coated nanoparticles are of interest as the coating prevents the nanoparticles from particle coarsening, surface oxidation, and agglomeration. From an application perspective, the coated nanoparticles have attractive potential application in high frequency soft magnetic materials and clinical drug delivery. In soft magnetic applications, the coating not only works as an insulate phase to achieve high electrical resistivity, but also behaves as a binder to ease the consolidation of the nanoparticles. In drug delivery applications, the coating protects the metal nanoparticles from leaching in an acidic environment.

A considerable amount of research has been conducted on the preparation and magnetic properties of insulator-coated ferromagnetic nanoparticles in the recent years, but most of them focused on Fe and Co nanoparticles [1-6]. We have recently synthesized SiO2-coated Ni75Fe25 nanoparticles and examined their structural and magnetic properties. The detailed synthesis procedure and structural properties have been presented elsewhere [7]. Here we present the magnetic properties of SiO2-coated Ni75Fe25 nanoparticles, especially the temperature-dependent saturation magnetization, coercivity, and exchange anisotropy.

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EXPERIMENTAL DETAILS

SiO$_2$-coated Ni$_{75}$Fe$_{25}$ nanoparticles were synthesized by a wet chemical technique [7]. Starting materials containing nickel, iron, and silicon were mixed in alcohol with controlled temperature and pH to form precomposite precipitates in solution. The alcohol was then removed by evaporation at elevated temperature. A further drying process was performed in an oven to obtain precomposite powder consisting of nickel oxide, iron oxide, and silica. The precomposite powder was then calcined in the presence of a reducing agent to form the SiO$_2$-coated Ni$_{75}$Fe$_{25}$ nanoparticles. The volume fraction of Ni$_{75}$Fe$_{25}$ in the synthesized nanoparticles was found to depend mainly on the precomposite concentration and calcination temperature. In this paper, nanoparticle sample T600, T700, T800, and T900 were prepared at different calcination temperatures of 600 °C, 700 °C, 800 °C, and 900 °C, respectively. The volume fraction of Ni$_{75}$Fe$_{25}$ in these nanoparticles was targeted at 50%.

The morphology of the synthesized nanoparticles was analyzed using high-resolution transmission electron microscopy (HRTEM). Structure was determined by powder x-ray diffraction (XRD) using Cu K$_\alpha$ radiation. The mean size of Ni$_{75}$Fe$_{25}$ particles was estimated from XRD main peak using the Scherer formula. Magnetic properties were studied using a Quantum Design SQUID magnetometer. Saturation magnetization was determined by $H^{-1} \rightarrow 0$ extrapolation using fields of $H \leq 55$ KOe.

RESULTS AND DISCUSSION

The XRD patterns for the Ni$_{75}$Fe$_{25}$ nanoparticles are shown in Figure 1. As can be seen, all of the diffraction patterns match only simple cubic Ni$_{75}$Fe$_{25}$ structure without peaks for SiO$_2$. The previous HRTEM and XRD studies revealed that the synthesized Ni$_{75}$Fe$_{25}$ nanoparticles were covered by amorphous SiO$_2$ [7]. The diffraction peaks broadened as the heat-treatment temperature decreased in Figure 1. It is well known that Ni$_{75}$Fe$_{25}$ has a diffusional phase transformation. The ordered Ni$_{75}$Fe$_{25}$ phase transforms to disordered Ni$_{75}$Fe$_{25}$ phase without any composition change when temperature increased around 500°C [8]. Correspondingly, the lattice parameter slightly expands when the disordered Ni and Fe solid solution formed [9]. The lattice parameter expansion resulted in the slight shift of the peaks towards lower angles. However, the usual diffraction techniques are ineffective to observe this slight shift due to very small changes in lattice parameter [10-11]. A slight shift of the main peak for sample T600 is observed, which

![Figure 1. X-ray diffraction patterns for sample T600, T700, T800, and T900](image-url)
might be caused by X-ray diffraction machine. The decrease in line broadening with increasing temperature is due to the increasing in grain size. The mean grain size of Ni$_{75}$Fe$_{25}$ has been determined by using the Scherer method and given in Table I. It is evident that sample T600, T700, and T800 have similar small sizes, but sample T900 has a relatively big size. This result indicates that when the calcination was performed at 800 °C or below, the SiO$_2$ coating remained as an unbroken shell and prevented the coarsening of Ni$_{75}$Fe$_{25}$ particles; at 900 °C, however, the coating no longer acted as a barrier to effectively prevent abnormal Ni$_{75}$Fe$_{25}$ particle growth. Similar result had been observed in the synthesis of SiO$_2$-coated Co nanoparticles [5].

**Table I.** Calcination temperature, mean particle size, and saturation magnetization at 5 K for four nanoparticle samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcination temperature ($^\circ$C)</th>
<th>Particle size (nm)</th>
<th>Saturation magnetization at 5 K (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T900</td>
<td>900</td>
<td>43.1</td>
<td>87.47</td>
</tr>
<tr>
<td>T800</td>
<td>800</td>
<td>11.5</td>
<td>81.29</td>
</tr>
<tr>
<td>T700</td>
<td>700</td>
<td>12.4</td>
<td>72.15</td>
</tr>
<tr>
<td>T600</td>
<td>600</td>
<td>11.1</td>
<td>65.75</td>
</tr>
</tbody>
</table>

Table I also gives the saturation magnetization at 5 K for four samples. It can be seen that the magnetization increased with the increasing calcination temperature. This result can be explained by the incomplete conversion from oxide to Ni$_{75}$Fe$_{25}$. During the synthesis procedure, the calcination caused a gradual conversion from Ni-oxide and Fe-oxide to metallic Ni$_{75}$Fe$_{25}$. For this reason, the as-synthesized Ni$_{75}$Fe$_{25}$ particles should have inner oxide cores if the conversion was not complete. It is obvious that the higher the calcination temperature, the more complete the conversion of oxide to Ni$_{75}$Fe$_{25}$. Consequently the nanoparticles calcined at higher temperature had smaller oxide cores and exhibited higher saturation magnetization. The existence of these oxide cores was confirmed by the presence of exchange anisotropy, which would be discussed later in this paper. It should be noted that there is no trace of oxide in all of the XRD patterns. This is because the Ni$_{75}$Fe$_{25}$ atoms, which had a high x-ray absorption coefficient, shielded the inner oxide cores. It also can be seen that the saturation magnetization of sample T900 almost reached the expected value of 89.37 emu/g indicating the almost complete conversion of oxide to Ni$_{75}$Fe$_{25}$ at 900 °C.

The variations of saturation magnetization as a function of temperature for four samples are shown in Figure 2 and are found to obey Bloch’s law [12-13]

$$M(T) = M(0)(1 - BT^b) \quad \text{(for } T < < T_c \text{)}$$

(1)

where $b$ is Bloch exponent and $B$ is Bloch constant. The values of $b$ and $B$ for bulk ferromagnetic metal were reported to be 1.5 and $\sim 10^{-6}$ K$^{-3/2}$, respectively. The values of $b$ and $B$ for four samples were obtained by fitting the measured data to Equation (1) and were given in Table II. As can be seen in Table II, the synthesized nanoparticles exhibited a strong dependence of magnetization on temperature. The Bloch exponent of all four samples fell from 1.5 to smaller values and decreased with increasing oxide content, while their Bloch constants were significantly bigger than $10^{-6}$ and drastically increased with increasing oxide content. One reason for those behaviors is that the nanoparticles have a high fraction of surface atoms and the fluctuation of surface moments is much larger than that of interior moments. Another reason lies
on the presence of inner oxide cores and their magnetic transition from ferrimagnetic or antiferromagnetic to superparamagnetic or paramagnetic with increasing temperature. Similar behaviors have been observed early in Co/oxide shell/core nanoparticles and oxide-coated Fe nanoparticles [5, 14].

Figure 3 shows the measured coercivities versus temperature for four samples. It can be seen from Figure 3 that the synthesized nanoparticles exhibited a strong dependence of coercivity on temperature: the value of coercivity decreased notably with increasing temperature. One reason for this behavior is that some of Ni$_{75}$Fe$_{25}$ particles was very small and underwent a magnetic transition from ferromagnetic to superparamagnetic as the temperature increased. The presence of the exchange anisotropy, which arose due to the ferromagnetic/anti-ferromagnetic (or ferrimagnetic) exchange coupling across Ni$_{75}$Fe$_{25}$/oxide interfaces, is believed to be another reason for that behavior. Due to small size the oxide cores underwent a transition from ferrimagnetic or anti-ferromagnetic to superparamagnetic or paramagnetic as the temperature increased from low temperature to room temperature. As a result, the exchange anisotropy weakened with increasing temperature leading to the decrease of coercivity. This explanation is supported by the measurement of exchange field versus temperature. Figure 4 shows the variation of exchange field as a function of temperature for sample T600. The exchange field was taken from the shifts of field-cooled hysteresis loops, which was measured after a field cooling from 350 K to the measurement temperature under a field of 55 kOe. It is evident that, for sample T600, the exchange field was notable at 5 K and insignificant at 100 K or above. The exchange anisotropy arising from ferromagnetic/anti-ferromagnetic (or ferrimagnetic) and its effect on coercivity were also observed early in nanostructured materials [15-17].

It also can be seen from Figure 3 that the nanoparticles calcined at lower temperature exhibited stronger temperature-dependent coercivity than those calcined at higher temperature. This result can be explained mainly by size effect. Compared to the Ni$_{75}$Fe$_{25}$ particles calcined at higher temperature, the Ni$_{75}$Fe$_{25}$ particles calcined at lower temperature were believed have
smaller effective size due to containing larger oxide cores and exhibited ferromagnetic at low temperature and superparamagnetic at high temperature, leading to stronger temperature-dependent coercivity. The difference in exchange anisotropy is believed to be another reason. The nanoparticles calcined at lower temperature had larger Ni$_{75}$Fe$_{25}$/oxide interfaces and exhibited stronger exchange anisotropy at low temperature and weaker exchange anisotropy at high temperature, while the nanoparticles calcined at higher temperature exhibit weaker exchange anisotropy in the whole temperature range due to containing smaller Ni$_{75}$Fe$_{25}$/oxide interfaces. Figure 5 shows the exchange field versus calcination temperature. Prior to the measurements, the samples were cooled from 350 to 5 K under a field 55 kOe. It can be seen from Figure 5 that the exchange field decreased notably with calcination temperature.

Figure 3 also reveals that the lower the calcination temperature was, the higher coercivity the nanoparticles exhibited. The above-discussed exchange anisotropy is believed to be one reason. Another reason lies on size effect. The effective Ni$_{75}$Fe$_{25}$ particle size in the samples calcined at lower temperature was smaller than that in the samples calcined at higher temperature. Smaller Ni$_{75}$Fe$_{25}$ particles exhibited higher coercivity according to the following equation [18]

$$ H_c = \frac{a}{r^2} - b $$

(2)

where $r$ is particle size and $a$ and $b$ are constants. Equation (2) was found for non-interacting single-domain particles. Most of the Ni$_{75}$Fe$_{25}$ particles in our samples were believed to be free of interaction and have single-domain structure. (To our knowledge, the single-domain critical size for Ni$_{75}$Fe$_{25}$ has never been reported, but it is believed to be larger than those for fcc Fe and fcc Co due to lower magnetocrystalline anisotropy.)

**CONCLUSIONS**

SiO$_2$-coated Ni$_{75}$Fe$_{25}$ nanoparticles were prepared. The SiO$_2$ material was in an amorphous state; the Ni$_{75}$Fe$_{25}$ nanoparticles were in a simple cubic state and contained an inner oxide core.
whose size decreased with increasing calcination temperature. The saturation magnetization of the synthesized nanoparticles increased with increasing calcination temperature, whereas their coercivity decreased with increasing calcination temperature. The nanoparticles exhibited strong temperature-dependent magnetic behaviors. The Bloch exponent fell from 1.5 for the bulk to smaller values and decreased with increasing oxide content, while the Bloch constant were much bigger than that for bulk and increased significantly with oxide content. The value of coercivity decreased with increasing temperature, and this decrease was more pronounced for the nanoparticles containing high oxide content. The exchange anisotropy arising from the exchange coupling across the Ni$_{75}$Fe$_{25}$/oxide interfaces was observed and was found to decrease with increasing temperature. The observed temperature-dependent magnetic properties were successfully interpreted by the magnetic transition of Ni$_{75}$Fe$_{25}$ particles and oxide cores and the presence of the exchange coupling across the Ni$_{75}$Fe$_{25}$/oxide interfaces.

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