Exchange-Coupled Soft Magnetic FeNi−SiO_2 Nanocomposite

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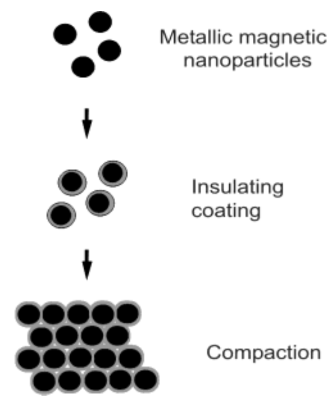
We report a method to make exchange-coupled soft magnetic FeNi−SiO_2 nanocomposite material composed of FeNi nanoparticles coated with a thin SiO_2 layer. Permeability is independent of frequency up to at least 100 MHz, with value as high as 16 in samples with density merely 93% of the ideal density. The quality factors are higher than conventional high-frequency CoNi ferrites after 10 MHz and decrease in a much slower fashion with increasing frequency. We ascribe these experimental observations to the exchange coupling among the magnetic particles.

Nanocomposite materials, composed of magnetic nanoparticles embedded in a dielectric matrix (e.g., polymer, alumina, or silica),[1] have attracted some research interest because of their potential applications as microwave absorbing and shielding materials[2] and in electromagnetic devices (e.g., inductors, dc-dc converters).[3] In particular, for the electromagnetic device applications at high frequencies,[4,5] researchers have long been searching for soft magnetic materials with high saturation magnetization (M_s), high permeability (μ), and low energy losses.[6−8] FeNi and FeCo alloys are common soft magnetic alloys with large saturation magnetization. However, due to their metallic nature, the eddy current generation severely limits their applications at high frequencies. On the other hand, soft magnetic ferrites have been traditionally used in high frequency applications because of their large permeabilities and low power losses. Ferrites usually have much smaller M_s compared with metallic ferromagnets. According to the Snoek's law, $\mu f_r \propto M_s$, where f_r is the ferromagnetic resonant frequency, materials with high M_s have potential to lead to high value of μ.[9] It is therefore conceivable that one may obtain high permeability in magnetic nanocomposites consisting of FeCo or FeNi nanoparticles embedded in an insulating matrix. In this case, the ferromagnetic exchange coupling must exist among ferromagnetic nanoparticles, which dramatically reduces anisotropy and significantly enhances permeability.[10−12]

In this Letter, we report a method to make exchange-coupled soft magnetic nanocomposite materialsby compacting FeNi nanoparticles coated with a thin layer SiO_2. Using a combustion-driven compaction process,[13,14] we have achieved about 93% of the ideal density. The experimental approach is schematically shown in Scheme 1. The nanocomposite samples have shown frequency-independent permeability spectra up to at least 100 MHz with permeability as high as 16. The experimental observations will be discussed in terms of exchange (dipole and direct) coupling among magnetic nanoparticles.

The commercial FeNi nanoparticles (Argonide Corp.) were used in our experiment. The particles have average diameters

SCHEME 1



of 100 nm with a large size distribution. To create a uniform amorphous SiO_2 layer coating on these particles, we employed a base-catalyzed sol−gel process.[15,16] The general coating procedures were as follows: 5 g of FeNi particles were dispersed into 100 mL of 2-propanol solution and sonicated for 10 min; 15 mL of tetraethoxysilane (TEOS) and 5 mL of 25% $NH_3 \cdot H_2O$ solution were added into the above dispersion, and the mixture was vigorously stirred for 1 h to complete the hydrolysis reaction. By means of magnetic decantation, the silica coated FeNi particles were separated from the supernatant solution. The coated particles were washed twice with 50 mL of acetone to remove any unreacted organic chemicals and finally dried in a desiccator. This procedure produces a very uniform SiO_2 coating of about 3 nm, as determined using a transmission electron microscope (see below). By changing the formulation of the coating solution, we can control the coating thickness, and we have obtained samples with 6 and 9 nm thick coatings. For thinner coatings (<3 nm), the silica prefers to nucleate on the surface of FeNi nanoparticles, which is quite similar to reported results of coating silica on Au nanoparticles.[15] We also note that the thicker coating layers (6 and 9 nm) are not as smooth as the thinner coating layer (3 nm). The thinner coating, as long as it is thick enough to prevent the electrical conductance, is always preferred in an exchange coupled system because the exchange length is only of the order of a few nanometers.[17] We have found 3 nm thick SiO_2 coating is sufficient for this purpose. For samples with different coating

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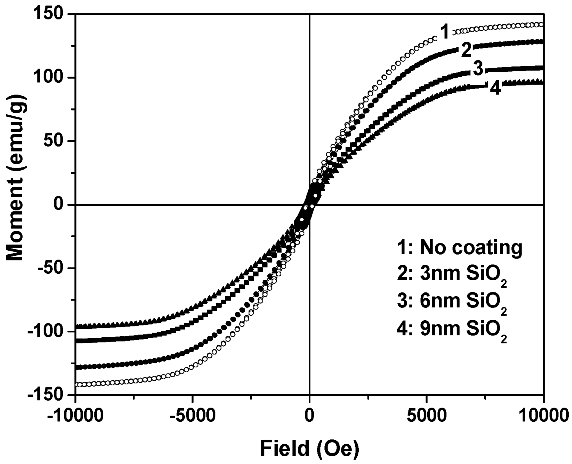

Figure 1. Room-temperature magnetization curves of FeNi nanoparticles coated with silica of different thickness.

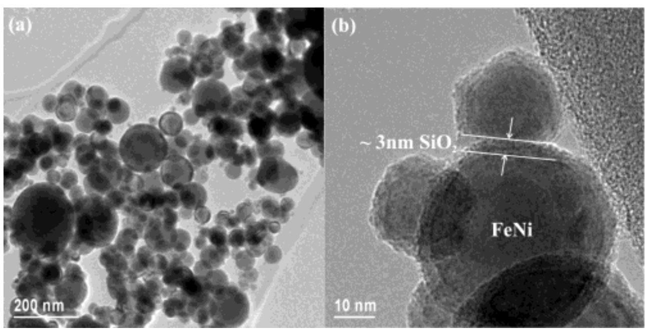

Figure 2. TEM graphs of FeNi nanoparticles coated with ~3 nm SiO_2.

thickness, the XRD patterns are almost identical to the sample without coating because of the amorphous nature of the silica layer. With increasing the coating thickness, the magnetic moment of the particles decreases accordingly, as expected, whereas the coercivity remains at the same level as the precursor FeNi nanoparticles (Figure 1).

The uniformity and coverage of the silica coating layer were examined by a JEM-2010f transmission electron microscope (TEM) operating at 200 kV. In Figure 2a, a low magnification TEM graph indicates that all FeNi nanoparticles were coated. In Figure 2b, a higher magnification TEM graph demonstrates the uniformity and full coverage of the silica coating with thickness of about 3 nm.

The FeNi nanoparticles coated with a 3 nm SiO_2 layer have been successfully compacted into toroid samples by using a combustion driven compaction technique[13,14] for high-frequency permeability measurement. In this technique, a pressurized mixture of natural gas and air creates preload pushing pressure and removes entrapped air from the powder. The gas mixture is then ignited to give a rapid pressure rise that further compresses the nanocomposite particles into its final shape. The preload pressure is in the range 207−276 MPa, and the peak pressure during combustion can vary from 414 MPa to 3.45 GPa. The process can also be cycled many times to enhance the density. With this technique, we have compacted a series of toroidal samples with different densities. The complex permeability μ and quality factor Q of the toroidal samples were measured using a HP 4294A Precision Impedance Analyzer with 16454A magnetic test fixtures in the frequency range from 100 kHz to 100 MHz.

The frequency spectrum of the real part of permeability, μ', for samples of different densities is plotted on the top panel of Figure 3a. For comparison, we also plot the data for a typical commercial high-frequency CoNi ferrite[18] in the bottom panel. There are two remarkable features. First, the frequency spectrum of the permeability μ' for FeNi/SiO_2 nanocomposites is independent of frequency up to at least 100 MHz whereas the CoNi ferrite enters the ferromagnetic resonance region at $f > 10$ MHz and its μ' decreases dramatically with further increasing frequency. Because of instrumentation limit, we cannot measure frequency above 100 MHz. However, it is obvious that the trend will extend to higher frequency. Second, there is a rapid increase in the value of μ' when the coating is thin (3 nm) and the density reaches about 90% of the ideal density. For example, in the upper two curves, the value of μ' changes from 12 to 16, a 33% increase, whereas the density only increased about 6% (from 5.81 to 6.15 g/cm^3). This illustrates that, once the density reaches certain critical value, a little increase in density will result in large increase in permeability. The fact that it is observed in samples with a thin coating also indicates that the exchange interaction, rather than the dipolar interaction, is responsible for such a large increase in permeability, as discussed below.

Although the value of μ' of our samples is still lower than that of commercial ferrites, a more important figure of merit is the quality factor Q, which is the inverse of energy loss. The results are plotted in Figure 3b. Clearly, all of our samples have higher Q values than that of commercial CoNi ferrite at $f > 10$ MHz and the Q values decrease much more slowly with increasing frequency.

To corroborate the results, we also used a hysteresis loop tracer (Walker Scientific Inc., AMH-401A) to measure ac hysteresis loops[19] up to 1 MHz for FeNi/SiO_2 samples with a

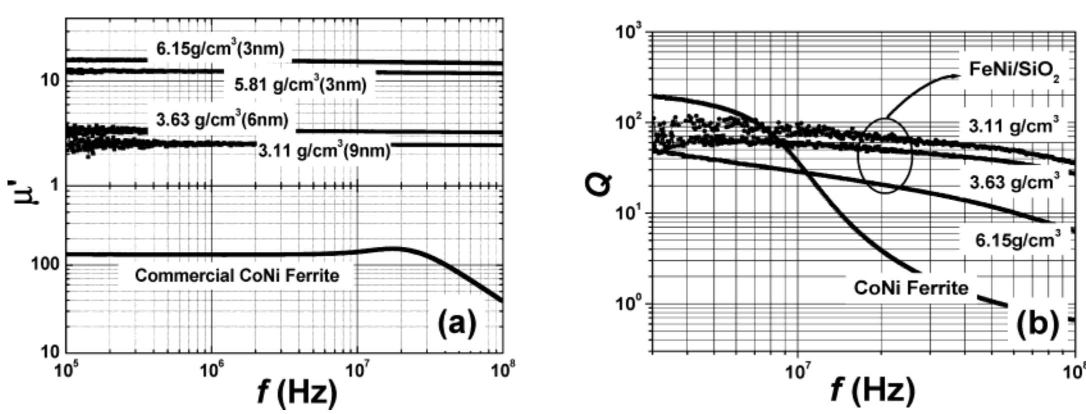

Figure 3. (a) Real part of permeability μ' as a function of the frequency for samples with different density (top panel, the silica coating thickness is indicated in the parentheses) in comparison with that of a commercial CoNi ferrite sample (bottom panel). (b) Quality factors as a function of the frequency for samples of difference density and the commercial CoNi ferrite.

density of 5.81 g/cm^3. The slope of the $B-H$ loops, thus the permeability, remains the same in the entire frequency range and the extracted value is about 13, which is consistent with the value shown above.

The permeability of powder based soft magnetic materials critically depends on the demagnetization factor in the sample. The relationship between the apparent permeability μ_{app} of an ellipsoid particle assembly and the true permeability μ of the material can be written as[20,21]

$$\mu_{app} = \frac{\mu}{1 + \frac{N}{4\pi}(\mu - 1)} \tag{1}$$

where N is the demagnetization factor of the ellipsoid particles in the direction of the measuring field. From this formula, one quickly finds the following conditions

$$N = 0 \qquad \mu_{app} = \mu$$

$$N = 4\pi \qquad \mu_{app} = 1$$

$$N = \frac{4\pi}{3} \qquad \mu_{app} = \frac{3\mu}{2 + u} \approx 3 \qquad \text{if} \qquad \mu \gg 1$$

For sphere particles as in our experiment, $N = 4\pi/3$ if the magnetic particles are not coupled. Even in a compacted sample, $N = 4\pi/3$ is still valid considering the random distribution of noninteraction particles. In other words, in materials with uncoupled particles, one would expect to see $\mu_{app} \sim 3$. This is exactly the case in our compacted samples with low densities, regardless of the coating thickness. On the other hand, if $\mu >> 1$, the demagnetization factor will be $N = 4\pi/\mu_{app}$. The highest μ_{app} we observed is 16 for a sample with 3 nm SiO_2 coating and a compaction ratio of 93%. Therefore the sample has an effective demagnetization factor $N = 4\pi/16$, which is 5 times smaller than $N = 4\pi/3$ as in the noninteracting particle assembly.

The reduction in the demagnetization factor arises from the coupling among particles. The coupling can be induced through direct exchange coupling and/or dipolar interaction. The direct exchange coupling will improve the soft magnetic properties, whereas the effect due to dipolar interaction is difficult to gauge. However, the dipolar interaction is a long range interaction and exists in all samples, including those with low density, suggesting the dipolar interaction is not the main contribution to improve the permeability. In addition, the dipolar interaction is unlikely to significantly increase the permeability by 33% when there is only a 6% change in density. The improvement in permeability most likely arises from the direct exchange coupling, which becomes more pronounced in samples with thin coatings and large densities. It should be pointed out that other experimental techniques such as small angle neutron scattering[22,23] may be useful to quantify the exchange coupling. The permeability in these materials can be further significantly improved by optimizing the coating thickness and most importantly the density. The method described here provides a promising route to achieve soft magnetic nanocomposite material with better magnetic properties than conventional soft ferrites in the high-frequency regime (>10 MHz).

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Supporting Information Available: Dynamic hysteresis loops of the FeNi/SiO_2 sample with density 5.81 g/cm^3. This material is available free of charge via the Internet at http://pubs.acs.org.

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