EXPRESS LETTER

Exchange-coupled Fe/Fe₃O₄ magnetic nanocomposite powder prepared by eutectoid decomposition of FeOSaeaki YAMAMURO^{1,†} and Toshiro TANAKA¹¹Department of Materials Science and Engineering, Faculty of Engineering, Ehime University,
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This report presents a new route to fabricating a ferrite-based magnetic nanocomposite consisting of a ferromagnetic metal (α -Fe) and a ferrimagnetic spinel ferrite (Fe₃O₄). The process is based on the eutectoid decomposition of FeO, leading to the formation of a lamellar nanostructure of α -Fe and Fe₃O₄. A sandwiched nanostructure of this type is preferable for exchange coupling between adjacent lamellae, because each lamella is subjected to exchange coupling via either side of the interface. It was found that decomposition of FeO takes place preferentially in the temperature range of 723–773 K, in which the decomposition is almost fully completed within 10 h. The room-temperature magnetization measurements gave rise to a high saturation magnetization above 100 emu/g, which is larger than that of single-phase Fe₃O₄. Since a smooth magnetization curve with single-phase-like behavior was observed despite the coexistence of two magnetic phases, the two phases could be magnetically exchange-coupled. Due to the ease of tuning the magnetic properties of the spinel ferrites with the substitution of constituent metal ions, the fabrication process described here could represent a potential route to making a variety of iron-based metal/ferrite magnetic nanocomposites.

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Since their discovery in 1930, ferrites have held a prominent position as technologically important materials, especially in the area of magnetic and electronic applications.^{1),2)} A good example of their applications is represented by hard ferrites (i.e., ferrite magnets), which are most commonly used as permanent magnets due to their chemical stability and cost effectiveness. Because these magnets are made entirely from iron-based oxides, the saturation magnetization is relatively low in comparison to such metal magnets as alnico magnets. In recent years, the concept of nanocomposite permanent magnets has attracted a great deal of attention^{3),4)} and has been investigated mainly with respect to rare-earth magnets^{5)–7)} and other hard magnetic materials such as L1₀-FePt.⁸⁾ These magnets comprise a nanoscale mixture of a hard magnetic phase with large magnetic anisotropy and a soft magnetic phase with high magnetization. The two phases are exchange-coupled via their interfaces, acting like a single magnetic phase. Such exchange coupling of the two phases is expected to yield enhanced remanence and hence, a high-energy product. Since exchange coupling is effective within the so-called “exchange-length scale”,^{3),4)} it is crucial to obtain a nanoscale composite of the magnetically hard/soft phases.

The concept of a nanocomposite magnet has also been applied to the ferrites (mainly hard ferrites) to improve their magnetic properties. Some attempts have been made to fabricate ferrite-based magnetic nanocomposites composed solely of iron-based oxides, i.e., a mixture of soft/hard ferrites, using powder metallurgical and/or colloidal approaches.^{9)–11)} Ferrite-based nanocomposites containing a magnetic metal (usually iron and/or an iron-based alloy) have also been fabricated by colloidal processes.¹²⁾ In the latter case, one of the major issues is ascribed to the difficulty of fabricating a suitable nanostructure consisting of a ferromagnetic metal and a specific iron oxide phase. This is largely owing to the chemical reactivity of metallic irons in the nanoscale dimension and the existence of many kinds of iron oxides.

In this report, we present a new route to fabrication of ferrite-based magnetic nanocomposites consisting of a nanoscale mixture of a ferromagnetic metal (α -Fe) and a ferrimagnetic spinel ferrite (Fe₃O₄). The process is based on the eutectoid reaction of wüstite (FeO), which decomposes into a lamellar nanostructure of Fe and Fe₃O₄, much like pearlite formation, which takes place during a slow cooling of austenite in an Fe–C system.¹³⁾ The sandwiched nanostructure appearing in the lamellar nanostructure is preferable for exchange coupling between neighboring lamellae, because the exchange coupling is effective on either side of each lamella’s interface. We investigated the

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optimum annealing conditions for the decomposition of FeO. Magnetic characterization of the nanocomposite powder formed was also performed by room-temperature magnetization measurement.

In the present experiments, Fe powder (99.9% purity, 45 μm pass) was purchased from Wako Pure Chemical Industries, Ltd., and Fe_3O_4 powder (90% purity, c.a. 1 μm) from Cojundo Chemical Laboratory Co., Ltd. To obtain the FeO phase, the Fe powder (0.169 g) and Fe_3O_4 powder (0.831 g) were mixed at an atomic ratio of $\text{Fe}:\text{O} = 49:51$, which is close to the eutectoid composition of FeO. The powder mixture was then ground with a mortar and a pestle for 15–20 min in a nitrogen atmosphere. It was then pressed into pellets ($\phi 10$ mm) by applying a mechanical load of 3.8 ton. The pellets were vacuum-sealed in a quartz tube at a base pressure of $(1-2) \times 10^{-4}$ Pa. The sealed quartz tube was heated in an electric furnace at 873 K for 10 h to promote a solid-phase reaction among the Fe and Fe_3O_4 powders. After the calcination was completed, the quartz tube was quickly taken out of the furnace, and air-cooled to room temperature.

To thermally decompose the FeO phase, each pellet was annealed again in an electric furnace at a predetermined temperature for 10 h without fracturing the quartz tube. The annealing temperature was varied from 573 to 823 K. During this annealing period, the FeO phase was decomposed into a mixture of Fe and Fe_3O_4 by eutectoid reaction. After the annealing was completed, the quartz tube was removed quickly from the furnace and air-cooled to room temperature.

The obtained products were removed from the quartz tube and crushed easily into powder using a mortar and a pestle in an inert atmosphere. The powder specimens were examined by X-ray diffraction (XRD) measurement to determine their crystal structure. We used a Rigaku GeigerFlex X-ray diffractometer, in which $\text{Cu K}\alpha$ radiation was irradiated. We also measured the magnetization curves at room temperature using a vibrating sample magnetometer in a field range from -8 to $+8$ kOe.

A representative XRD pattern of the FeO powder obtained by calcinating a mixture of starting powders at 873 K for 10 h is shown in **Fig. 1(a)**. The referenced peak data for FeO are also shown as a bar chart in **Fig. 1(b)**. The profile in **Fig. 1(a)** exhibits a series of sharp peaks, which closely match the FeO phase (depicted with closed circles in the figure). Based on an analysis conducted by extrapolating the lattice spacings for all these peaks in a plot of lattice spacings versus $\cos^2\theta$, the lattice constant was found to be 0.430 nm. This value is closely consistent with the referenced value of FeO, which generally ranges from 0.428 to 0.431 nm, depending on the iron deficiency in a nonstoichiometric Fe_xO crystal ($x < 1$).^{14),15)} A broad, weak shoulder peak is also seen at around $2\theta = 30-35^\circ$, moreover (depicted as a closed upturned triangle). Since Fe_3O_4 has a (311) main peak at $2\theta = 35.4^\circ$ together with a (220) peak at $2\theta = 30.1^\circ$, the broad peak may originate from a slight amount of Fe_3O_4 with poor crystallinity.

Fig. 1. (a) XRD pattern of FeO powder obtained by calcination of the starting powder mixture at 873 K for 10 h, and (b) bar chart of the referenced peak data of FeO. The inset shows an enlarged profile of the FeO powder.

Fig. 2. XRD patterns of the specimens after thermal decomposition of FeO at different temperatures.

Figure 2 shows the XRD patterns of the specimens after thermal decomposition of the FeO powder at different temperatures. When decomposed at 823 K, which is just below the eutectoid temperature (843 K) of FeO, the most intense peak at $2\theta = 35.4^\circ$ is assigned to the main peak of Fe_3O_4 (the closed upturned triangle). Peaks from Fe are also detected at $2\theta = 44.7$ and 65.0° (the closed squares), indicating that decomposition of FeO into Fe and Fe_3O_4 takes place. Since the peaks from the initial FeO phase still remain to some extent (the closed circles), however, it can be said that the thermal decomposition of the FeO phase is not yet completed under these annealing con-

ditions. This is due to insufficient supercooling to drive the decomposition.

By contrast, the specimens that were decomposed at 773 and 723 K show a series of sharp peaks corresponding almost entirely to Fe and Fe₃O₄, although a faint peak from FeO is also detected at the position of its main peak ($2\theta = 35.4^\circ$). This result suggests that the decomposition of FeO is nearly complete. When the annealing temperature is decreased further from 723 to 573 K, the intensity of the Fe₃O₄ peaks is gradually reduced. At 573 K, the most intense peak comes instead from FeO. This is attributed to suppressed atomic diffusion among the powders in the mixture due to the lowered annealing temperature.

To estimate the lamellar width, Scherrer analysis was applied to a specimen that was decomposed under the optimum annealing temperature (773 K). The crystallite size was estimated as 40–50 nm using several peaks of Fe₃O₄ from (111) to (440). Scherrer analysis was also applied to the three representative peaks of Fe in the same specimen, ranging from (110) to (211), resulting in an estimated crystallite size of about 40 nm. Though details of the crystallographic relation between the two phases are unknown, all these values are on the order of tens of nanometers and, hence, could be comparable to the lamellar width. This result is consistent with the result for the other group where the lamellar widths of Fe and Fe₃O₄, prepared by the eutectoid reaction of FeO, are 20 nm and 60 nm, respectively.¹⁶⁾

The room-temperature magnetization curves for the as-made FeO powder and a representative Fe/Fe₃O₄ nanocomposite powder decomposed at 723 K are shown in **Fig. 3**. The inset shows an enlarged magnetization curve for the as-made FeO powder. The magnetization curve for the as-made FeO powder shows significantly reduced magnetization (about 4 emu/g at 8 kOe) owing to the antiferromagnetic nature of FeO. A weak ferromagnetic feature is also observed, however, as a nonlinear enhancement of magnetization and a magnetic hysteresis (see the

Fig. 3. Room-temperature magnetization curves of the as-made FeO powder and Fe/Fe₃O₄ nanocomposite powder, the latter of which was made by decomposition of the FeO powder at 723 K for 10 h. The inset shows an enlarged magnetization curve for the as-made FeO powder.

inset). Since FeO is intrinsically an antiferromagnet, this ferromagnetic feature is possibly attributable to the existence of a slight ferrimagnetic Fe₃O₄-like phase.

When the as-made FeO powder is thermally decomposed at 723 K for 10 h, the ferromagnetic behavior is considerably enhanced, as shown in **Fig. 3**. The magnetization reaches 101 emu/g at 8 kOe, and the coercive force is 340 Oe. The magnetization value is much larger than the room-temperature saturation magnetization of Fe₃O₄ (~92 emu/g),¹⁾ even though the magnetization curve is not saturated at 8 kOe. Such high magnetization is ascribed to the presence of the Fe phase, which has a large saturation magnetization (217 emu/g) at room temperature.¹⁷⁾ It should be noted that the magnetization of the decomposed specimen shows a smooth curve with no shoulders, despite the coexistence of two magnetic phases. Since the deficiency in exchange coupling in a magnetic nanocomposite often results in the appearance of shoulders in its magnetization curve,^{9),10)} this smooth curve could be an indication that the two phases are exchange-coupled.

Figure 4 shows the saturation magnetization as a function of the decomposition temperature. As shown in this figure, the specimens decomposed at 673–773 K show high saturation magnetizations, indicating that the decomposition of FeO takes place preferentially. Of particular note, a high saturation magnetization above 100 emu/g is obtained at the decomposition temperatures of 723–773 K. This result is consistent with the XRD result shown in **Fig. 2**.

In the present work, the values of the first-order magnetocrystalline anisotropy K_1 for Fe and Fe₃O₄ at room temperature are 4.8×10^4 and -0.9×10^4 J/m³,¹⁸⁾ respectively; thus, Fe₃O₄ is slightly softer than Fe in the bulk state. The critical dimension, within which the exchange coupling is effective in the soft phase, is given by^{3),4)}

$$b_{cs} = \pi \sqrt{A_s / 2K_h},$$

where A_s is the exchange stiffness constant of the soft magnetic phase, and K_h the magnetocrystalline anisotropy of the hard magnetic phase. Here, A_s for Fe₃O₄ is assumed to be $\sim 1.0 \times 10^{-11}$ J/m,¹⁹⁾ and K_h for Fe to be 4.8×10^4

Fig. 4. Room-temperature saturation magnetization of the specimens decomposed at different temperatures for 10 h. The applied magnetic field was 8 kOe.

J/m^3 . Using these values, b_{cs} is estimated to be ~ 30 nm. If a sandwiched nanostructure consisting of hard/soft magnetic phases is formed, the actual dimension required for the soft phase is $2b_{\text{cs}} \sim 60$ nm. Since this value is comparable to the estimated dimension of the crystallite size for Fe_3O_4 (i.e., 40–50 nm), exchange coupling between the Fe and Fe_3O_4 phases would be effective in the present specimens.

In conclusion, Fe/ Fe_3O_4 nanocomposite powders were prepared by eutectoid decomposition of FeO powder. The annealing temperature suitable for the decomposition of FeO was determined to be 723–773 K, at which the decomposition is almost fully completed within 10 h. Owing to the presence of Fe, the Fe/ Fe_3O_4 nanocomposite gave rise to a high saturation magnetization above 100 emu/g, which exceeds the value for Fe_3O_4 . A smooth magnetization curve with single-phase-like behavior was also observed, despite the coexistence of two magnetic phases, suggesting exchange coupling between the two phases. The present fabrication process can be applied to other spinel ferrites to make a variety of iron-based metal/ferrite magnetic nanocomposites by substituting the constituent metal ions in the ferrites.

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