Direct Iron Coating onto Nd-Fe-B Powder by Thermal Decomposition of Iron Pentacarbonyl

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Abstract. Iron-coated Nd-Fe-B composite powder was prepared by thermal decomposition of iron pentacarbonyl in an inert organic solvent in the presence of alkylamine. Though this method is based on a modified solution-phase process to synthesize highly size-controlled iron nanoparticles, it is in turn featured by a suppressed formation of iron nanoparticles to achieve an efficient iron coating solely onto the surfaces of rare-earth magnet powder. The Nd-Fe-B magnetic powder was successfully coated by iron shells whose thicknesses were of the order of submicrometer to micrometer, being tuneable by the amount of initially loaded iron pentacarbonyl in a reaction flask. The amount of the coated iron reached to more than 10 wt.% of the initial Nd-Fe-B magnetic powder, which is practically sufficient to fabricate Nd-Fe-B/α-Fe nanocomposite permanent magnets.

1. Introduction
Nanocomposite permanent magnets currently gain a growing attention because of their potential superiorities of enhanced remanence and high energy product in the range of reduced rare-earth content [1-3]. These magnets are comprised of a fine mixture of a magnetically hard phase with a large magnetic anisotropy and a magnetically soft phase with a high magnetization. The two phases are preferred to have intimate contacts to be exchange-coupled via their interfaces. Since such interaction is effective at the exchange length scale, the two phases are preferably mixed in the nanoscale order [1]. Since the strict nanostructural control of such a bulk nanocomposite is hardly achieved by the metallurgical processes, the fabrication of soft/hard magnetic composite powder is an alternative approach that is followed by their subsequent consolidation and sintering. Some attempts have been made to prepare composite magnetic powders consisting of rare-earth magnetic powder (either Sm-Co or Nd-Fe-B system) mixed/coated by metallic α-Fe using mechanical [4-6], sonochemical [7] and colloidal approaches [8]. A major difficulty ascribes to the highly reactive nature of both rare-earth

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magnet and $\alpha$-Fe phases, which restricts the available processes to make composite powders. A sufficiently low content of impurities such as oxygen is also strongly required.

Here, we present a new solution-phase coating process of soft magnetic iron onto the surfaces of rare-earth magnet powders. Since the coating reaction is carried out under the inert conditions using hydrocarbon solvent and argon atmosphere, severe oxidation and undesired reactions between rare-earth magnet powder and reagents are largely suppressed. The process is also characterized by the use of highly anisotropic Nd-Fe-B powder that is prepared by the hydrogenation-disproportionation-desorption-recombination (HDDR) process. Such HDDR-processed Nd-Fe-B powder is anticipated to ensure a high magnetic coercivity even in the reduced size range of powder particles and lead to a magnetically anisotropic bulk nanocomposite [3].

2. Experimental

The present method of iron coating is based on a modified wet process that is used for high-quality iron nanoparticles synthesis via thermal decomposition of iron pentacarbonyl (Fe(CO)$_5$) [9,10]. However, the process used here is featured by the suppressed formation of iron nanoparticles to achieve an efficient iron coating onto the surfaces of rare-earth magnet powder. This carbonyl complex is used as an iron source that generates neutral iron atoms when it is thermally decomposed in an inert organic solvent in the presence of surfactant. These iron atoms give rise to a direct coating without any reducing treatment of metal ions. The chemical stability of organic reagents at elevated temperature is also important to avoid undesirable reactions with highly reactive Nd-Fe-B magnet powders. After a series of examinations, hydrocarbons and alkylamines were found to be suitable for solvent and surfactant, respectively. Even after a mixture of these reagents (either dodecane or dioctylamine) and HDDR powder was heated at 200 °C for 2 h in an argon gas atmosphere, a severe damage was not detected in the x-ray diffraction profiles and demagnetization curves of the reacted HDDR powder, though a slight decrease in remanence and coercivity was observed (see Fig. 1(a) and 1(b)). In this reaction, the surfactant plays a crucial role to preferentially coat onto the rare-earth magnet powder.

![Figure 1](image_url)

**Figure 1.** The chemical reactivity between HDDR magnetic powder and chemical reagents (dodecane and dioctylamine) after being heated at 200 °C for 2 h: (a) x-ray diffraction patterns and (b) demagnetization curves.

In a typical reaction, 4 g of Nd-Fe-B powder (50–100 μm) was mixed in 30 mL of dodecane with 0.2 mL of dioctylamin in a flask. The solution mixture was mechanically stirred for 1 hour under an Ar gas flow, and then rapidly heated to 100 °C. 1–5 mL of Fe(CO)$_5$ was then introduced into the flask via a syringe and the temperature was hold in a couple of minutes. Temperature was then increased to 180 °C and was hold for 4 h. On the reaction, the yellow color originating from Fe(CO)$_5$ was gradually diminished in the flask. After the reaction was finished, the solution was air-cooled to
room temperature. The powder is then collected via filtration and washed by hexane under nitrogen gas atmosphere. The product was examined with a Carl Zeiss Crossbeam 1540 energy selective backscattered scanning electron microscope (SEM). The compositional analysis was carried out by the inductively coupled plasma (ICP) method.

3. Results and Discussion
The appearance of Fe-coated HDDR magnetic powder exhibited an increased gray color. When these powder samples were handled in air, they were rapidly oxidized with a smoke due to the existence of highly reactive Fe surface layers. Since the coated iron formed by this process has an amorphous-like crystal structure [10], the x-ray diffraction measurement does not provide a meaningful result. The SEM observation was instead performed for Fe-coated HDDR powders. As shown in Fig. 2(a), the surface of each powder particle is attached by a number of small granules that are presumably the fragments of the coated iron layers. One of these particles is etched with a focused ion beam (FIB) of Ga ions and the cross section is observed with a backscattered electron (BSE) SEM. As shown in Fig. 2(b), the surface of the particle is covered by an iron shell that has a bumpy morphology and does not uniformly coat over the entire surface of the particles (see the upper dark region in Fig. 2(b)). However, it can be seen that the iron surface layer fills well into the morphologically uneven surface of the HDDR particle. The thickness of the Fe shell is estimated to be about submicrometer-to-micrometer order (The arrows in Fig. 2(b) show the cross-sectional thickness of coated iron layer). Since such a thick layer of soft magnetic iron is apparently too large for exchange coupling in comparison to the theoretically estimated dimension [1], the fabrication of finer HDDR powders and thinner iron layers is strongly desirable.

![Figure 2](image)

**Figure 2.** (a) Low magnification SEM image of Fe-coated HDDR magnetic powder and (b) cross-sectional BSE image of a Fe-coated HDDR particle etched by a focused Ga ions beam. The images were taken by tilting the specimen by an angle of 35 °. 1 mL of Fe(CO) 5 was used in the Fe coating reaction.

To examine the tuneability of coated Fe amount, a straightforward way is varying the amount of iron source during the reaction. As shown in Fig. 3, the mass of coated Fe layers is increased by increasing the amount of initially loaded Fe(CO) 5 into the reaction flask. In the present experiments, the maximum value reached to more than 10 wt.% of the initial Nd-Fe-B magnetic powder when 5 mL of Fe(CO) 5 was served for the coating reaction. Though this value is comparable to the one required for the fabrication of Nd-Fe-B/α-Fe nanocomposite permanent magnets, the coating efficiency is not satisfactory yet; our simple calculation showed that only 1/4–1/3 of loaded Fe(CO) 5 was used for Fe coating onto HDDR powder. The major cause of such a low efficiency is ascribed to the undesirable coating onto the inner wall of flask. Another issue is the incorporation of impurities such as oxygen and carbon elements into the Fe-coated HDDR powder though inert environment was employed.
during the reaction. This largely deteriorates the magnetic properties. The EPMA mapping analysis showed that these elements are preferentially accompanied by the coated Fe phase. The minimization of these impurities is currently underway.

![Figure 3. The relation between the amounts of loaded Fe(CO)_5 and coated Fe.](image)

4. Conclusion
A new solution-phase technique of iron coating onto Nd-Fe-B magnetic powder was reported. This is based on a modified process to synthesize high-quality iron nanoparticles by thermal decomposition of iron pentacarbonyl in an inert organic solvent in the presence of alkylamine. The Nd-Fe-B magnetic powder was successfully coated by iron shells that are bumpy and uneven in thickness. The typical thickness of the coated iron shell was of the order of submicrometer to micrometer. The amount of coated Fe was tuneable by the amount of initially loaded iron pentacarbonyl in a reaction flask. The maximum amount of the coated iron reached to more than 10 wt.% of the initial Nd-Fe-B magnetic powder, which is practically sufficient to fabricate Nd-Fe-B/α-Fe nanocomposite permanent magnets.

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