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# Microwave absorption properties of the nano-composite powders recovered from Nd–Fe–B bonded magnet scraps

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## Abstract

Nd–Fe–B bonded magnet scraps were recovered as the nano-composite powders composed of α-Fe, $Fe_xB$ and $Nd_2O_3$ by a disproportionation method and their electromagnetic wave absorption properties at the GHz range were characterized to recycle them as efficient absorbers. The bonded magnet scraps decomposed to $NdH_2$, $Fe_xB$ and α-Fe at 873 K for 30–60 min in $H_2$, of which $NdH_2$ was converted to the corresponding fine particles of $Nd_2O_3$ by the subsequent oxidation at room temperature for 120 min in air. Resin-bonded discs prepared from the composites powders of α-Fe/$Fe_xB$/$Nd_2O_3$ (mean diameter ≅ 20 nm), $Fe_xB$ (amorphous) and $Nd_2O_3$ particles showed the excellent electromagnetic wave absorption ability in a frequency range of 4.0–6.7 GHz, which shifted to the high GHz region side compared with binary composite ones of α-Fe/rare earth oxide.

*Keywords:* Recycling; Rare earth bonded magnets; Nd–Fe–B intermetallic compound; Magnet scraps; Electromagnetic microwave absorbers

## 1. Introduction

Recently, electromagnetic waves (EM) have been used in various industrial applications, such as satellite broadcasting, local area network (LAN) system and mobile phone, so that the demand for the utilization of GHz range microwaves has drastically increased and some electromagnetic interference (EMI) problems, as a result, have become serious as well as the baneful influences on human bodies. To dissolve the above problems, spinel type ferrites have been used as magnetic materials for EM absorbers for instance. However, such spinel type ferrites are limited in the applied frequency range because their Snoek's limit [1] is so small that the imaginary part of permeability is considerably lowered in GHz range. On the other hand, metallic soft-magnet powders certainly have excellent EM absorption ability in the high frequency range than spinel type ferrites because the former materials is free from such Snoek's limit at GHz ranges.

Sugimoto and co-workers [2,3] have reported that the good EM absorption properties in the 0.73–1.30 GHz range are observed on the α-Fe/SmO composite powders by preparing the disproportionation processes of hydrogenation and oxidation for $Sm_2Fe_{17}$. In the α-Fe/SmO nano-composite, the fine α-Fe particles were electrically isolated from one another by the insulating barrier of SmO to reduce the eddy current loss. Liu et al. [4,5] have also similarly prepared composites with rare earth oxides, such as α-$Fe_3N$/$Y_2O_3$ and FeCo/$Y_2O_3$, prepared and found the good EM absorption properties in the 0.6–4.4 and 2.7–8.1 GHz, respectively.

The Nd–Fe–B sintered magnets have been widely used as various powerful and/or small-sized motors, magnetic field generators and so on due to excellent magnetic properties. In the former case, however, a large amount of the magnet scraps, such as slug or sludge, are consequently generated in the mass production processes for melting the raw metals and cutting into the small pieces with demanded sizes. Yamashita [6] have reported that the scraps of the bonded magnet collected from the waste electric devices can be effective used again as the same bonded magnets from the recovered magnetic powders by dissolving the resin using the chemical process.

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Recently, Machida et al. [7] have applied the above mentioned disproportionation processes to recycle the slug or sludge scraps of Nd–Fe–B sintered magnets as α-Fe/$Fe_xB$/$Nd_2O_3$ nano-composite powder for EM absorbing materials in the GHz range. The Nd–Fe–B bonded magnets with good of molding formability are also widely used in the industrial fields and the main small-sized motors. In the present study, we proposed a simple recycle process for the bonded magnet scraps to the nano-composite magnet powders as the EM absorbers.

## 2. Experimental

The Nd–Fe–B bonded magnet scraps were ground into coarse powders with a diameter of several hundred micrometers under an Ar atmosphere by a tungsten carbide mortar. The powder obtained was packed into a stainless pot (50 ml) with a small amount of dioctyl sulfosuccinate sodium as a surfactant and 10 metal balls (9.5 mm Ø) and 10 ml of dehydrated *n*-hexane pulverized by the planetary-type apparatus (FRITSCH Japan P-7) ball mill at 400 rpm for 10 h. After ball-milling, powders were washed several times by the dehydrated *n*-hexane to remove the surfactant and then dried in vacuum. Hydrogenation disproportionation (HD) treatments for the above magnet scrap powders were carried out at 423 K for 60 min and subsequently at 873–973 K for 10–60 min in $H_2$ stream. After the HD treatments, the powders were oxidized at room temperature for 120 min in air. The XRD measurements were performed on the RIGAKU RINT 2200 diffractmeter equipped with a Cu Kα radiation. From the (1 1 0) peak of α-Fe in the XRD patterns, the mean diameter of α-Fe crystalline size was evaluated according to the Scherrer's formula.

$$t = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where *t* is the crystalline size of particle (Å), λ the wave length of Cu Kα radiation (1.54050 Å), *β* the full width of half maximum (FWHM) of the peak and *θ* is the scan angle for X-ray diffraction (XRD). Scanning electron microscope (SEM) images were obtained by HITACHI X-650. Magnetic properties of the obtained powder were measured with a vibrating sample magnetometer (VSM, TAMAKAWA TM-VSM2014-MHR type) in a range of magnetic field up to 1.6 MA/m at room temperature. To characterize the EM absorption properties over the GHz region, the disc shaped compacts with ∼2.5 mm thickness were prepared from the mixture of magnet powder and 30 wt% of epoxy resin by heating them at 403 K for 30 min and subsequently heating at 453 K for 30 min. Then, the discs were cut into ring-shaped samples with 7.00 mm outer diameter and 3.04 mm inner diameter using the ultrasonic cutter (CHO-ONPA KOUGYOU UM-2-7D). EM absorption properties of the resulting resin composite were characterize by Agilent Technology 8720B network analyzer in a range of 0–8 GHz. The complex permeability ($\mu_r = \mu' - j\mu''$) and the permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) were determined the reflection parameters ($S_{11}$, $S_{22}$) recorded and the transmitting parameters ($S_{12}$, $S_{21}$) on the network analyzer. The normalized input impedance in the foreface of absorber ($Z_{in}$) and the reflection loss (RL) of absorber was evaluated with following equations.

$$Z_{in} = Z_0\left(\frac{\mu_r}{\varepsilon_r}\right)^{1/2}\tanh\left\{j\left(\frac{2\pi fd}{c}\right)(\mu_r\varepsilon_r)^{1/2}\right\} \tag{2}$$

$$RL = 20\log\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right| \tag{3}$$

where *f* is the frequency of EM, *d* the thickness of absorber, $Z_0$ the impedance of air and *c* is the velocity of the light. These calculations were conducted by using a model of impedance matching type for microwave absorbing material.

## 3. Results and discussion

In this study, the resins of Nd–Fe–B bonded magnets were pyrolyzed by HD treatments. The XRD patterns of nano-composite powders recovered by the HD treatment at various reaction conditions and subsequent oxidation are shown in Fig. 1 together with the as-obtained powders after ball-

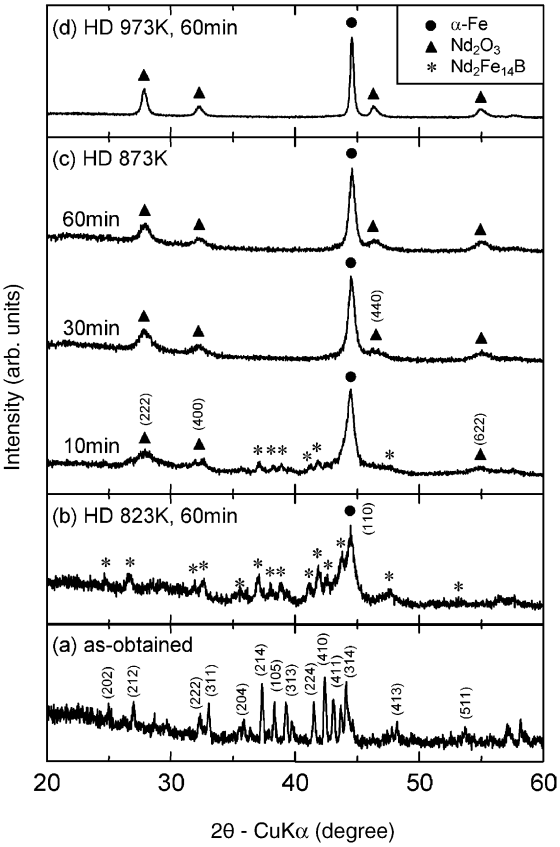

Fig. 1. X-ray diffraction patterns of (a) as-obtained powder after ball-milling, (b) after hydrogenation–disproportionation at 823 K for 60 min, (c) at 873 K for 10–60 min and (d) at 973 K for 60 min.

Table 1
HD reaction conditions and FWHM of (1 1 0) reflection of α-Fe, mean diameter of α-Fe and coercivity of resulting sample powders

| HD reaction condition | | FWHM (°) | Mean diameter (nm) | Coercivity (kA/m) |
|---|---|---|---|---|
| Temperature (K) | Time (min) | | | |
| As-obtained | | – | – | 605 |
| 823 | 60 | – | – | 154 |
| 873 | 10 | 0.568 | 15.1 | – |
| | 30 | 0.533 | 16.0 | 15.9 |
| | 60 | 0.513 | 16.7 | 19.7 |
| 923 | 60 | 0.363 | 23.6 | 16.0 |
| 973 | 60 | 0.313 | 27.4 | 26.5 |
| 1073 | 180 | 0.344 | 25.0 | – |

milling. Table 1 summarizes the FWHMs of (1 1 0) diffraction peak of α-Fe, mean diameters of α-Fe particle and coercivity ($H_{cJ}$) values for the above samples. The as-obtained scrap powder gave a typical diffraction pattern of $Nd_2Fe_{14}B$ primary phase as labeled by asterisks. After the HD treatment at 823 K for 60 min and subsequent oxidation, a broad peak of α-Fe labeled by the close circle symbol was observed at around $2\theta = 44°$. However, the peaks of $Nd_2Fe_{14}B$ primary phase were still observed and this sample showed the high $H_{cJ}$ value (154 kA/m), suggesting that the HD reaction was not completely finished. For the samples hydrogenated at 873–973 K and oxidized, the peaks of α-Fe and $Nd_2O_3$ (symbols of the close triangle) were observed. As listed in Table 1, their low $H_{cJ}$ (15.9–26.5) values were responsible for the complete decomposition of Nd–Fe–B phase. For the series of above powders hydrogenated at various temperatures, Nd–Fe–B sample powders firstly uptake large amount of $H_2$ at 423 K, then decompose into $NdH_2$, α-Fe and $Fe_xB$ composite at high temperature [7]. However, an excessive hydrogenation at high temperature treatment may results in a growth of primary particle (Table 1). For the EM absorbing material, smaller particle size is favorable to prevent the decrease of permeability induced by the eddy current. Thus, the optimum reaction temperature in this study was found to be 873 K, which led the complete decomposed of the Nd–Fe–B phase with the small size of primary particle of α-Fe. After the oxidation treatment of sample powders, α-Fe/$Fe_xB$/$Nd_2O_3$ composites were obtained because of the higher reactivity of $NdH_2$ against oxygen than that of α-Fe. Fig. 1(c) shows the series of the XRD patterns of sample powders after HD treatments for various reaction time (10–60 min) and the following oxidation. For the sample hydrogenated for 10 min, peaks of α-Fe and $Nd_2Fe_{14}B$ primary phases were co-existed because of the short HD treatment time. The longer time for HD treatments of (30 and 60 min) provides the formation of α-Fe/$Fe_xB$/$Nd_2O_3$ nano-composites, while the mean diameter of α-Fe particle increases along with increasing reaction time (Table 1). From these results, the HD treatment at 873 K for 30 min is the optimal condition and the smallest of α-Fe particle (16 nm) was obtained in this reaction condition. Peaks of $Fe_2O_3$ were not observed by the HD and oxidization treatments in this study. In addition, no peak assigned to the $Fe_xB$ phase was observed in the diffraction patterns of α-Fe/$Fe_xB$/$Nd_2O_3$ nano-composites. It is considered that the amount of $Fe_xB$ in nano-composite is too small to detect by the XRD measurement. The formation of $Fe_xB$ phase, however, was confirmed in the other nano-composite material α-Fe/$Fe_xB$/$Y_2O_3$ prepared by $Y_5Fe_{77.5}B_{17.5}$ metal ribbons using the similar method in own precious study [8].

Fig. 2 shows the SEM images (a) as-obtained, (b) HD treated at 873 K for 60 min and (c) subsequently oxidized at room temperature for 120 min. As shown in Fig. 2(a), average of secondary particle size of the sample powders was about 1–3 μm. The secondary particle size was not changed both after hydrogenation (b) and oxidation (c). This suggests that the growth of the particle is effectively suppressed by the optimization of preparation condition of the above nano-composite, especially by gradual oxidation at room temperature. Furthermore, it is considered that the fine α-Fe particles were surrounded by the $Nd_2O_3$ particles, their conditions were similar to the transmission electron microscope (TEM) image on $Fe_3N/Y_2O_3$ [4], which prepared by the similar disproportionation method reported previously.

Frequency dependences of EM absorption properties of the samples: (a) as-obtained, (b) the HD treated at 873 K for 30 min and oxidized at room temperature for 120 min and (c) the HD treated at 1073 K for 180 min and oxidized at room temperature for 120 min, are shown in Fig. 3. For the sample (a), the effective RL was not observed in 0–8 GHz region because of a high natural resonance frequency of $Nd_2Fe_{14}B$ (190 GHz). The slight RL value (∼−6 dB) observed at around 7 GHz may come from a little amount of α-Fe phase precipitated during the ball-milling process. Sample (b) shows excellent RL values in 2.2–7.2 GHz. Especially, RL values smaller than −20 dB at 4.0 and 6.7 GHz were attained when the matching thickness ($d_m$) were 3 and 2 mm, respectively. The good absorption properties in these regions are ascribed to the precession movement of α-Fe under the EM field; however, the regions obtained in this study are rather higher than the natural resonance frequency value of a spherical Fe particle (1.5 GHz). The shift to the highest region (over 1.5 GHz) on this sample is due to the shape anisotropy of the lamella structure consisted of nano-sized α-Fe, $Fe_xB$ and $Nd_2O_3$ [3]. This microstructure could be achieved by the effective HD and oxidation treatments performed in this study. In fact, the natural resonance frequency for a rod-like Fe particle is calculated to be ∼9 GHz. The natural resonance frequency of $Fe_3B$ is also located at high range of 14 GHz. The amount of $Fe_3B$ in the nano-composite is, however, vanishingly very small compound to that of α-Fe, so that the anisotropic α-Fe particle in shape can be estimated as a or the main medium to absorb electromagnetic wave. Sample (c) shows worse RL values, poor EM absorption properties, in contrast to the sample (b). Small RL values were observed at 1.2–4.2 GHz region

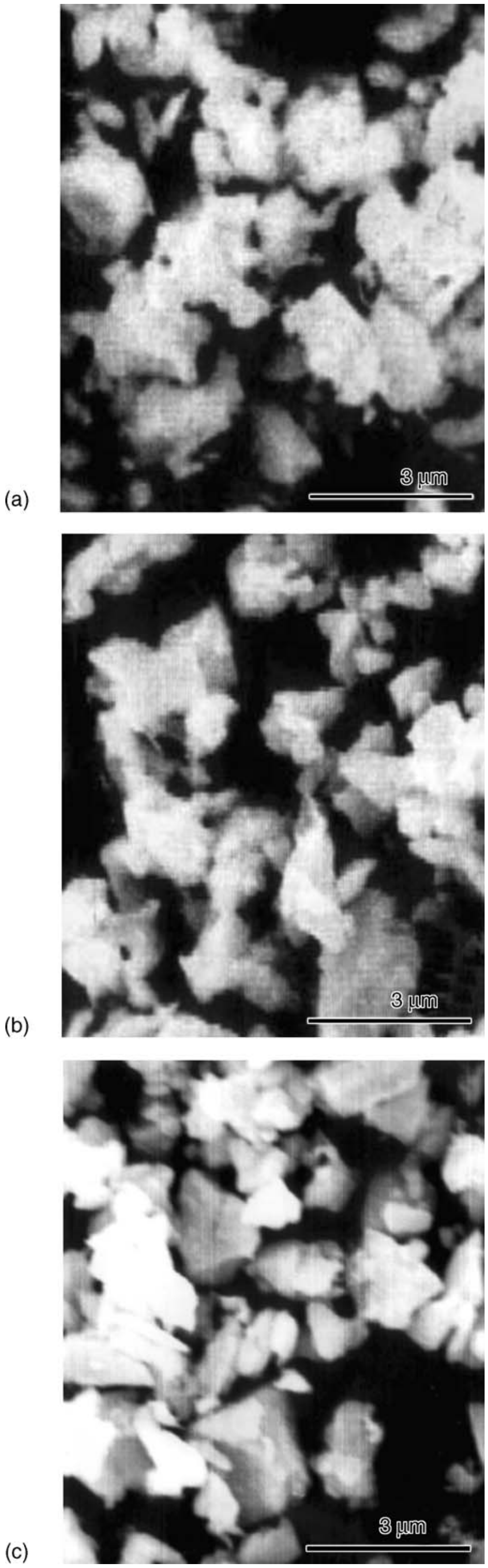

Fig. 2. SEM images of (a) as-obtained, (b) HD treated at 873 K for 60 min and (c) subsequently oxidized at room temperature for 120 min.

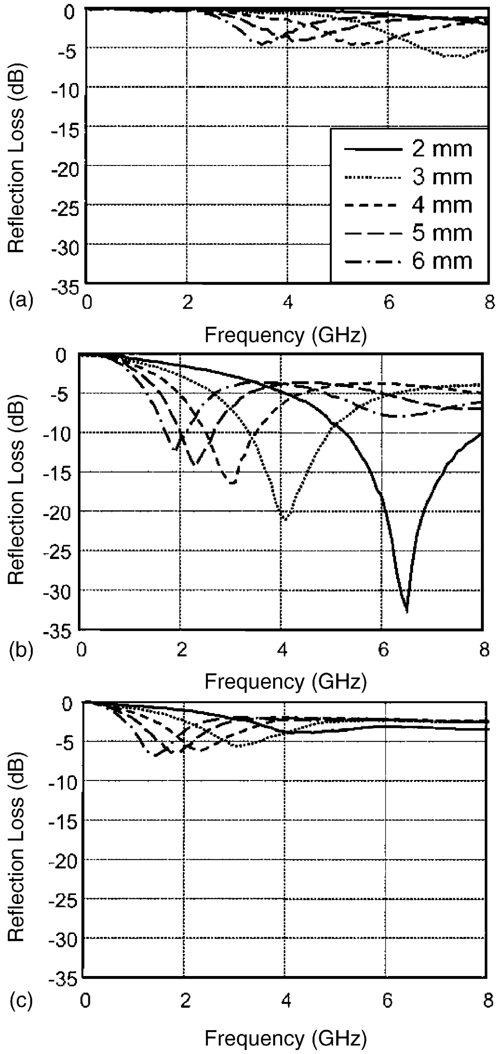

Fig. 3. Frequency dependence of EM absorption properties for resin composites with (a) as-obtained, (b) HD treated at 873 K for 60 min and subsequently oxidized at room temperature for 120 min and (c) HD treated at 1083 K for 180 min and subsequently oxidized at room temperature for 120 min.

(−7.5 to −5 dB). This is due to the large size α-Fe particle (25 nm) in the composite caused by the growth of the primary particles during the excessive high temperature and long time for HD treatment (1073 K, 180 min).

## 4. Conclusions

The conclusions obtained in this work are as follows:

(1) Through the hydrogenation and subsequent oxidation, the Nd–Fe–B magnet scraps are recovered to the nano-composites powders of α-Fe/Fe$_x$B/Nd$_2$O$_3$.

(2) The magnetic anisotropy of such nano-composite powders is high compared with those of α-Fe/rare earth oxides derived from rare earth–iron intermetallic compounds, so that the effective EM absorption proper-

ties of α-Fe/$Fe_xB$/$Nd_2O_3$ are observed in the higher range (4.0–6.7 GHz) than those of the α-Fe/rare earth oxides.

(3) It can be seem from these results that the used rare earth bonded magnet scraps are effectively recycled as the EM absorption materials to suppress the EMI for the used of related devices or systems.

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