Effective Recovery of Nd–Fe–B Sintered Magnet Scrap Powders as Microwave Absorbing Materials

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Effective recovery processes for the Nd–Fe–B sintered magnet scrap (sludge) powders as α-Fe/Nd_2O_3 nanocomposite magnetic particles were established, so that the resin-bonded sheets produced from them showed good microwave absorption properties over a range of 4–8 GHz.

Rare earth sintered magnets based on the $Nd_2Fe_{14}B$ primary phase possess the most excellent performance among the permanent magnets produced up to date,[1–3] so that they are currently the key parts for fabricating efficient small-sized motors with high torque rates and other equipments.[4] However, large amounts of scraps such as "slug" and "sludge" are necessarily produced in the processes for melting the raw metals (Nd, Fe, B, and some additives) and grinding or polishing the as-sintered magnet bulks. Among them, the sludge is one of the main scraps of Nd–Fe–B sintered magnets and the total amount produced per year is estimated to be 2000–2500 tons.[5] The fine powders of sludge are inevitably contaminated with impurities such as oxygen and carbon and, hence, only the rare earth components in them are practically recovered by the solution processes followed by ion-exchange or solvent extraction.[6]

Recently, direct recovery processes to Nd–Fe–B sintered or bonded magnets have been proposed for the sludge powders by applying Ca metal reduction technique.[7,8] Among them, the present authors[8] have succeeded in fabricating isotropic bonded magnets with the same magnetic properties as the commercially available magnets of Magnequench International Co, Ltd. However, the total yield is about 50% for the starting scrap powder. In the present paper, new effective usage of the sludge is proposed as the microwave absorbers covering GHz region, which are required to solve the serious electromagnetic interference problems accompanied by using the advanced systems such as LAN (local area network), ETC (electronic toll collection system), etc.

The sludge powder (particle size = ca. 3 μm) produced from Nd–Fe–B sintered magnets for voice coil motors (VCM) was employed without any further treatment. Some of the fine scrap powders were hydrogen-disproportionated to form nanosized composite powders of α-Fe, Fe_3B, and NdH_2 by heating at 1073 K for 3 h in H_2. The resulting powders were oxidized under conditions of 573 K for 3 h in air to form composite powders mainly consisting of nanosized α-Fe and Nd_2O_3 particles. The samples obtained were characterized by XRD analysis using Cu Kα radiation. Epoxy resin-bonded composites were prepared by molding the intimate mixtures of the recovered nanocomposite powders with 25% epoxy resin by pressing into cylindrical-shaped compacts with ca. 10 mm in diameter and 1–2 mm in thickness, followed by curing at 453 K for 30 min. They were cut into toroidal-shaped samples of 7.00 mm in outer diameter and 3.04 mm in inner one, respectively.

Reflection loss values were obtained by the indirect method based on absorber models with various thickness values as attached with a metal sheet reflector at the back side.[9] Scattering parameters (S_{11} and S_{21}) of the toroidal-shaped disks were measured on a Hewlett–Packard 8720B network analyzer in a range of 0.05–20.05 GHz, which were converted to relative permeability (μ_r) and permittivity (ε_r) values. The reflection loss (*RL*) values were calculated from the μ_r and ε_r values for the above models with various thickness values over the measured GHz range according to the following equations:

$$Z_{in} = Z_o(\mu_r/\varepsilon_r)^{1/2} \tanh\{j(2fd/c)(\mu_r\varepsilon_r)^{1/2}\} \quad (1)$$

$$RL = 20 \log |(Z_{in} - Z_o)/(Z_{in} + Z_o)| \quad (2)$$

where f is the frequency of microwave, d the thickness of absorber, Z_o the impedance of air, and c the velocity of light.

Figure 1 shows a series of XRD patterns recorded on the nanocomposite powders recovered from the sludge powder by hydrogenation (in H_2, 1073 K, 3 h) and/or oxidation (in air, 573 K, 3 h), together with that of the as-obtained (sludge) one. The sludge powder provided the typical XRD pattern of the $Nd_2Fe_{14}B$ primary phase in Nd–Fe–B sintered magnets, but a few unknown peaks derived from impurities such as whetstone were also observed. The particle sizes were so small that the

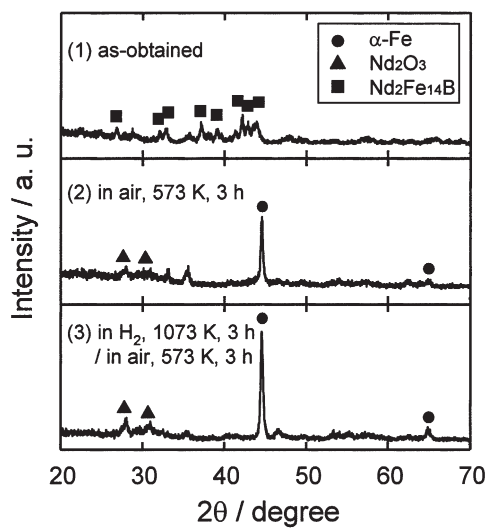

Figure 1. X-ray diffraction patterns of (a) the sludge (as-obtained) and the recovered powders by (b) oxidation and (c) hydrogenation/oxidation.

peak intensity was considerably low. By oxidizing the sludge powder, reflection peaks derived from α-Fe were grown up, together with those of Nd_2O_3 (see Figure 1b), where the mean particle size of α-Fe was evaluated to about 60 nm from the corresponding (111) reflection peak according to Scherrer's equation. Such nanocomposite powders were also prepared in two disproportionation steps of hydrogenation and oxidation as identified by XRD profile (see Figure 1c). The evaluated mean particle size of α-Fe was relatively small (ca. 50 nm) compared with that of the one step disproportionated (oxidized) sample. Particularly, the finer composite powders produced by the disproportination processes of hydrogenation and oxidation resulted in the much more enhancement of microwave absorption properties.

Sugimoto et al.[10,11] and the present authors[9] have reported that rare earth intermetallic compounds such as Sm_2Fe_{17} and Y_2Fe_{17} provide the same nanocomposite powders of α-Fe and Sm_2O_3 or Y_2O_3 via the disproportionation processes of hydrogenation and oxidation, of which the α-Fe particles are electrically isolated from one another by the rare earth oxides with insulating properties. Consequently, they can have good electromagnetic wave absorption properties.[9–11]

Calculated reflection loss (*RL*) patterns for the resin-bonded composite prepared from the nanocomposite powders (particle size = ca. 50 nm for α-Fe) recovered by the two step process of hydrogenation and oxidation for disproportionation are shown in Figure 2. The *RL* profiles were distributed over a wide range of 2–8 GHz and the *RL* value of resin-bonded composite sheets below −20 dB was obtained in the range of 5–8 GHz. The similar results were observed on samples of the nanocomposite powders recovered only by oxidation although their peak

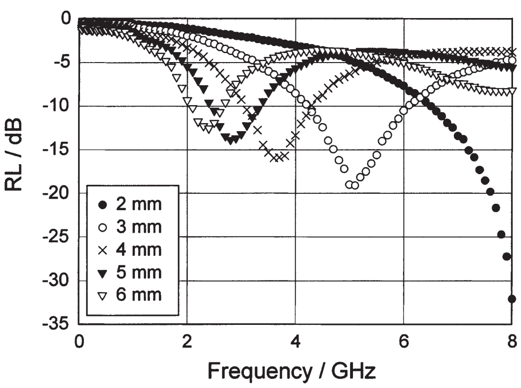

Figure 2. Frequency dependences of the calculated reflection losses for resin composite sheets with 75 wt% of the recovered sludge powder by hydrogenation (in H_2, 1073 K, 3 h) and subsequent oxidation (in air, 573 K, 3 h).

intensities were somewhat lower than those of the absorption peaks shown in Figure 2.

Unfortunately, since one cannot calculate the *RL* values in the range above 8 GHz because of the operation limitation on the apparatus used in this work, the minimum reflection loss (RL_{min}) and matching thickness (d_m) values were not observed on the *RL*-frequency profiles. However, these values should be located at the lower or thinner positions ($RL_{min} < -32$ dB; $d_m < 2$ mm) on the profiles than those of the nanocomposite particles derived from Y_2Fe_{17} ($RL_{min} = -36$ dB; d_m = ca. 4 mm)[9] and Sm_2Fe_{17} ($RL_{min} = -54$ dB; d_m = ca. 9.5 mm).[10] Therefore, the recovered nanocomposite powders possess excellent electromagnetic absorption properties in the region around 8 GHz. This must be due to the high magnetic anisotropy of Fe_3B[12] although the XRD profile of Fe_3B was not apparently observed on the oxidized samples.

In conclusion, the sludge powders as one of the main scraps of Nd–Fe–B sintered magnets are effectively recovered as the nanocomposite powders for microwave absorbers owing to their excellent electromagnetic absorption abilities in the range of 5–8 GHz.

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