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# Effective recycling for Nd–Fe–B sintered magnet scraps

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**Abstract**

Rare earth sintered magnet scrap powders ($Nd_2Fe_{14}B$ sludge) were melted and solidified with Si or Ti to produce Fe-based intermetallic compounds and coproducts of rare-earth-oxide slugs. After separating them, oxygen content measurements and energy dispersive X-ray analysis (EDX) observations demonstrated that about 60% of the rare earth components in the raw scrap powders were efficiently collected as rare-earth-oxide slugs during the melting process. The former compounds were ground into fine powders and some of them were heated at 100–250 °C for 1–12 h in air. The epoxy resin composites with 80–83 wt% of these powders showed good microwave absorption properties at GHz range. For Fe–Si (18.5 at% Si) and heat-treated (250 °C, 3 h) Laves phase $Fe_2Ti$ intermetallic compound, the minimum reflection loss (RL) values of −38.8 and −39.4 dB were observed at 3.3 and 12.3 GHz, respectively.


*Keywords:* Nd–Fe–B sintered magnet scrap; Sludge; Fe-based intermetallic compound; Microwave absorption; Recycle

## 1. Introduction

Rare earth magnets ($Nd_2Fe_{14}B$) have been widely used because of their excellent magnetic properties since its discovery in 1984 [1,2]. However, for the $Nd_2Fe_{14}B$ sintered magnets, 20–30% of the raw magnets were wasted as scrap powders (sludge) in order to cut and grind to desired shapes (1500–2500 t/year) [3]. Similarly, Si and Ti metals and alloys have been used for a variety of commercial applications, such as the semiconductor, aerospace, biomedical industry and so on, and large amounts of these scraps were also produced as industrial wastes. Thus, an economical and convenient method for the recycling of these materials is in demand. On the other hand, the microwave absorbing materials have been attracting much attention because of the electromagnetic interference problems become more serious along with the development and extensive applications of electromagnetic wave communication devices. Concerning these points, recently the present authors have discovered the effective recycling processes for the sludge powders to recover as raw materials for isotropic bonded-magnets, and also for microwave absorbing materials for GHz range [4,5].

It is known that there are some kinds of soft magnetic Fe–Si intermetallic compounds, which possess high permeability value, such as silicon steel (∼3% Si), FINEMET [6,7], Sendust [8], Super Sendust [9,10] and some other compounds [11,12]. Yoshida et al. reported a high permeability value for the Fe–Si–Al alloy flakes-polymer composite, and resulting good microwave absorbing properties in a quasimicrowave range (1 MHz–1 GHz) [8]. Ding et al. also reported soft magnetic properties of the nanocrystalline Fe–Si and resulting good permeability values of $Fe_{75}Si_{25}$ powder as high as that of pure bcc-Fe powder [12].

For the Fe–Ti intermetallic compounds, the present authors have recently found that the resin composites of the powders derived from $Fe_2Ti$ Laves phase (hexagonal C14) by grinding show good microwave absorbing properties in 10–17 GHz range [13] based on a magnetocrystalline anisotropy of $Fe_2Ti$ phase.

In this study, rare earth sintered magnet scrap powders ($Nd_2Fe_{14}B$ sludge) were used as a source of Fe, and prepare a variety of Fe-based intermetallic compounds of Fe–Si and Fe–Ti. For these materials, effects of composition, structure and heat treatment on microwave absorbing properties were investigated.

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## 2. Experimental

For raw materials, the sludge powders (particle size = ∼3 μm) produced from $Nd_2Fe_{14}B$ sintered magnets were employed together with Fe powders (325 mesh), Si shot (purity > 99.99) and Ti rod (99.95), which played roles as alloy formers. Firstly, the sludge powders (1 g) were compressed with/without Fe powders into cube compacts using a steel die under 20 MPa.

For the preparation of Fe–Si compounds, 5 g of sludge-Fe cubes and Si (3–25 at% for Fe) were charged in a quartz nozzle, and then inductively melted in Ar, followed by rapidly quenching on a melt-spun apparatus at a roll surface velocity of 25 m/s. During this process, thin-ribbon-shaped Fe–Si intermetallic compound was formed, and the rare earth component was remained inside the quartz nozzle as rare-earth-oxide slugs. The Fe–Si ribbons obtained were ground into fine powders by ball-milling at 400 rpm for 2 h. At this process, since the ribbon sample of 3 at% Si was hardly ground, the samples were nitrogenated at 500 °C for 2 h followed by a subsequent nitrogenation at 400 °C for 2 h before ball-milling, and hydrogenated at 450 °C for 2 h after ball-milling.

For the Fe–Ti materials, 5 g of sludge cubes and Ti (Fe:Ti = 2:1.2) were arc-melted in Ar for each process. The ingots were usually remelted five times to melt them intimately. The resultant samples were mechanically separated into the main alloy ingot portions of Fe–Ti intermetallic compounds and coproducts of rare-earth-oxide slugs. The alloy was then ground into fine particles (particle size < 38 μm) with WC mortar in Ar. Some of these powders were heat treated in air at 100–250 °C for 1–12 h.

Epoxy resin composites with 80 wt% of Fe–Si or 83 wt% of Fe–Ti powders were pressed into disc-shaped compacts of about 2.0 mm thickness, and then heated at 130 °C for 30 min and subsequently 170 °C for 30 min. The compacts were cut into toroidal-shaped samples of 3.04 mm inner diameter and 7.00 mm outer diameter for measurements of microwave absorbing properties on a network analyzer (Agilent technology 8720ES) at 0–18 GHz. The *S* parameters for each sample were measured based on an impedance matching model. The frequency dependence of reflection loss (RL) values were estimated from the complex permittivity ($\varepsilon_r = \varepsilon'_r - j\varepsilon''_r$) and permeability ($\mu_r = \mu'_r - j\mu''_r$) derived from the *S* parameters measured. The crystal structure, magnetic properties, elemental compositions and oxygen content of obtained sample powders were characterized by X-ray diffraction (XRD, RIGAKU, RINT2200), vibrating sample magnetometer (VSM, Tamakawa, TM-VSM2014-MHR type) with an applied field up to ±1.6 MA/m, an energy dispersive X-ray analysis (EDX, Hitachi, S-3000HXS) and oxygen/nitrogen analyzer (Horiba, EMGA-550), respectively.

## 3. Results and discussion

The assignments for samples, nominal compositions of raw materials and microwave absorbing properties obtained are summarized in Table 1.

The amounts of rare-earth-oxide slugs were 12.3 and 17.5% of total weight of raw materials in the case of Si and Ti addition, respectively. In the XRD patterns of the slugs, almost peaks were well indexed as $Nd_2O_3$, and a little amount of FeO was observed. The oxygen content of the raw sludge powders and slugs, obtained with samples D and E, were 3.88, 10.72 and 10.53 wt%, respectively. From the atomic compositions estimated by EDX measurements, the weight ratio in the raw sludge, Nd:Fe = 25.64:69.50, was in good agreement with the composition of $Nd_2Fe_{14}B$. The Nd and Fe contents were almost the same between these two slugs (73.53–73.70 wt% for Nd and 15.05–15.31 wt% for Fe), and these results were consistent with XRD patterns of them. From these results, it was calculated that 62.1 and 64.3% of Nd component in the raw sludge powders were efficiently collected as rare-earth-oxide slugs during the melting and solidification processes of Fe–Si and $Fe_2Ti$ compounds, respectively.

Fig. 1 shows the XRD patterns for powders of samples A, B, C, D and E. Firstly, sample A was prepared based on

Table 1
Nominal compositions, atomic ratios of Si or Ti for Fe and microwave absorbing properties for resin composites with 80–83 wt% of sample powders

| Sample | Nominal composition | Ratio of Si/Ti for Fe (at%) | Microwave absorbing properties for resin composites | | | | | Comment[a] |
|---|---|---|---|---|---|---|---|---|
| | | | RL < −20 dB | | Minimum RL | | | |
| | | | Frequency range (GHz) | $d_m$ (mm) | RL (dB) | $f_m$ (GHz) | $d_m$ (mm) | |
| A | $Nd_2Fe_{14}BSi_{3.5}$ | 25 | NA | NA | −5.4 | 16.5 | 1.0 | |
| B | $NdFe_{14}B_{0.5}Si_{0.42}$ | 3 | 1.0–3.9 | 10.1–3.0 | −34.5 | 2.0 | 5.4 | |
| C | $NdFe_{14}B_{0.5}Si_{1.4}$ | 10 | 0.9–2.2 | 8.0–3.7 | −33.0 | 1.6 | 5.1 | |
| D | $NdFe_{14}B_{0.5}Si_{2.59}$ | 18.5 | 2.2–4.6 | 6.2–3.4 | −38.8 | 3.3 | 4.5 | |
| E | $Nd_2Fe_{14}BTi_{8.4}$ | 66.7 | 10.5–15.9 | 1.52–1.0 | −36.5 | 11.7 | 1.4 | |
| F | $Nd_2Fe_{14}BTi_{8.4}$ | 66.7 | 8.2–16.8 | 2.0–1.0 | −39.4 | 12.3 | 1.35 | Heat treated |
| G | $Fe_2Ti_{1.2}$ | 66.7 | 5.9–17.6 | 2.5–0.9 | −34.1 | 14.6 | 1.1 | |
| H | $Fe_2Ti_{1.2}$ | 66.7 | NA | NA | −13.7 | 3.1 | 4.0 | Heat treated |

[a] Heating condition: 250 °C, 3 h.

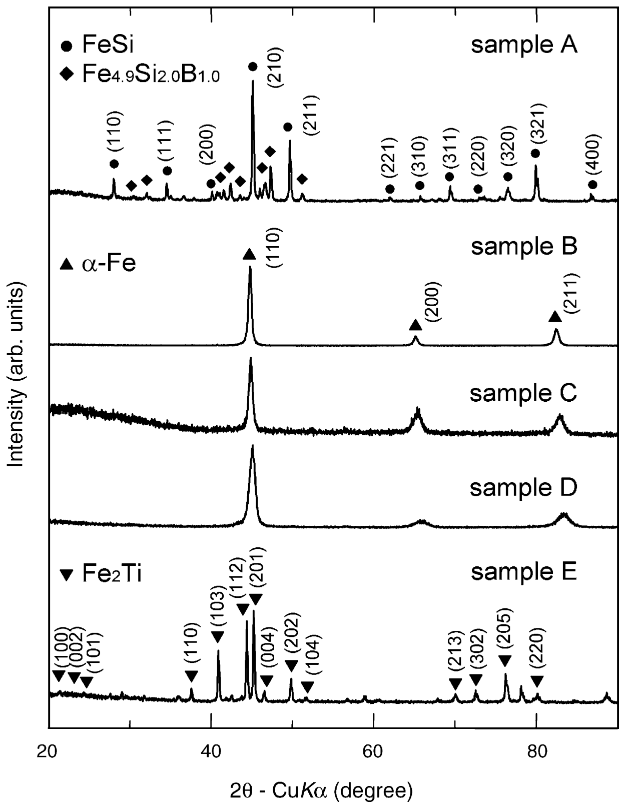


Fig. 1. XRD patterns of sample powders A, B, C, D and E listed in Table 1.

the high permeability value reported by Ding et al. [12]. In the XRD pattern of resultant sample powders, peaks of FeSi were mainly observed and weak peaks of $Fe_{4.9}Si_{2.0}B_{1.0}$ appeared. The RL values were larger than −5 dB in all frequency range measured, suggesting very poor absorption properties due to the low saturation magnetization ($M_s$) value of 17.1 emu/g. On the other hand, Fe–Si intermetallic composites with 3–18.5 at% of Si (samples B, C and D) showed good microwave absorbing properties. For sample B, because of a low Si content, the XRD pattern was almost the same as that of α-Fe, and the high $M_s$ value of 195 emu/g was also close to that of α-Fe (214 emu/g). The resulting microwave absorption properties were good. For sample C, despite the Si content was increased to 10 at% and the $M_s$ value decreased to 152 emu/g, RL values were still small. Finally, sample D was prepared with 18.5 at% of Si, which was equal to that of Sendust alloy. The peaks in the XRD pattern shifted to the higher degree and became close to that of $Fe_3Si$ for sample D due to the larger amount of Si content than that of sample B and C. The lattice constant value of 0.2846 nm for sample D was almost equal to that of $Fe_3Si$ (0.2841 nm). It is well known that nanocrystalls of Fe-based soft magnetic materials show high permeability as well as low eddy current loss, and these materials are very suitable for high frequency applications [6,14,15]. The crystalline size of sample D was estimated to be about 10 nm from peak widths of XRD pattern according to the Scherrer's formula, suggesting a good suppression ability of the eddy current induced in fine sample

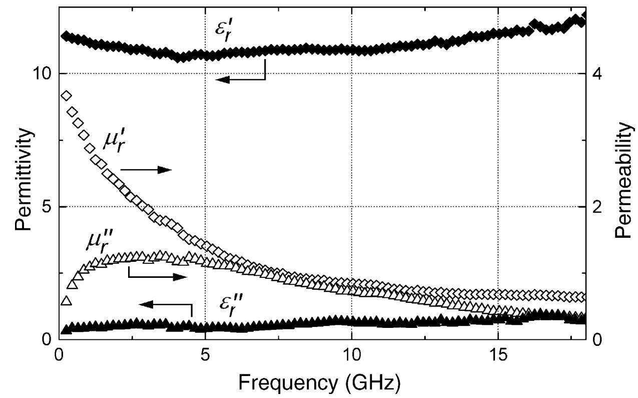


Fig. 2. Frequency dependence of the relative permittivity and permeability for the resin composites with 80 wt% of sample powders derived from sludge and 18.5 at% of Si (sample D).

particles. In the result, low permittivity and high permeability values and the resulting most excellent microwave absorbing property were obtained as shown in Figs. 2 and 3. The frequency range where RL < −20 dB covered 2.2–4.6 GHz, and the minimum RL value of −38.8 dB was obtained at matching frequency ($f_m$) and thickness ($d_m$) of 2.0 GHz and 4.5 mm, respectively.

For Fe–Ti compound of sample E, the XRD pattern was close to that of $Fe_2Ti$ with slight peak shifts to the lower degree, indicating an increase in lattice constant due to an excess amount of Ti content compared to stoichiometric $Fe_2Ti$ [16].

Fig. 4 shows the frequency dependence of the relative permittivity and permeability of the resin composites of samples E or F. The real and imaginary parts $\varepsilon_r'$ and $\varepsilon_r''$ were almost constant at 0–13 GHz for both resin composites. However, at higher frequency range, as shown by open symbols in Fig. 4(a), $\varepsilon_r'$ and $\varepsilon_r''$ values for sample $E$ were increased with frequency to 27 and 8, respectively. On the other hand, for sample F, both values kept constant as shown by solid symbols in Fig. 4(a). This indicates the resistivity was enhanced due to the improvement of isolation of particles induced by

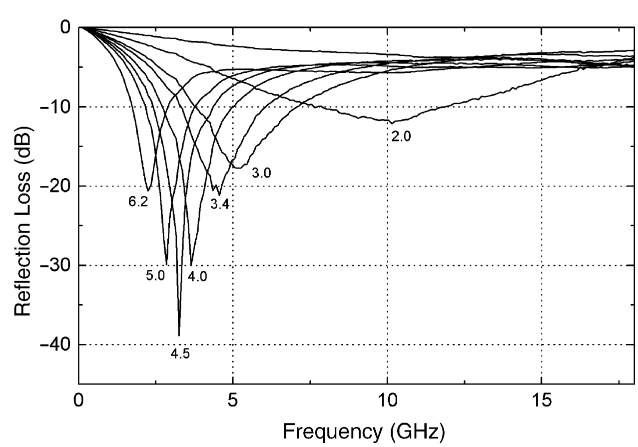


Fig. 3. Frequency dependence of the RL values for the resin composites with 80 wt% of sample powders derived from sludge and 18.5 at% of Si (sample D). The numbers represents the $d_m$ value for each curve.

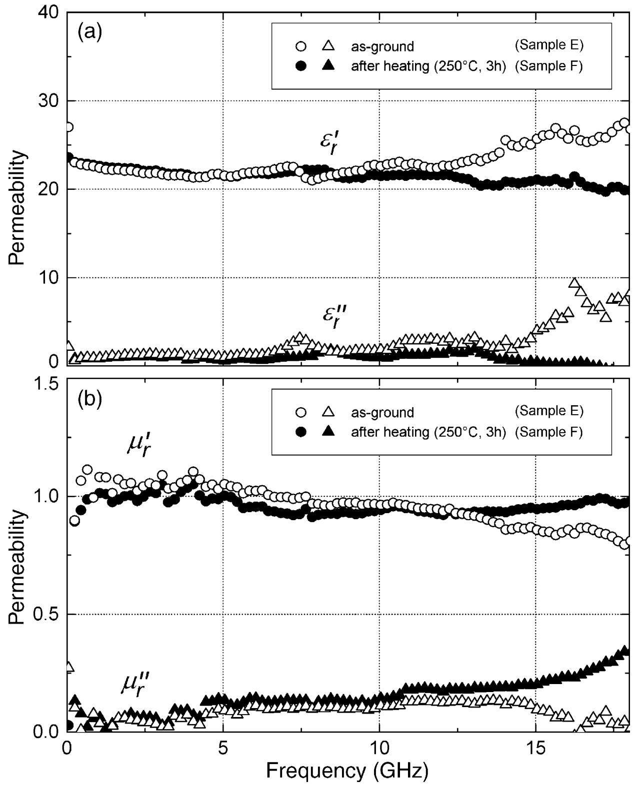


Fig. 4. Comparison of changes in (a) relative permittivity and (b) relative permeability between as-ground (sample E) and heat-treated (sample F) $Fe_2Ti$ powders derived from sludge.

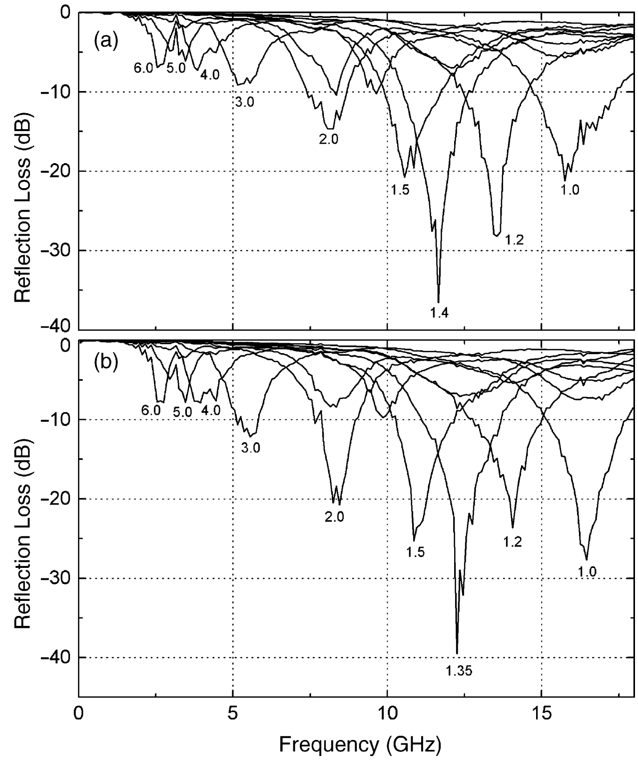


Fig. 5. Frequency dependence of the RL values for (a) the resin composites with 83 wt% of as-ground $Fe_2Ti$ sample powders derived from sludge (sample E) and (b) that of heat-treated powders (sample F).

an efficient oxidation, and the resulting suppression of the eddy current leads to the increase in $\mu_r''$ value. In Fig. 4(b), while the imaginary part $\mu_r''$ for sample *E* (open triangles) showed a broad peak which covered 5–16 GHz range with the maximum value of 0.14 at 12.5 GHz, the $\mu_r''$ for sample *F* (solid triangles) showed the larger peak than that for sample *E*. Since the latter peak lies in wider frequency ranges than studied, the top of the peak was not determined and the maximum value obtained was 0.36 at 18 GHz.

The resulting RL values for both resin composite with samples *E* or *F* are shown in Fig. 5. The microwave absorbing property for sample *E*, which was prepared using the sludge powders, showed similar characteristics compared to that for $Fe_2Ti$ prepared from pure Fe and Ti [13]. Moreover, after heating at 250 °C for 3 h (sample *F*), the frequency range where RL < −20 dB was widened to 8.2–16.8 GHz. In particular, the minimum RL became smaller value of −39.4 dB at 12.3 GHz. The enhancement of the absorbing property observed for sample F was due to the lower values in $\varepsilon_r$ and the larger values in $\mu_r''$ compared to sample *E* as shown in Fig. 4. Additionally, for sample *F*, considering the broadness of the $\mu_r''$ peak, it is expected that excellent absorbing properties will be also observed at frequency range above 18 GHz.

The effect of oxidation was investigated in detail. For comparison with samples *E* and *F*, samples *G* and *H* in Table 1 were prepared from the fresh metals of Fe and Ti. While the oxygen content was increased from 0.33 wt% (sample E) to 1.42 wt% (sample *F*), the value showed a less increase from 0.16 wt% (sample *G*) to 0.48 wt% (sample H) after heating at 250 °C for 3 h. In contrast to sample F, absorption properties for sample H were very poor as listed in Table 1. From these results, it is concluded that the powders of $Fe_2Ti$ compound derived from the sludge powders have a higher oxidation resistivity than that prepared using pure Fe. These results are presumably explained as follows: For sample *F*, the residual Nd components were preferentially oxidized than Fe or Ti, and then the resultant $Nd_2O_3$ prevented from further oxidation of the $Fe_2Ti$ phase. Meanwhile, for sample H, the $Fe_2Ti$ phase was directly damaged by an oxidation because of the lack of Nd components. The study on this point is in progress. These results indicated that Si can be introduced into the sludge powders up to 18.5 at% to form Fe–Si compounds. Since these Si-rich or Laves $Fe_2Ti$ compounds are mechanically brittle and easy to grind, such a characteristic becomes a great advantage in the convenient process for recycling.

## 4. Conclusions

From this study, it was revealed that rare earth sintered magnet scrap powders ($Nd_2Fe_{14}B$ sludge) can be effectively recycled as Fe–Si or $Fe_2Ti$ intermetallic compounds, which possess efficient microwave absorbing properties in GHz range, by melting and solidification processes. Especially, good absorbing properties at frequency range above 18 GHz are also expected for the latter material. These excellent absorbing properties are based on the large electric resistivity and $\mu_r''$ values due to the insulating effect of rare-earth-oxides, such as $Nd_2O_3$. In addition, good oxidation resistivity is realized by using the sludge powders as a Fe source, because of the preferential oxidation of Nd component. Moreover, about 60% of Nd component in the raw sludge powders can be efficiently collected as rare-earth-oxide slugs. Thus, the present processes are concluded to be effective recycling processes for $Nd_2Fe_{14}B$ rare earth sintered magnet scrap powders, Si and Ti materials.

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