Electromagnetic Microwave Absorption of \( \alpha \)-Fe Microstructure Produced by Disproportionation Reaction of Sm\(_2\)Fe\(_{17}\) Compound \(^1\)

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The electromagnetic wave absorption properties of a magnetic powder with a fine \( \alpha \)-Fe structure, produced by the disproportionation of Sm\(_2\)Fe\(_{17}\), were investigated in the GHz frequency range. A fine, sub-micrometre \( \alpha \)-Fe/SmH\(_2\) structure was formed from the Sm\(_2\)Fe\(_{17}\) compound after disproportionation in a hydrogen atmosphere. The grain size of the \( \alpha \)-Fe phase was calculated by X-ray diffraction line broadening analysis, to be about 30 nm. In this way, a magnetic powder with a fine structure of \( \alpha \)-Fe was obtained. This powder was then heated in air in order to oxidize the SmH\(_2\), with the result that an \( \alpha \)-Fe/SmO two-phase microstructure was obtained. Toroidally shaped epoxy-resin composites were made from this powder, and the microwave absorption properties of these samples were measured. As a result, the disproportionated samples (heated in hydrogen at 873 K for 1 hour, nilled for 30 minutes and oxidized at 473 K for 2 hours in the air) exhibited electromagnetic wave absorption (\( R_L \sim -20 \) dB) in the frequency range 0.75 to 1.3 GHz, for absorber thicknesses ranging from 12.5 to 7.5 mm, respectively. An undisproportionated sample did not show any electromagnetic wave absorption in this frequency range.

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1. Introduction

Recently, there has been a great increase in the number of communication devices that utilize 1–5 GHz-range microwave radiation, largely due to the high data transfer rates possible in this higher frequency range. In particular, the use of mobile phones and LAN systems, is rapidly increasing. Unfortunately, this has lead to electromagnetic interference (EMI) becoming a serious problem.\(^1\) One promising technique to help to prevent EMI, is the use of electromagnetic wave absorption materials. In the 1–5 GHz frequency range, resin composites of either Spinel-type ferrite\(^2\),\(^3\) or metallic magnetic material,\(^4\)–\(^6\) can be used as electromagnetic wave absorbers. However, because the latter materials have larger values of saturation magnetization, their Snook’s limit\(^7\) are at a higher frequency and so their values of relative complex permeability remain high in this frequency range. Therefore, it is possible to make thinner absorbers from metallic magnetic materials. However, there are two problems with the use of electrically conductive magnetic materials as absorbers. One is that the magnetization of these materials, induced by electromagnetic waves, decreases due to eddy current losses. For this reason, it is best to use smaller particles, compared to the skin-depth, when making electromagnetic wave absorbers from such materials. The second problem is that of insulation: due to the high conductivity of these materials, the particles must be insulated by a non-conductive material, such as resin or rubber.

In the 1–5 GHz frequency range, the skin-depth has been calculated to be about 1 \( \mu \)m, and so it is effective to use magnetic metallic materials with a sub-micrometre grain size for the production of resin composite microwave absorbers. In the conventional process, mechanically pulverized Fe-based powders or carbonyl iron powders have been used, however, in this study an alternative processing route has been investigated, using a R—Fe (R: rare-earth element) compound. It is well known that a fine \( \alpha \)-Fe microstructure can be produced by disproportion reactions in many R—Fe compounds. For example, the Sm\(_2\)Fe\(_{17}\) compound disproportionates into a two-phase, \( \alpha \)-Fe/SmH\(_2\) microstructure after heating in hydrogen at temperatures from 873 to 1373 K.\(^8\),\(^9\) The grain-size of this disproportionated mixture can be controlled by changing the hydrogen treatment conditions: at around 873 K, it is possible to obtain a sub-micrometre scale lamella structure. In addition, R\(_2\)Fe\(_{17}\) compounds have the largest amount of Fe within the binary rare-earth iron compounds, which indicates that a high volume fraction of \( \alpha \)-Fe can be obtained after disproportionation, to give a high permeability microwave absorption material. Therefore, the purpose of this study is to investigate the possibility of using the disproportionation reaction of a R\(_2\)Fe\(_{17}\) compound, to produce a fine \( \alpha \)-Fe microstructure for use as a microwave absorption materials.

The SmH\(_2\) phase produced by the disproportionation reaction in hydrogen, only has low resistivity (3 \( \times \) 10\(^{-7}\) \( \Omega \)-m),\(^10\) and so it is necessary to increase the resistivity by oxidizing Samarium hydride to form Samarium oxide. Therefore, in this study, resin composites using a disproportionated powder, which was heat-treated at 873 K for 1 hour in hydrogen and oxidized at 323–773 K temperatures for 2 hours in air, were prepared, and their microwave absorption properties were investigated.

2. Experimental Procedure

The composition of the studied alloy was Sm\(_2\)Fe\(_{17}\). The

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alloy was induction-melted using high purity samarium and iron, under an argon atmosphere, and was then homogenized at 1273 K for 50 hours. After crushing into powder with a particle size of 63–500 μm, the Sm₂Fe₁₇ powders were compacted into cube-shaped samples. The heat treatments for disproportionation and oxidation, were carried out as follows; the Sm₂Fe₁₇ samples were heated up to 873 K at 400 K/h, in a hydrogen gas flow (H₂ flow rate: 5.0 × 10⁻⁴ m³/min). After keeping at this temperature for 1 hour, the atmosphere was changed from hydrogen to argon and the samples were cooled to room temperature. The disproportionated powders were then heat-treated at 323–773 K for 2 hours in air, in order to oxidize the Samarium hydride. The powders were mixed with an epoxy resin at a ratio of 80 mass% and then pressed into cylindrical shaped compacts. These compacts were cured by heating up to 453 K in argon atmosphere, and then they were formed into the toroidally shaped samples (φ_out: 7.00, φ_in: 3.04, t: 0.5–1.5 mm²).

The phases present in these powders were characterized by X-ray diffraction (XRD), and the microstructures were observed using a field emission scanning electron microscope (FE-SEM). The scattering parameters (S₁₁, S₂₂) were measured by the coaxial method using a Hewlett-Packard HP8720D vector network analyzer in the frequency range, 0.05 to 20.05 GHz. These parameters were then used to determine the relative complex permeability (μ_re) and permittivity (ε_re), and also used to calculate the frequency (f) dependence of reflection loss (R.L.) at a thickness (d) with the following formulae, which characterize the electromagnetic wave absorption properties.

\[ R.L. = 20 \log \left| \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right| \]  

\[ Z_{in} = Z_0 \sqrt{\mu_0 / \varepsilon_0} \tanh \left( \frac{-j \mu_0 f d / c}{\mu_0 / \varepsilon_0} \right) \]

where \( Z_{in} \): input impedance of absorber, \( Z_0 \): impedance of air, c: velocity of light.

3. Results and Discussion

Before measuring the microwave absorption properties, the phases present in, and the microstructures of, the samples were examined by X-ray diffraction and field emission scanning electron microscopy. Figure 1 shows X-ray diffraction patterns of the homogenized Sm₂Fe₁₇ ingot powders after disproportionation at 873 K for 1 hour in hydrogen. It was confirmed that the Sm₂Fe₁₇ compound decomposed into α-Fe and samarium dihydride (SmH₂) after the hydrogen heat treatment. The grain sizes of the α-Fe and SmH₂ phases were calculated, by line broadening analysis of the X-ray diffraction peaks using the Scherrer equation, to be about 30 and 15 nm, respectively. However, as these values contain information relating to both the grain size and the crystallinity, it is thought that these values do not correspond to the real grain size of the α-Fe and SmH₂ phases. Therefore microstructural observations were carried out. Figure 2 shows a back-scattered SEM micrograph of the disproportionated sample. The phases with bright and dark contrast correspond to the SmH₂ and α-Fe phases, respectively, and have a sub-micrometre size lamella structure.

In order to convert the SmH₂ into samarium oxide, the disproportionated samples were heated in air at 323–773 K for 2 hours: the X-ray diffraction patterns for these samples are shown in Fig. 3. The sample heated at 673 K was composed of α-Fe and SmH₂ phases, and the sample heated at 773 K consisted of three phases of α-Fe, samarium monoxide (SmO) and hematite (α-Fe₂O₃). Under these oxidation conditions, a two-phase microstructure composed of α-Fe and samarium oxide, was not obtained. At the lower temperature (673 K), it is considered that the oxygen can not diffuse through the whole powder because the particle size (63–500 μm) is too large. At the higher temperature (773 K), the oxidation of α-Fe also occurred. Therefore, in order to oxidize SmH₂ phase more efficiently, the disproportionated powders were pulverized into finer powders with particle sizes of about 20 μm using a planetary ball mill, before the heat treatment in air.

Figure 4 shows the X-ray diffraction patterns of the sam-
Fig. 3 X-ray diffraction patterns of a disproportionated Sm$_2$Fe$_{17}$ sample, and of disproportionated samples that were then oxidized at 673, 773 K for 2 h in air.

Fig. 4 X-ray diffraction patterns of a disproportionated Sm$_2$Fe$_{17}$ samples pulverized to give a particle size of about 20 μm, and oxidized at 423–773 K for 2 h in air.

Samples heated at several temperatures for 2 hours in air after pulverization. The sample heated at 423 K, was still composed of the α-Fe and SmH$_2$ two-phase mixture. However, at 473 K the sample consisted only of the α-Fe and SmO phases, and the X-ray diffraction peaks of the α-Fe$_2$O$_3$ phase were not observed. This shows that only the SmH$_2$ was oxidized and that the α-Fe remained largely unreacted under these conditions. In the case of the sample heat-treated at 773 K, α-Fe$_2$O$_3$ peaks were observed, which suggests that not only the SmH$_2$ but also the α-Fe phase was oxidized. Therefore, it was found that it is possible to obtain an α-Fe/SmO two-phase microstructure

by milling the disproportionated powder and then oxidizing it at 473 K.

Resin composites were prepared using this powder by mixing with epoxy resin at a ratio of 80 mass% powder (54 vol%), and the high-frequency electromagnetic absorption properties of this material were measured using a network analyzer. (In this resin composite, the volume fraction of Fe phase was calculated to be 34 vol%.) In order to evaluate the properties of this sample, an epoxy resin composite made from carbonyl iron powder (particle size: 3.5 μm, made by BASF Aktiengesellschaft, Germany), in which the volume fraction of Fe was about 35 vol%, was also prepared.

The relative complex permittivity of the disproportionated sample was almost constant in the frequency range 1–5 GHz ($\varepsilon_r = 21 - 1.5 j$). However, the undisproportionated sample nearly behaved as a conductor, which suggests that the disproportionated composite had a higher resistivity (The resistivity increased from $\sim 10^{-1}$ Ω-m to $\sim 10^2$ Ω-m after disproportionation). Figure 5 shows the frequency dependence of relative complex permeabilities of the disproportionated sample, in compared with those of the undisproportionated and carbonyl iron samples. The disproportionated sample showed higher values than the undisproportionated sample in both the real ($\mu'_r$) and imaginary ($\mu''_r$) parts of permeability. This sample exhibited a maximum $\mu'_r$ value of 1.31 at 1.37 GHz, which is 25% higher than that of the carbonyl iron composite. This $\mu'_r$ peak is considered to be due to the natural resonance of iron, whose resonance frequency is 1.6 GHz. From this result, it can be said that the microstructure of the disproportionated sample is effective in restraining a decrease in magnetization.
induced by eddy current losses.

The electromagnetic wave absorption properties of the resin composites were estimated from the reflection loss (R.L.). Figure 6 shows the frequency dependence of R.L. for the disproportionated sample. The R.L. of the undisproportionated sample was nearly zero due to its high permittivity and low permeability. However, the disproportionated sample had R.L. values less than −20 dB at the frequencies from 0.75 to 1.3 GHz. In particular, the minimum R.L. value of −52 dB was obtained at 0.98 GHz with a matching thickness ($d_m$) of 9.33 mm, and the minimum $d_m$ value of 7.5 mm was obtained at 1.3 GHz.

To conclude, an α-Fe/SmO two-phase microstructure was obtained by disproportionating the Sm$_2$Fe$_{17}$ compound in hydrogen and oxidizing the milled powder in air: a resin composite of this oxidized powder exhibited good electromagnetic wave absorption properties in the 1−5 GHz frequency range. To our knowledge, this is the first study to demonstrate the possible use of a rare-earth iron compound as an electromagnetic wave absorber.

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