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GHz microwave absorption of a fine α-Fe structure produced by the disproportionation of Sm_2Fe_{17} in hydrogen

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Abstract

In this study, the possibility of using the disproportionation reaction of the Sm_2Fe_{17} compound for the production of powders with a fine α-Fe structure was investigated, for use as electromagnetic wave absorbers that can operate in the GHz frequency range. A fine α-Fe/SmH_2 or α-Fe/SmO structure with a sub-micrometer size is formed from the Sm_2Fe_{17} compound after disproportionation in hydrogen or air, respectively. In this way, magnetic powders with a fine structure of α-Fe were obtained. The powders disproportionated in hydrogen, were heated in air in order to oxidize the Sm hydride, to give a α-Fe/SmO two-phase microstructure, and thereby increase the resistivity of the powders. Toroidally shaped epoxy-resin composites were made from this powder, and the microwave absorption properties of these samples were measured. An undisproportionated sample did not show any electromagnetic wave absorption in this frequency range. However, the disproportionated samples (heated in hydrogen at 873 K for 1 h, milled for 30 min and oxidized at 473 K for 2 h in air) exhibited electromagnetic wave absorption ($RL < -20$ dB) in the frequency (f_m) range 0.73–1.30 GHz, for absorber thicknesses (d_m) ranging from 13.1 to 7.9 mm, respectively. The disproportionated samples in air (heated at 473 K for 2 h and milled for 30 min) also showed good electromagnetic wave absorption properties (f_m=1.21–2.50 GHz and d_m=8.0–4.2 mm). It is concluded that the disproportionation reaction, in either hydrogen or in air, is a useful method for the production of powders with a fine α-Fe structure, which can be used for microwave absorbers that operate in the several GHz range.

Keywords: Electromagnetic wave absorber; Samarium–iron compound; Disproportionation reaction; α-Fe fine structure; Epoxy resin composite; Complex relative permeability; Reflection loss

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1. Introduction

Recently, as the number of communication devices using 1–5-GHz range microwave radiation, such as mobile phones and LAN systems, have greatly increased, serious electromagnetic interference (EMI) problems have become apparent [1]. This has led to a search for suitable electromagnetic wave absorption materials that can prevent EMI. In the 1–5-GHz frequency range, both spinel-type ferrites [2,3] and metallic magnetic materials [4–7] can be used as electromagnetic wave absorbers. However, because the latter materials have larger values of saturation magnetization, their Snoek's limit [8] are at a higher frequency and so the relative values of complex permeability remain high in this frequency range. Therefore, it is possible to make thinner absorbers from bulk metallic materials. However, there are two problems with the use of metallic magnetic materials as absorbers. Firstly, because of their high

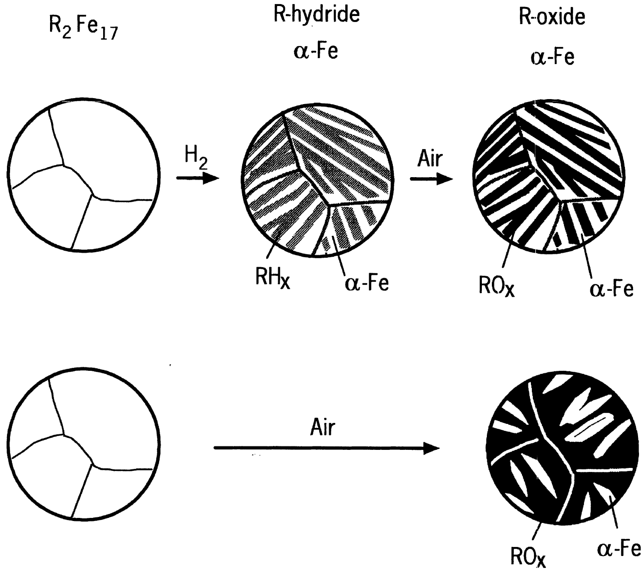

Fig. 1. Schematic illustration of the expected microstructural changes within the R_2Fe_{17} compound during hydrogen-disproportionation and oxidation in air (above), and during oxygen-disproportionation (below).

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conductivity of these materials, they must be pulverized into small particles, which are insulated by a non-conductive material, such as resin or rubber. Secondly, because the magnetization of these materials is induced by electromagnetic waves, it decreases due to eddy current losses. For these reasons, it is better to use smaller particles, compared to the skin-depth, when making electromagnetic wave absorbers from such materials. For iron, the skin-depth in the 1–5-GHz frequency range has been calculated to be about 1 μm, hence it is effective to use powders with a sub-micrometer grain size for the production of resin composite microwave absorbers. Mechanically pulverized Fe-based powders [5–7] or carbonyl iron powders [4] have been the most commonly used electromagnetic wave absorption materials.

However, in the present study, an alternative processing route has been investigated, using an R-Fe (R=rare-earth element) compound. It is well known that a fine α-Fe microstructure can be produced by disproportionation reactions in many R-Fe compounds. For example, Zhong et al. [9] and Nakamura and co-workers [10,11] reported that the Sm_2Fe_{17} compound disproportionates into a two-phase, α-Fe/SmH_2 microstructure after heating under a hydrogen atmosphere (hydrogen-disproportionation) at temperatures from 873 to 1373 K. The grain-size of this disproportionated mixture can be controlled by changing the hydrogen treatment conditions. A sub-micrometer scale lamellar structure composed of SmH_2 and α-Fe is obtained after a heat treatment at temperatures close to 873 K. However, at higher temperatures, the SmH_2 lamellae grow to form spheres several hundred micrometers in diameter, embedded within an α-Fe phase. Judging from the difference in free energy change for the formation of oxide between rare earth elements and iron, a similar disproportionated microstructure can be expected when the heat treatment is performed in oxygen or air (oxygen-dispropor-

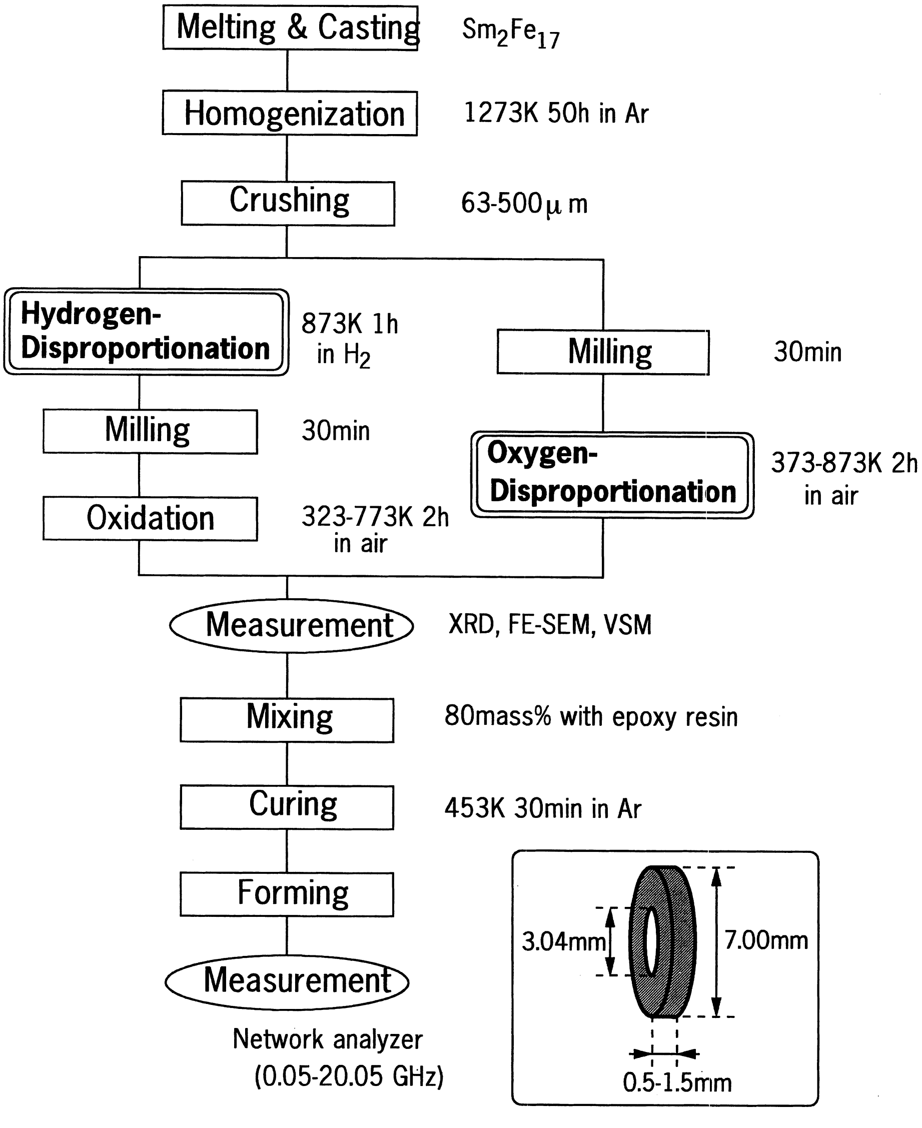

Fig. 2. Experimental procedure.

tionation). In addition, the R_2Fe_{17} compounds exhibit the largest amount of Fe within the series of binary rare-earth iron compounds, which indicates that a high volume fraction of α-Fe can be obtained upon disproportionation.

Therefore, the purpose of this study is to investigate the possibility of using the disproportionation reaction of an R_2Fe_{17} compound, to produce a fine α-Fe microstructure with high microwave absorption properties. However, the resulting RH_2 phase has only a low resistivity (3×10^{-7} Ωm) [12], so it is necessary to increase the resistivity, for example, by oxidizing the R-hydride to form R-oxide. Fig. 1 shows a schematic illustration of the expected microstructural changes within the R_2Fe_{17} compound during (i) hydrogen-disproportionation followed by oxidation in air, and (ii) oxygen-disproportionation. In this study, powders with microstructures consisting of a fine mixture of α-Fe and samarium oxide phases, were produced by the process described above, and using these powders, resin composites were prepared to investigate their microwave absorption properties.

2. Experimental procedure

Fig. 2 shows the experimental procedure. The composition of the studied alloy was chosen as Sm_2Fe_{17}, because the hydrogen absorption and desorption characteristics of this compound are well known [9–11]. The alloy was induction-melted using high purity samarium and iron, under an argon atmosphere, and was then homogenized at 1273 K for 50 h. After being crushed to a particle size of 63–500 μm, the Sm_2Fe_{17} powders were compacted into cube-shaped samples. In the case of the hydrogen-disproportionation+oxidation treatment, the Sm_2Fe_{17} samples were heated up to 873 K at 400 K/h, in a hydrogen gas flow (H_2 flow rate: 5.0×10^{-4} m^3/min). After holding at this temperature for 1 h, the atmosphere was changed from hydrogen to argon and the samples were cooled to room temperature. In order to oxidize the SmH_2 phase more efficiently, the hydrogen-disproportionated powders were pulverized into finer powders with particle sizes of about 20 μm using a planetary ball mill; this was

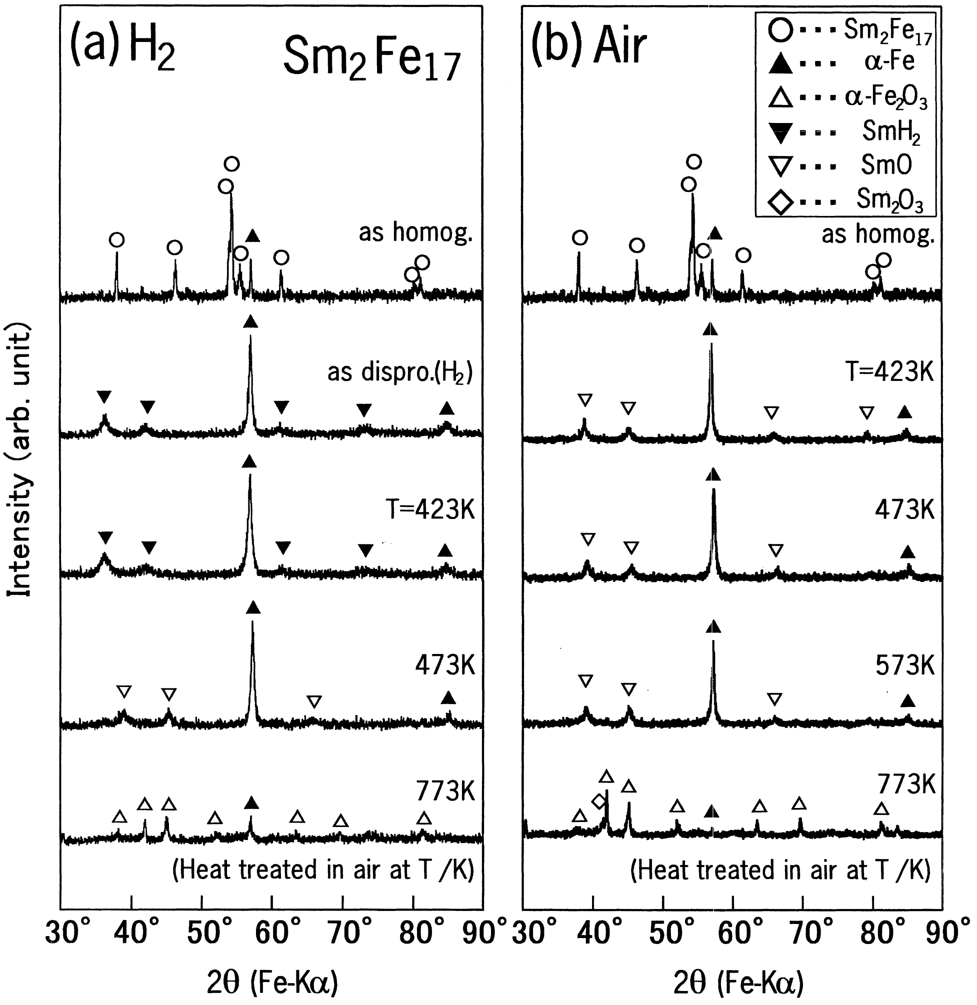

Fig. 3. X-ray diffraction patterns of the Sm_2Fe_{17} ingot powders (a) after hydrogen-disproportionation at 873 K for 1 h and then oxidation at 323–773 K for 2 h in air, and (b) after oxygen-disproportionation at 423–773 K for 2 h.

carried out before the heat treatment at 323–773 K for 2 h in air. In the case of the oxygen-disproportionation treatment, the crushed Sm_2Fe_{17} powders were ball-milled into powders of about 10 μm before heat-treating at 373–873 K for 2 h.

These disproportionated powders were mixed with an epoxy resin at a ratio of 80 mass% (powder) and then pressed into cylindrical shaped compacts. These compacts were cured by heating up to 453 K in an argon atmosphere. Then they were formed into toroidally shaped samples (ϕ_{out}=7.00, ϕ_{in}=3.04, t=0.5–1.5 mm^3).

The powders were characterized by X-ray diffraction (XRD), and the microstructures were analysed using a field emission scanning electron microscope (FE-SEM). The magnetic properties were measured using a vibrating sample magnetometer (VSM). The scattering parameters (S_{11}, S_{21}) were measured by the coaxial method using a Hewlett-Packard HP8720D vector network analyzer in the frequency range, 0.05–20.05 GHz. These parameters were then used to determine the relative complex permeability (μ_r) and permittivity (ε_r), and also to calculate the frequency (f) dependence of reflection loss (RL) at a thickness (d) with the following formulae which characterize electromagnetic wave absorption.

$$\mathrm{RL} = 20\log|(Z_{in} - Z_O)/(Z_{in} + Z_O)| \quad (1)$$

$$Z_{in} = Z_O\sqrt{\mu_r/\varepsilon_r}\,\tanh\{j(2\ fd/c)\sqrt{\mu_r\varepsilon_r}\} \quad (2)$$

where Z_{in} is the input impedance of absorber, Z_O is the impedance of air, and c is the velocity of light.

3. Results and discussion

Before measuring the microwave absorption properties, the phases present in the samples were examined by X-ray diffraction. Fig. 3 shows X-ray diffraction patterns of the homogenized Sm_2Fe_{17} powders (a) after hydrogen-disproportionation at 873 K for 1 h followed by oxidation at 323–773 K for 2 h in air, and (b) after oxygen-disproportionation at 423–773 K for 2 h. From Fig. 3a, it is confirmed that Sm_2Fe_{17} decomposes into α-Fe and samarium dihydride (SmH_2) after application of the hydrogen heat treatment. The grain sizes of the α-Fe and SmH_2 phases were determined from the line broadening of the X-ray diffraction peaks using the Scherrer formula, to be about 30 and 15 nm, respectively. The hydrogen-disproportionated sample was still a two-phase mixture of α-Fe and SmH_2 after of the oxidation heat treatment at 423 K in air. However, at 473 K, the X-ray diffraction peaks of SmH_2 disappeared and the sample was found to consist only of the α-Fe and SmO phases. In the case of the sample heat-treated at 773 K, α-Fe_2O_3 peaks were observed, which suggests that not only the SmH_2 but also the α-Fe phase was oxidized.

In the case of the oxygen-disproportionation, as shown in Fig. 3b, the powders were composed of both the SmO and α-Fe phases after heat treatment at temperatures between 423 and 573 K. However, X-ray diffraction peaks of α-Fe_2O_3 were only observed above 773 K, which suggests that the α-Fe oxidized above this temperature. Therefore, a two-phase microstructure of α-Fe/SmO can be obtained by the oxygen-disproportionation at temperatures below 573 K.

Resin composites were prepared using these powders by mixing with epoxy resin at a ratio of 80 mass% powder (54 vol%). In this resin composite, the volume fraction of α-Fe was calculated to be 34 vol%. Fig. 4 shows the magnetization of resin composites at an applied field of 1.2 MA m^{-1} ($M_{1.2}$) against the oxidation temperature after hydrogen-disproportionation, and against the oxygen-disproportionation temperature. The hydrogen-disproportionated samples show a high $M_{1.2}$ value due to the formation of α-Fe; however, $M_{1.2}$ decreases with increasing oxidation temperature since oxidation of α-Fe results in the formation of α-Fe_2O_3. The $M_{1.2}$ values of the oxygen-disproportionated samples exhibit almost the same thermal treatment dependence.

The high-frequency electromagnetic absorption properties of the epoxy resin composites were measured using a network analyzer. In order to evaluate the properties of the samples, an epoxy resin composite made from carbonyl iron powder (made by BASF Aktiengesellschaft, Ger-

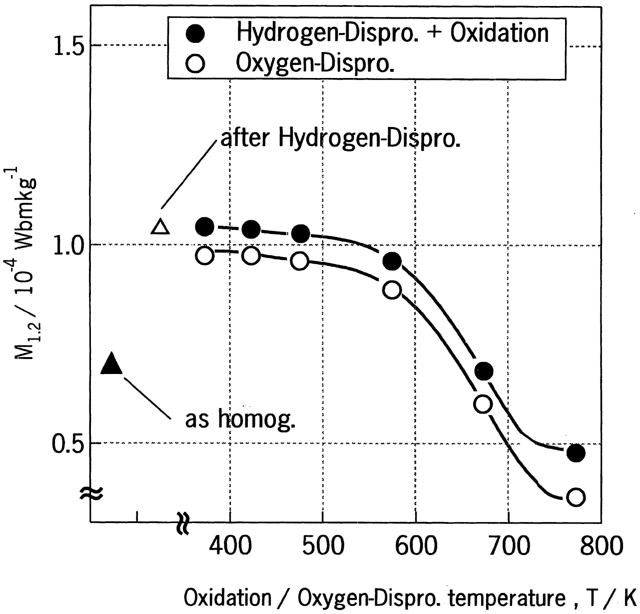

Fig. 4. Variation of magnetization values of resin composites at an applied field of 1.2 MA m^{-1} ($M_{1.2}$), with respect to the oxidation temperature after hydrogen-disproportionation, or to the oxygen-disproportionation temperature.

many), was also prepared in which the volume fraction of Fe was about 35 vol% and the particle size 3.5 μm. Fig. 5a shows the frequency dependencies of relative complex permittivities and permeabilities of samples after hydrogen-disproportionation and the following oxidation at 473 K for 2 h, compared with those of undisproportionated and carbonyl iron samples. The undisproportionated sample exhibits a high value of relative complex permittivity, and nearly behaves as a metal conductor (see inset in Fig. 5a). However, that of the hydrogen-disproportionated and oxidized sample remains almost constant in the frequency range 1–5 GHz ($\varepsilon_r = 21 - 1.5j$), which indicates that the disproportionated composite has a higher resistivity. This resistivity was measured to be 1×10^2 Ωm. The disproportionated sample shows higher values than the undisproportionated sample in both real (μ_r') and imaginary (μ_r'') parts of permeability. This sample exhibits a maximum μ_r'' value of 1.31 at 1.37 GHz, which is 25% higher than that of the carbonyl iron composite. This μ_r' peak is attributed to the natural resonance of iron, which has a resonance frequency (f_r) of 1.6 GHz; this value was calculated using the expression $2\pi f_r = \gamma H_A$, where H_A is the anisotropy field and γ is the gyrometric ratio. The high permeability in the disproportionated samples is ascribed to a reduction in eddy current losses, due to the grain size of the α-Fe phase being smaller than the skin depth.

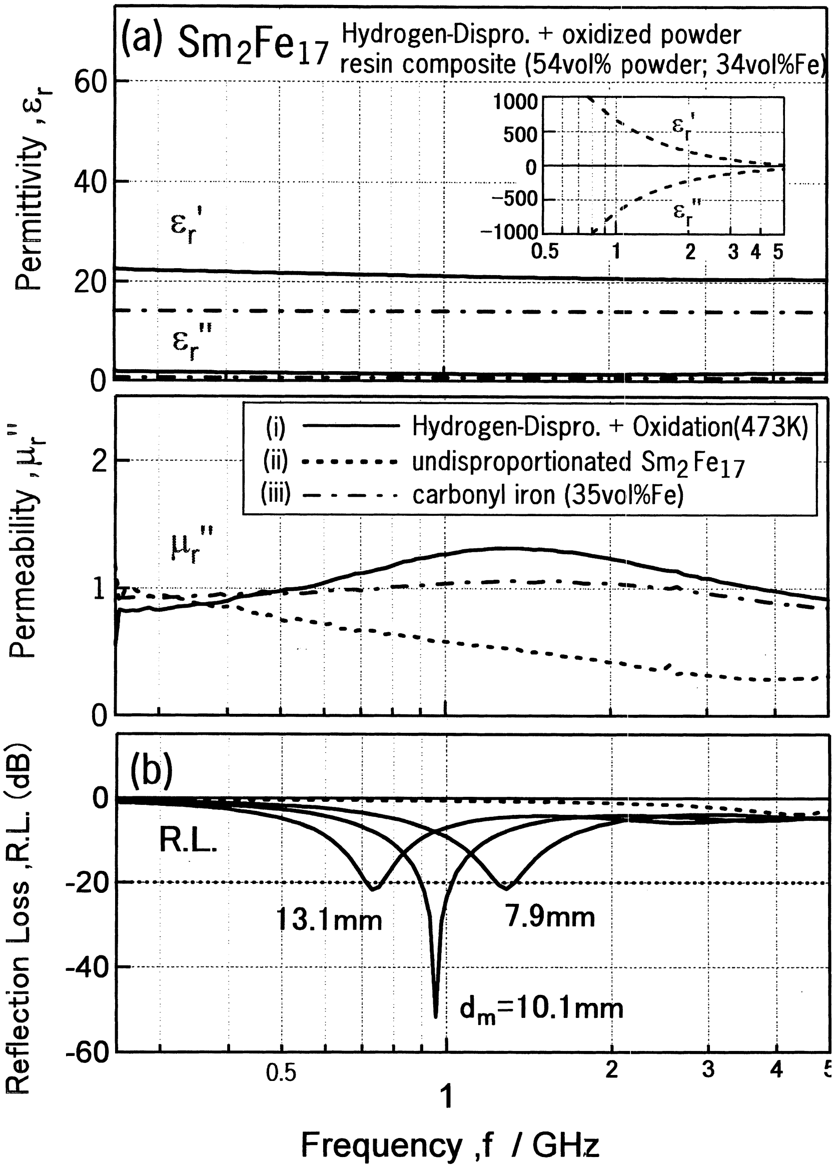

Fig. 5. (a) The frequency dependencies of the complex relative permittivity and permeability of resin composites of: (i) hydrogen-disproportionated and oxidized Sm_2Fe_{17} (54 vol% powder), (ii) undisproportionated Sm_2Fe_{17} (54 vol% powder), and (iii) carbonyl iron with an Fe content equivalent to the volume fraction of Fe found in the other samples (35 vol% powder). (b) The frequency dependence of RL of the hydrogen-disproportionated and oxidized samples.

The RL of the hydrogen-disproportionated and subsequently oxidized sample was calculated from the complex permittivities and permeabilities, and its frequency dependence is shown in Fig. 5b. The RL of the undisproportionated sample is nearly zero due to a high permittivity and a low permeability. However, the disproportionated sample has RL values less than −20 dB in the 0.73–1.30-GHz frequency range (matching frequency, f_m). In particular, a minimum RL value of −53 dB is obtained at 0.95 GHz with a matching thickness (d_m) of 10.1 mm, and the minimum d_m value of 7.9 mm is obtained at 1.30 GHz.

The electromagnetic wave absorption properties of oxygen-disproportionated samples were also investigated in the same manner, and the results are summarized in Fig. 6, versus the oxygen-disproportionation temperature. In order to compare their microwave absorption properties, the results obtained for the hydrogen-disproportionated samples are also shown in Fig. 6. Almost all of the hydrogen-disproportionated or oxygen-disproportionated samples, which were only composed of an α-Fe/SmO two phase microstructure, showed an RL less than −20 dB and a minimum RL of about −50 dB. This suggests that these resin composites can be used as electromagnetic wave absorbers in this frequency range. The f_m values of hydrogen-disproportionated samples are almost constant around 0.7–0.9 GHz, however, those of the oxygen-disproportionated samples increase from 0.75 to 4.0 GHz with increasing oxygen-disproportionation temperature (d_m decreases from 13.9 to 3.9 mm). This difference in properties, with respect to treatment temperature may be due to differences in the disproportionated microstructures, however, more detailed microstructural observations are needed. This shift of the f_m values to a higher frequency in the oxygen-disproportionation samples, should result in a decrease in d_m, because of the inverse proportional relationship between the frequency and the thickness of absorber.

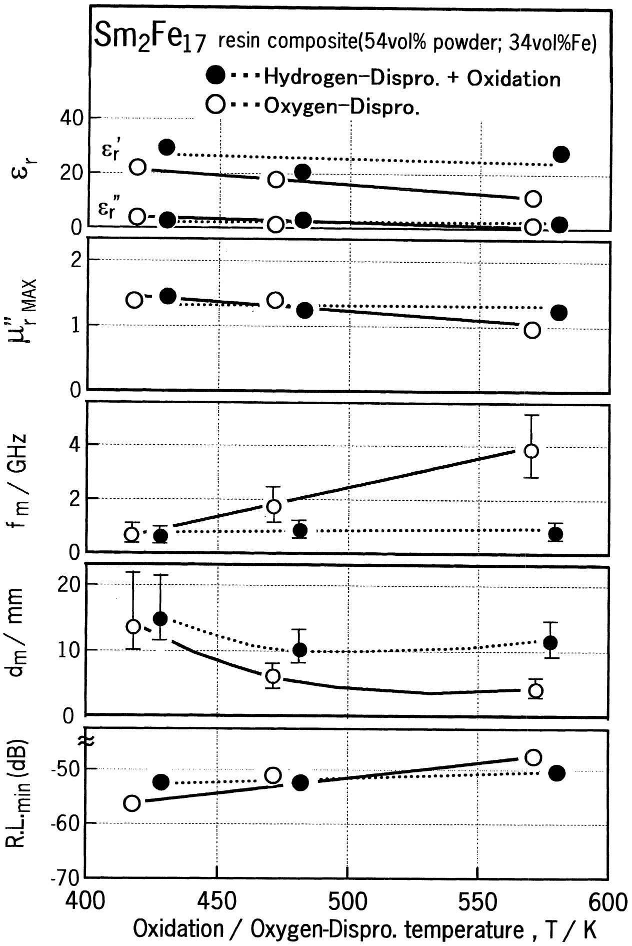

Fig. 6. The electromagnetic wave absorption properties of oxygen-disproportionated samples, compared with those of hydrogen-disproportionated and then oxidized samples.

To conclude, an α-Fe/SmO two-phase microstructure was obtained by disproportionating the Sm_2Fe_{17} compound in hydrogen and then oxidizing the milled powder in air (or by disproportionating the compound in air). A resin composite of this oxidized powder exhibited good electromagnetic wave absorption properties in the 1–5-GHz frequency range.

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