Synthesis of Fine $Mg_{1-x}Ca_xFe_2O_4$ Ferrite Powder Having High Heat Ability under AC Magnetic Field

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Fine $Mg_{1-x}Ca_xFe_2O_4$ ferrite powders for local thermal coagulation therapy were synthesized by a reverse coprecipitation method. The enhancement of temperature under an AC magnetic field was improved by the partial Ca^{2+} substitution. A high heat ability was obtained for the samples calcined at 300 and 800 °C.

Thermal coagulation techniques have become important treatments for cancer tissues. One of the new methods is the application of a magnetic material under an alternating magnetic field from external coils. Up to now, magnetite ($FeFe_2O_4$) has been investigated for this therapy, since fine magnetite powders having a good heat ability can be easily prepared using chemical methods.[1] It was reported that the heating property of magnetite in an AC magnetic field is improved by the preparation of fine particles.[2,3] In addition, the heat ability of the magnetite decreases with oxidation of the Fe(II) ion in the magnetite. We investigated the selection of an appropriate material from many commercialized ferrite powders (MFe_2O_4, M = Mg, Mn, Fe, Co, Ni, Cu, and Sr) having large particle sizes ($>1\,\mu$m).[4,5] In these ferrites, the $MgFe_2O_4$ powder showed the maximum enhancement of the temperature under the AC magnetic field. The reason for this enhancement of the temperature was attributed to the large hysteresis loss in the magnetic properties. We considered that the heat ability could also be influenced by the chemical preparation method in order to reduce the particle size for the $MgFe_2O_4$. Furthermore, the substitution of larger Ca^{2+} ions into the Mg^{2+} sites in cubic $MgFe_2O_4$ ferrite might effectively increase the hysteresis loss.

In this study, we examined the heat ability in an AC magnetic field of a fine $Mg_{1-x}Ca_xFe_2O_4$ powder prepared using the reverse coprecipitation method.

The precursors for the $Mg_{1-x}Ca_xFe_2O_4$ were prepared by a reverse coprecipitation method.[6] Stoichiometric mixtures of $MgCl_2{\cdot}6H_2O$ ($(1-x)/10$ mol), $CaCl_2$ ($x/10$ mol) and $FeCl_3{\cdot}6H_2O$ (0.20 mol) were dissolved in 200 mL of pure water. The mixed metal solution was dropped into an NaOH (6 mol/L, 140 mL) solution in a water bath at 100 °C with stirring and held at the same temperature for 30 min. The precipitation was filtered and washed with pure water until pH < 9, and then it was sufficiently dried at 100 °C. The precursors were calcined at various temperatures for 10 min. in ambient air (heating rate 2 °C/min). In order to characterize the materials, their X-ray diffraction (XRD) patterns with Cu Kα radiation were recorded using a Rigaku Rint 2000 at a scanning rate of 2°/min at 40 kV and 20 mA. Figure 1 shows the apparatus for the measurement of the temperature in the AC magnetic field. The sample powder (1.0 g) was placed in a glass case (Pyrex: 20 mm ϕ, 45 mm). The AC magnetic field was applied to the sample using an external coil. The coil consists of loops of copper pipe (6 mm ϕ) wound around a polypropylene (PP) bobbin. The copper pipe was cooled by flowing water to maintain its temperature. The coil was connected to a power supply source (T162-5712B, Thamway Co., Ltd.) through an impedance tuner. The output power of 200 W at 370 kHz corresponds to 4 kA/m at the center of the coil. An infrared thermometer (505s, Minolta Co., Ltd.) was used for the measurement of the sample temperature (accuracy is ±2 °C). A commercial $MgFe_2O_4$ powder sample (99.9%, Kojundo Chemical Lab. Co., Ltd.) was also measured to compare the heating properties.

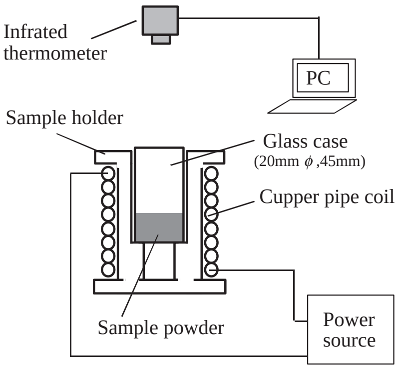

Figure 1. Apparatus for measuring temperature in AC magnetic field.

Figure 2 shows the XRD powder diffraction patterns for the $x = 0.7$ sample calcined at various temperatures. The results of the commercialized $MgFe_2O_4$ and synthesized $CaFe_2O_4$ (sintered at 1000 °C) are also shown in the figure. The XRD patterns showed the broad peaks of the $MgFe_2O_4$-type cubic ferrite for the samples calcined below 800 °C. The FWHM (full width at half hight) decreased with an increase in the calcining temperature. The crystal size was estimated to be ca. 5 and 10 nm for the samples calcined at 300 and 800 °C, respectively. Small peaks of NaCl from the starting materials were detected as an impurity. The cubic crystal structure was changed to orthorhombic $CaFe_2O_4$-type by the calcination at 900 °C.

Figure 3 shows the typical results for the heating properties under an AC magnetic field (370 kHz, 4 kA/m) for the powder samples (1.0 g) calcined at 800 °C. The temperature increased by applying the AC magnetic field to all of the examined samples. The sample temperature almost reached a constant value after 20 min. The increased temperature (ΔT) for some of the

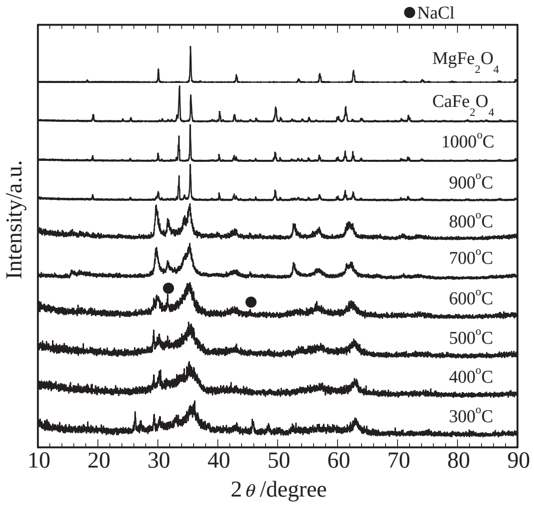

Figure 2. Typical XRD results for $Mg_{0.3}Ca_{0.7}Fe_2O_4$ samples prepared by the reverse coprecipitation method. The calcining temperatures are shown in the figure.

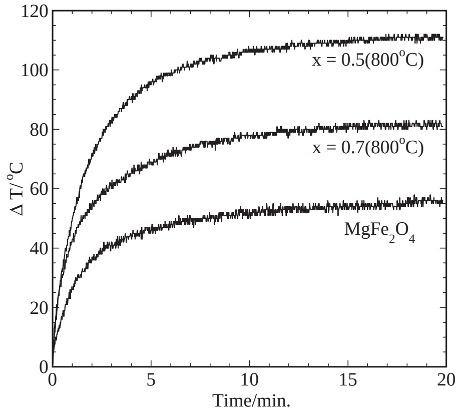

Figure 3. Temperature of the samples (1.0 g) vs time under AC magnetic field (370 kHz, 4 kA/m) in ambient air for typical samples.

Ca^{2+} substituted samples was higher than $\Delta T = 56\,°C$ for the commercialized $MgFe_2O_4$ ferrite powder as shown in Figure 3.

Figure 4 plots the relationship between the calcining temperature and ΔT values under the AC magnetic field after 20 min. for the $x = 0.5$ and 0.7 samples. A high temperature was obtained for the samples calcined at around 300 and 800 °C. This tendency was very similar for the $x = 0.2$–0.8 samples.

Figure 5 shows the relationship between the x value and ΔT for the samples calcined at around 300 and 800 °C. In the case of $MgFe_2O_4$ ($x = 0$), the heat ability was lower than that of the commercialized $MgFe_2O_4$ powder ($\Delta T = 56\,°C$). However, the ΔT value was significantly increased with an increase in the x value. A high temperature was obtained even for $CaFe_2O_4$ ($x = 1.0$) calcined at 300 °C, since the cubic structure was obtained for the samples calcined below 700 °C. The reason for the high ΔT value for the samples calcined at 300 °C would be ascribed to fine particle size for the cubic ferrite. For the samples calcined at 800 °C, the ΔT value decreased for $x > 0.8$. The crystal distortion with the phase transition at around 800 °C might be very effective due to the partial substitution of large Ca^{2+} ions into the Mg^{2+} sites.

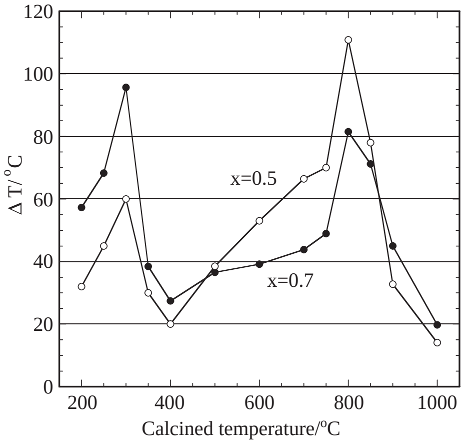

Figure 4. Relationship between the calcining temperature and increased temperature (ΔT) for $x = 0.5$ and 0.7.

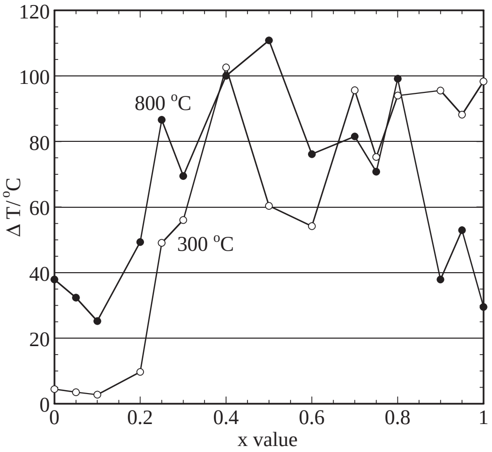

Figure 5. ΔT value for the $Mg_{1-x}Ca_xFe_2O_4$ system calcined at 300 and 800 °C.

As a conclusion, we obtained a good candidate as a material for the local thermal coagulation therapy. The suitable calcination temperature for the precursors prepared by the reverse coprecipitation method was 300 or 800 °C. However, we could not clarify the reason for the high ΔT of these Ca^{2+} substituted samples. We will clarify this mechanism in the future.

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