Effects of Mg Doping and Sintering Temperature on the Magnetoresistance of Sintered Fe_3O_4 Ferrites

C. T. Lie, P. C. Kuo, A. C. Sun, C. Y. Chou, S. C. Chen, I. J. Chang, T. H. Wu, and J. W. Chen

***Abstract*—Fe_3O_4 powder was mixed with MgO powder and then sintered in an atmosphere of argon at various temperatures for 3 h to form Mg-doped Fe_3O_4 ferrites. The effects of the sintering temperature, microstructure, and Mg content on the magnetoresistance of sintered Fe_3O_4 ferrites were investigated. X-ray diffraction and chemical titration analysis of Fe^{2+} and Fe^{3+} ions indicate that the nonstoichiometric phases of Fe_3O_{4+x} and $MgFe_2O_{4-x}$ coexisted in the sintered sample. The temperature dependence of resistivity was examined. A plot of log ρ against $T^{-1/2}$ of the sintered samples exhibits a linear relationship, indicating that the dominant magnetoresistance effect is spin-dependent tunneling. The maximum magnetoresistance of the sintered sample is about 7.3% at room temperature at a magnetic field of 12 kOe. The Mg content of this sample is 0.93 at.%.**

***Index Terms*—Magnetoresistance, sintered Fe_3O_4 ferrites, spin-dependent tunneling.**

I. Introduction

SEVERAL GROUPS have examined the magnetoresistance (MR) of pure Fe_3O_4 [1]–[3]. The MR value of Fe_3O_4 in these studies was found to be very low at room temperature ($MR = 0 \sim 1.7\%$). The MR value of the sintered Fe_3O_4 ferrite depended on the microstructure and sintering conditions. In this work, the MR value of the sintered Fe_3O_4 ferrite at room temperature is 5.4% and can be improved to about 7.3% by adding a small amount of Mg. The effects of Mg content, sintering temperature (T_s), and microstructure on the magnetoresistance of ferrite at room temperature were investigated.

II. Experiment

High-purity Fe_3O_4 powder was mixed with various amounts of MgO powder (0∼25 mol.%), according to the formula $(MgO)_\delta(Fe_3O_4)_{1-\delta}$. After full mixing, the powder was compressed into a pellet (10-mm diameter, 1-mm thick) under a pressure of 3757 kg/cm^2, and then sintered in an atmosphere of argon at temperatures between 1050 °C and 1200 °C for 3 h. The composition of the sintered sample was analyzed using energy dispersive spectroscopy (EDS). The crystalline structure of the sintered sample was determined by X-ray diffraction (XRD) using Cu–Kα radiation. The microstructure was observed by a scanning electron microscope (SEM). The Fe^{2+} and Fe^{3+} ion contents of the sintered sample were examined by chemical titration [4]. The magnetoresistance of the sintered sample was measured at various temperatures using a four-probe method. The maximum applied field was 12 kOe.

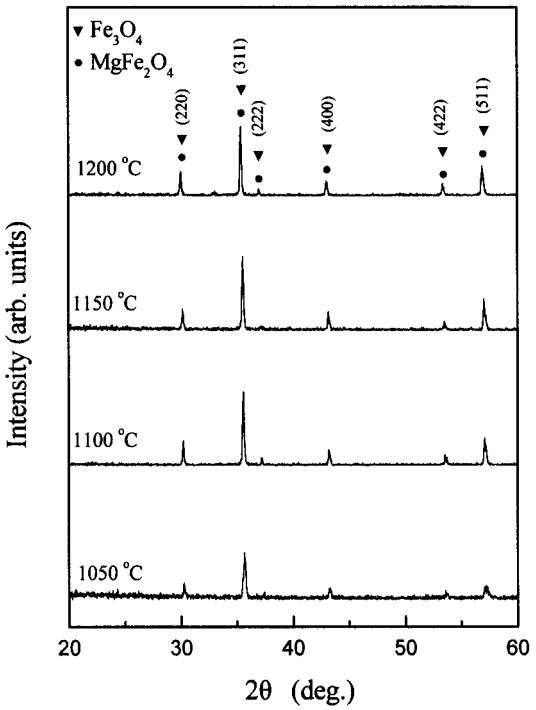

Fig. 1. XRD patterns of the sintered samples for various T_s. MgO powder in the mixed powder of these sintered samples is 5 mol.%.

III. Results and Discussion

Fig. 1 shows the XRD patterns of the sintered samples for various temperatures, T_s. The two phases, Fe_3O_4 and $MgFe_2O_4$, coexist at these sintering temperatures, indicating that the MgO oxide reacts with some Fe_3O_4 to form $MgFe_2O_4$ ferrite after sintering. However, the XRD peaks of $MgFe_2O_4$ ferrite are very close to those of Fe_3O_4 and almost overlap. Magnifying the XRD patterns at a specific angle reveals that the peaks of $MgFe_2O_4$ and Fe_3O_4 are separated, as shown in Fig. 2. Fig. 2 shows the (311) peaks of Fe_3O_4 and $MgFe_2O_4$ ferrites of the sintered sample at T_s of 1100 °C; the MgO

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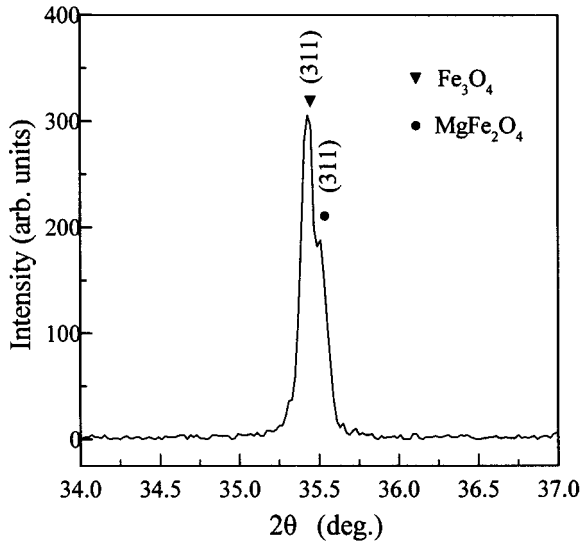

Fig. 2. XRD pattern of the (311) peaks of Fe_3O_4 and $MgFe_2O_4$ ferrites of the sintered sample.

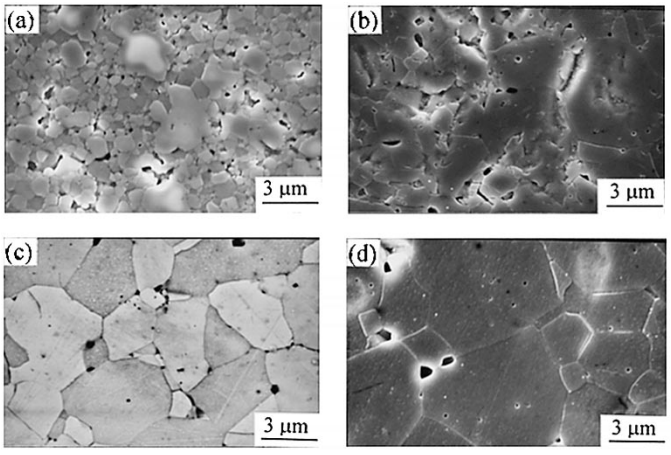

Fig. 3. SEM micrographs of sintered samples with 5 mol.% MgO in the mixed powder. Sintering temperature of (a) is 1050 °C, of (b) is 1100 °C, of (c) is 1150 °C, and of (d) is 1200 °C, respectively.

powder content in the mixed powder of this sintered sample is 5 mol.% and the Mg content in this sintered sample is 0.93 at.%, respectively.

Fig. 3 shows SEM micrographs of the sintered samples for various T_s. The grain size and densification of these samples increase with increasing T_s. The grain size is about 0.75 μm at T_s of 1050 °C and increases to about 5.4 μm at T_s of 1200 °C, as shown in Fig. 3(a) and (d). The pores disperse uniformly in the sintered sample and the number of pores decreases as T_s increases.

The SEM element mapping analysis indicates that the Mg ions are distributed uniformly in all sintered samples. Fig. 4 shows the relationship between MR value and T_s of sintered samples with various Mg contents at room temperature. The MR value was found to depend on both T_s and Mg content. The MR values of all the samples increased with T_s to an optimum temperature and then decreased as T_s is further increased. The optimum T_s is that at which the maximum MR value can be obtained and is around 1100 °C for all samples, as shown in

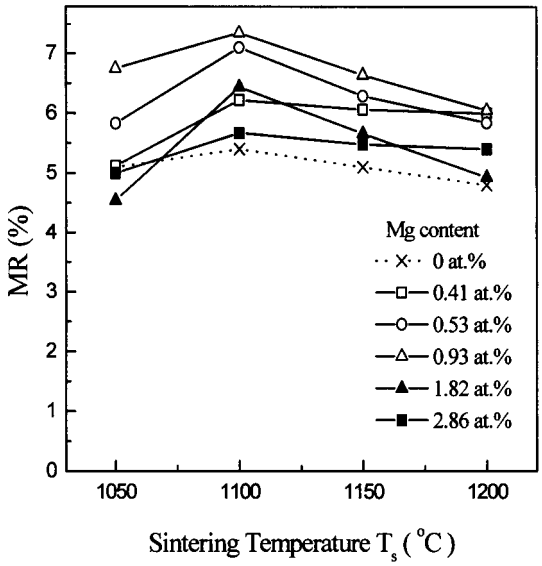

Fig. 4. Relationship between MR value and T_s of various sintered samples for various Mg contents.

Fig. 4. Berkowitz *et al.* [5] showed that the MR value depends inversely on the grain size. The surface/volume ratio decreases as the grain size is increased. Once the surface/volume ratio reduces, the spin-dependent interfacial scattering is decreased, and then the MR value is also dropped. The grain size and densification of the samples in Fig. 3 increase with T_s. The MR value of the sample sintered at 1050 °C is lower than that of the sample sintered at 1100 °C because it has more pores, and therefore a smaller surface/volume ratio. However, the MR value decreases as T_s exceeds 1100 °C, because the grain size increases, and the surface/volume ratio falls. We speculate that the MR value is dominated by the number of pores at lower T_s, but dominated by the grain size at higher T_s. The optimum T_s corresponds to the temperature to get an optimum magnetic grain size and densification and also corresponds to the temperature to exhibit the maximum MR value.

Chemical titration analysis of Fe^{2+} and Fe^{3+} ions indicates that nonstoichiometric phases of Fe_3O_{4+X} and $MgFe_2O_{4-X}$, except Fe_3O_4 and $MgFe_2O_4$, also exist in the sintered samples. The electric resistivity, ρ, of the sintered sample was measured by the four-probe method at temperatures between 80 K and room temperature. Fig. 5 indicates the plots of log ρ versus $T^{-1/2}$ for sintered samples with various Mg contents. $T^{-1/2}$ is linearly related to log ρ for all samples, implying that the magnetoresistance effect of these sintered samples is mainly spin-dependent tunneling [6], and implying that the insulators Fe_2O_3, $MgFe_2O_4$, and $MgFe_2O_{4-X}$ act as tunneling barriers and thus increase the MR value of Fe_3O_4 itself.

Fig. 6 shows the relationship between MR value and Mg content of the sintered sample at T_s of 1100 °C measured at room temperature. The maximum MR value is about 7.3%, which occurs at an Mg content of 0.93 at.%. The grain size of this sample is about 2.5 μm and its density is 4.95 g/cm^3, which is about 94% theoretical density of pure Fe_3O_4 (5.24 g/cm^3). The MR value of pure sintered Fe_3O_4 is about 5.4% and increases with Mg content when Mg content is less than 0.93 at.%. $MgFe_2O_4$

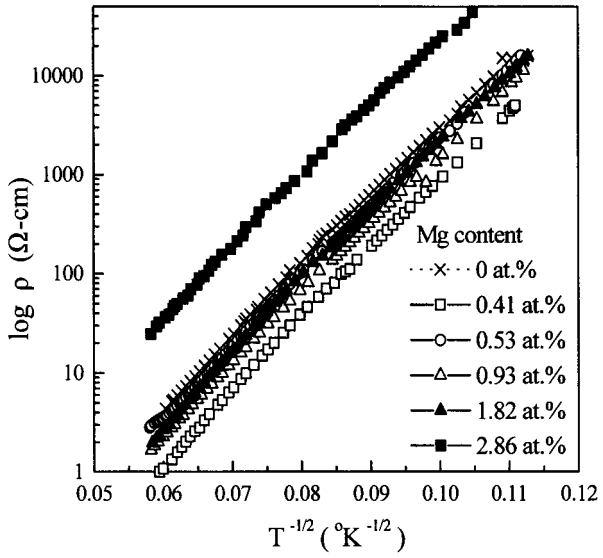

Fig. 5. Log ρ versus $T^{-1/2}$ for various samples sintered at 1100 °C.

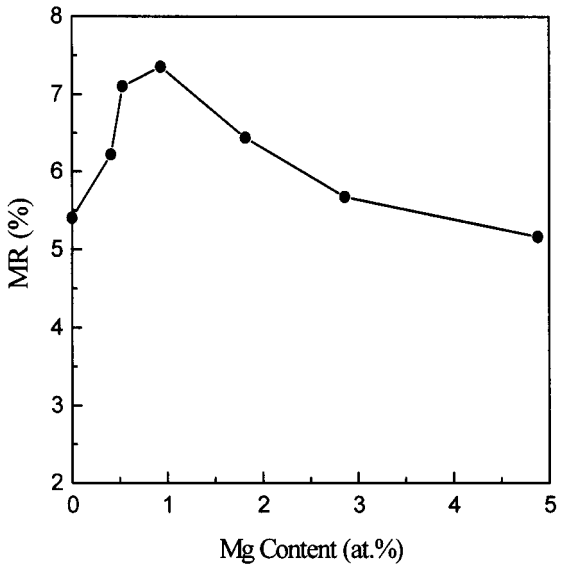

Fig. 6. Relationship between MR value and Mg content of the sintered sample. The sintered temperature is 1100 °C.

ferrite and $MgFe_2O_{4-X}$ ferrite will form in the sintered sample after Mg is added. $MgFe_2O_4$ ferrite and $MgFe_2O_{4-X}$ ferrite are tunneling barriers, because they are insulators. When the doping amount of Mg is more than 0.93 at.%, the spin-dependent tunneling barrier thickness is too wide to increase the MR value because the tunnel effect cannot occur when the energy barrier is too wide. Therefore, the MR value is decreased when the Mg content is higher than 0.93 at.%, as shown in Fig. 6.

IV. Conclusion

The effect of sintering temperature and Mg doping on the MR value of sintered Fe_3O_4 ferrite is examined. The optimum sintering temperature that yields the highest MR value is about 1100 °C. The maximum MR of the sintered samples at room temperature is about 7.3%, and the Mg content is then 0.93 at.%.

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