Magnetoresistance and Microstructure of the Sintered Ni Doped Fe_3O_4 Ferrites

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***Abstract*—Sintered Ni doped Fe_3O_4 ferrites were prepared by mixing Fe_3O_4 powder with NiO powder and compressing into pellet, then sintering in argon atmosphere. The contents of Ni in the sintered samples were between 0 at.% and 5.08 at.%. The effects of the Ni content, sintering temperature and sintering time on the magnetoresistance (MR) and microstructure 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 $NiFe_2O_{4-Y}$ were co-existed in the Ni doped sample. The optimum sintering temperature, at which the maximum MR value could be obtained, is around 1100 °C and the optimum sintering time is about 9 h for all samples. After sintering at 1100 °C for 9 h, the MR value of the undoped Fe_3O_4 ferrite is about 6% at room temperature. Maximum MR value is about 7.5% when 1.12 at.% Ni was doped. It was found that the log ρ versus $T^{-1/2}$ curves of all the samples exhibit a linear relationship from the measurement of the electrical resistivity (ρ) of the sintered samples between 80 K and room temperature. This implies that the MR effect is mainly spin-dependent tunneling where the electrons flow through insulating barriers of Fe_2O_3, $NiFe_2O_4$ or $NiFe_2O_{4-Y}$.**

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

I. Introduction

RECENTLY, the transport properties of the half metallic oxide material Fe_3O_4, [1]–[4], have been extensively studied due to its potential application in spintronic devices. Fe_3O_4 has electrons of a single spin polarization at the Fermi level [5] (100% spin polarization), therefore, it has been suggested to be a good candidate of the magnetoresistance (MR) materials. The MR behavior in the magnetite of different forms including epitaxial films, single crystals, polycrystalline films, and compact powder has been investigated [1]–[4]. However, the largest MR value of Fe_3O_4 bulk obtained at room temperature is only 1.2% [4]. In this paper, we made effort to increase the MR value of the Fe_3O_4 bulk at room temperature by doping Ni into sintered Fe_3O_4 ferrite and investigated the effects of the Ni content, sintering temperature (T_s) and sintering time (t_s) on the MR and microstructure of sintered Fe_3O_4 ferrites.

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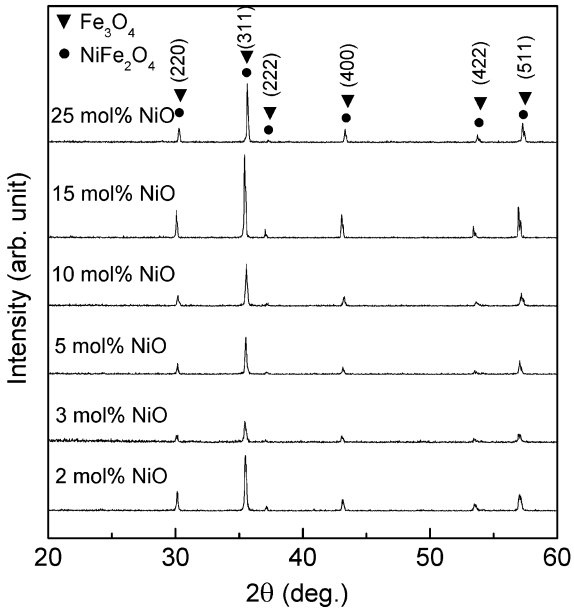

Fig. 1. X-ray diffraction patterns of the sintered samples with various amounts of NiO powder in mixed powder. The T_s is 1100 °C and the t_s is 3 h.

II. Experiment

Sintered Ni doped Fe_3O_4 ferrites were prepared by mixing high purity Fe_3O_4 powder with various amounts of NiO powder (0–25 mol.%) according to the formula of $(NiO)_x(Fe_3O_4)_{1-x}$. The full mixed powder was compressed into pellet under a pressure of 3757 kg/cm^2, then sintering in argon atmosphere. The T_s was varied from 1050 °C to 1200 °C and the t_s was between 3 and 12 h. The composition of the sintered sample was analyzed by energy dispersive spectroscopy (EDS). The chemical titration method was used to examine the Fe^{2+} and Fe^{3+} ion contents of the sintered sample [6]. The microstructure and crystal structure of the sintered sample was investigated by scanning electron microscope (SEM) and X-ray diffractometer (XRD) with Cu-K_α radiation. The electric resistivity (ρ) and MR value of the sintered sample was measured by the four-probe method. The maximum applied field is 8.8 kOe and the applied field is parallel to the current direction. Magnetic properties of the sintered sample were measured by a vibrating sample magnetometer (VSM) at room temperature.

III. Results and Discussion

Fig. 1 shows the X-ray diffraction patterns of the sintered samples with various amounts of NiO powder (2–25 mol%) in mixed powder. The T_s is 1100 °C and the t_s is 3 h. We can observe that the two phases, Fe_3O_4 and $NiFe_2O_4$, coexisted in

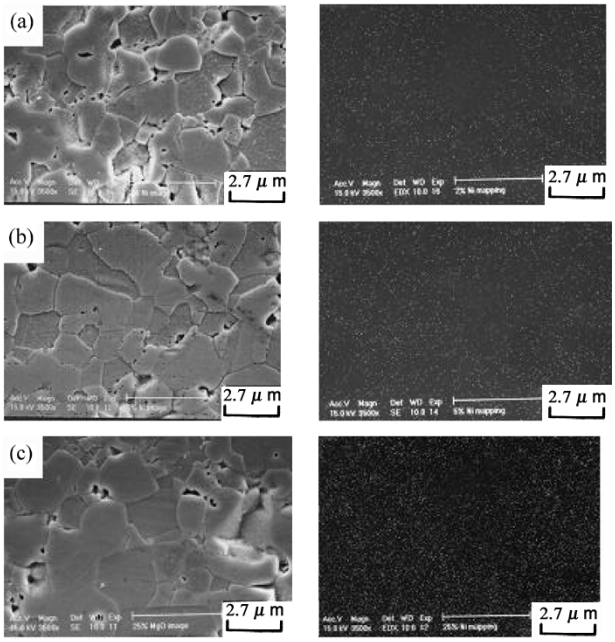

Fig. 2. SEM micrographs and their Ni element mapping.of the sintered samples with various Ni contents. The Ni content is (a) 0.41 at% Ni, (b) 1.12 at% Ni, and (c) 5.08 at% Ni, respectively.

all sintered samples. This indicates that the NiO oxide reacts with parts of Fe_3O_4 to form $NiFe_2O_4$ ferrite during sintering. From the Joint Committee on Power Diffraction Standards (JCPDS) cards, it can be seen that the X-ray diffraction peaks of $NiFe_2O_4$ ferrite are very close to those of Fe_3O_4 and they almost overlapped. However, we can exactly observe the separated (311) peaks of Fe_3O_4 and $NiFe_2O_4$ ferrites in the Magnified XRD patterns at the specific angle as the NiO powder content in mixed powder is >5 mol%. From the analysis of Fe^{2+} and Fe^{3+} ion contents in the sintered sample by the chemical titration method, the (Fe^{2+}/total Fe) value is about 27 mol% which is lower than that of pure Fe_3O_4 (33 mol%). This means that some Fe_3O_4 were oxidized to Fe_2O_3 during sintering. Accordingly, the NiO oxide would combine with Fe_2O_3 or Fe_3O_4 ferrite to form $NiFe_2O_4$ ferrite or nonstoichiometric $NiFe_2O_{4-Y}$ ferrite during sintering. Therefore, the nonstoichiometric phases of Fe_3O_{4+X} and $NiFe_2O_{4-Y}$, except Fe_3O_4 and $NiFe_2O_4$, coexisted in the Ni doped sample.

SEM micrographs of the sintered samples with various Ni contents and their Ni element mapping are shown in Fig. 2(a)–(c). The T_s is 1100 °C and the t_s is 3 h. We can see that there are some pores disperse in the samples and the average grain size is about 3 μm for all samples. By comparing the SEM micrograph and corresponding Ni mapping image, it can be seen that the Ni ions disperse uniformly in the grains. This means that the $NiFe_2O_4$ ferrite or nonstoichiometric $NiFe_2O_{4-Y}$ ferrite are uniformly dispersed in all sintered samples.

Fig. 3 shows the variation of the MR value with T_s of sintered samples with various Ni content at room temperature. The MR value was defined as $\mathrm{MR}(\%) = (R_H - R_0)/R_0$, where R_H is the resistance in maximum applied magnetic field H and R_0 is the resistance in zero magnetic field. The contents of Ni in the

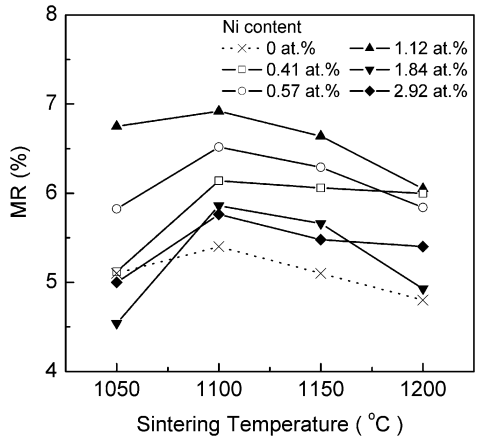

Fig. 3. Relationship between MR value and T_s of various sintered samples with various Ni contents.

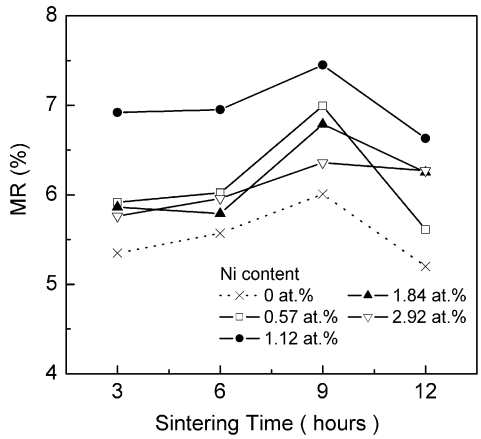

Fig. 4. Relationship between MR value and t_s of various sintered samples with various Ni contents.

sintered samples were between 0 at.% and 5.08 at.% and the t_s is 3 h for all samples. We can see that the MR values of all the samples with various Ni contents increased with T_s to a maximum MR value and then decreased as T_s is further increased. The various doping amounts of the Ni will change the tunneling barrier thickness of the $NiFe_2O_4$ ferrite or $NiFe_2O_{4-Y}$ ferrite and affect the MR value. Because the grain size and densification of the samples were increased with T_s [7]. The lower MR value of the sample sintered below 1100 °C is due to more pores dissolved in it. As the T_s is higher than 1100 °C, the MR value is decreased due to the larger grain size. More amount of pores in the sintered sample and the increase of grain size both will decrease the surface/volume ratio. Therefore, the spin-dependent interfacial scattering is reduced and the MR value is decreased. The optimum T_s, at which the maximum MR value could be obtained, is around 1100 °C for all samples.

Fig. 4 shows the variation of the MR value with t_s for various sintered samples at room temperature. The T_s is 1100 °C. We can see that the MR values of all the samples with various Ni contents increased with t_s to a maximum MR value and then decreased as t_s is increased further. The optimum t_s is about 9 h for all samples. After sintering at 1100 °C for 9 h, the MR value of the undoped Fe_3O_4 ferrite is about 6% at room temperature. The MR value was enhanced by doping Ni. Maximum MR value

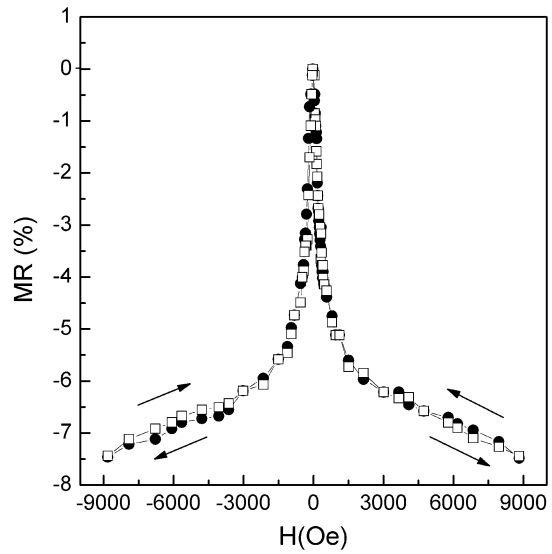

Fig. 5. MR curve of the sintered sample with 1.12 at.% Ni.

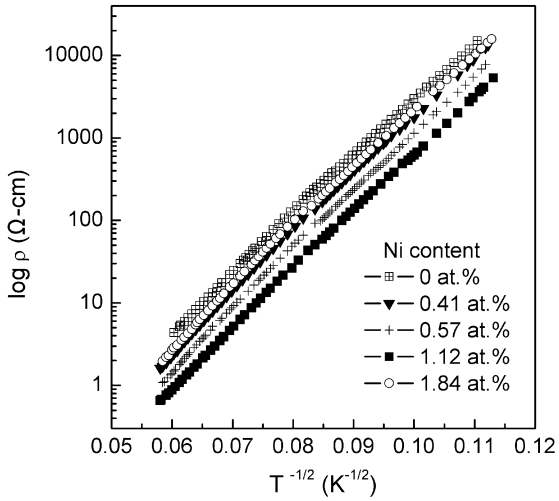

Fig. 6. Log ρ versus $T^{-1/2}$ of various samples which sintered at 1100°C for 9 h.

is about 7.5% when 1.12 at.% Ni was doped. The MR curve of this sintered sample is shown in Fig. 5.

Fig. 6 shows the variations of electrical resistivity (ρ) with temperature of the sintered samples with various Ni contents. It was found that the log ρ versus $T^{-1/2}$ curves of all the samples exhibit a linear relationship between 80 K and room temperature. This implies that the MR effect is spin-dependent tunneling dominant [8] where the electrons flow through insulating barriers of Fe_2O_3 [9], $NiFe_2O_4$ or $NiFe_2O_{4-Y}$. Therefore, the MR values were dramatically improved in the pure Fe_3O_4 sample or Ni doped Fe_3O_4 ferrites comparing with other research groups.

IV. Conclusion

We have investigated the magnetic and electron transport properties of sintered Ni doped Fe_3O_4 ferrite. It is found that MR value of the bulk Fe_3O_4 can be enhanced by doping Ni. The MR effect of sintered Ni doped Fe_3O_4 ferrite is mainly spin-dependent tunneling where the electrons flow through insulating barriers of Fe_2O_3, $NiFe_2O_4$ or $NiFe_2O_{4-Y}$. The maximum MR value at room temperature is about 7.5% after sintering at 1100 °C for 9 h when 1.12 at.% Ni was doped.

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