Tunneling Magnetoresistance in Sintered Fe$_3$O$_4$ Samples Diluted with Fe and α-Fe$_2$O$_3$

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Electric transport and magnetoresistance characteristics were investigated for Fe$_3$O$_4$ - x Fe ($x=0, 10, 20$ wt.%) samples and Fe$_3$O$_4$-α-Fe$_2$O$_3$ samples sintered at 500°C. For composition dependence of Fe$_3$O$_4$ - x Fe samples, the largest room temperature MR, 3.3% at 10 kOe, was obtained from a Fe$_3$O$_4$-10 Fe sample. For the surface heat treatment dependence of Fe$_3$O$_4$ powders, the largest room temperature MR, 4% at 10 kOe, was obtained from a Fe$_3$O$_4$-α-Fe$_2$O$_3$ sample sintered with Fe$_3$O$_4$ powders heated at 200°C in air. It was found that these enhanced MR ratios always appear together with the appropriate excess resistance which is regarded as the tunneling barrier. These enhanced MR ratios of Fe$_3$O$_4$-10 Fe and Fe$_3$O$_4$-α-Fe$_2$O$_3$ samples can be explained by the increased interparticle contact sites and the appropriate thickness of α-Fe$_2$O$_3$, respectively.

Keywords: Fe$_3$O$_4$, tunneling magnetoresistance, sintered body, electric transport

1. INTRODUCTION

Since low-field negative magnetoresistance (MR), associated with interparticle transport, was observed in polycrystalline oxide samples of ferromagnetic manganite [1-3], other half metallic oxides such as La$_2$(FeMo)O$_6$, CrO$_2$ and Fe$_3$O$_4$ have attracted great interest, and have been expected to exhibit high MR. Among the half metallic oxides, magnetite (Fe$_3$O$_4$) is perhaps one of the oxides most expected to achieve the high room temperature MR because of its high Curie temperature ($T_c=580°C$) compared with the other ferromagnetic oxides mentioned above.

The room temperature MR of Fe$_3$O$_4$ has been reported in polycrystalline thin films [4, 5] and powder compacts [6]. Adachi et al. [4] observed that the polycrystalline Fe$_3$O$_4$ film with the addition of 1% Pt exhibited a large MR of 8.7% at 2.5 kOe. Nishimura et al. [5] observed that the synthesized Fe$_3$O$_4$ film from FeCl$_3$ solution exhibited a MR of 7.4% at 9 kOe. Coey et al. [6] observed that Fe$_3$O$_4$ bulk prepared by powder compact exhibited a MR of 1.2% at 5 kOe. These results reported that the MR effect is associated with a tunneling transport of spin-polarized electrons through the interparticle barrier, and also suggested that appropriate control of the interparticle structure may improve the MR effect.

On the other hand, the interparticle structure in Fe$_3$O$_4$ sintered bodies could be controlled by powder parameters such as the powder size, shape, density, powder composites and surface heat treatment of powders. However, in spite of their high scientific potential, the magnetoresistance behaviors for Fe$_3$O$_4$ sintered bodies have not been investigated.

In this study, we have prepared sintered Fe$_3$O$_4$ - x Fe ($x=0, 10, 20$ wt.%) samples and Fe$_3$O$_4$-α-Fe$_2$O$_3$ samples sintered with the Fe$_3$O$_4$ powders heat-treated in the temperature range of 100°C and 400°C in air. This paper describes how the MR and the electric transport properties of sintered Fe$_3$O$_4$ samples depend on Fe composition and the surface heat treatment temperature of Fe$_3$O$_4$ particles.

2. EXPERIMENTAL PROCEDURE

The powder sizes of both elemental Fe$_3$O$_4$ and Fe were less than 5 μm and 2 μm, respectively. A vibration ball mill was filled with the powder mixtures having the nominal compositions of Fe$_3$O$_4$ - x Fe ($x=0, 10, 20$ wt.%) for milling, and milled for 150 h in a highly purified argon atmosphere with a frequency of 25 Hz and amplitude of 2.5 mm. The size of the milled Fe$_3$O$_4$ powders was about 200 nm as shown by observation of scanning electron microscopy. On the other hand, to form α-Fe$_2$O$_3$ layer at the surface of Fe$_3$O$_4$ powders, the milled Fe$_3$O$_4$ powders were heated in the temperature range between 100°C and 400°C in air. For pulse discharge sintering, a graphite mold with two TiAl punches pressed into it were filled with the heat treated Fe$_3$O$_4$ powders and Fe$_3$O$_4$-γ-X Fe powders separately, then pressed to make pellets. Disc-shaped pellets 20 mm in diameter and 5 mm in thickness were sintered at 500°C for 10 minutes in vacuum under the pressure of 100 MPa. The rel-
ative densities of sintered pellets were above 95%.

The microstructures of both the milled powders and the sintered pellets were investigated by X-ray diffraction analysis with monochromatic Cu-Ka radiation. The resistance of Fe$_3$O$_{4-x}$ Fe samples was measured in the range between 77 K and 300 K. The room temperature MR of the sintered samples were measured by a conventional D. C. four point probe method in the field range of ±10 kOe.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the Fe$_3$O$_{4-x}$ Fe ($x=0$, 10, 20 wt.%) samples sintered at 500°C for 10 minutes. The Fe$_3$O$_4$ sample indicated the randomly oriented Fe$_3$O$_4$ polycrystalline. For Fe$_3$O$_{4-10}$, 20 Fe samples, the Fe as well as the Fe$_3$O$_4$ peaks was observed. It can be seen from the figure that the Fe peak varies from a small and broad Fe peak in the Fe$_3$O$_{4-10}$ Fe sample to a sharp peak with high intensity in Fe$_3$O$_{4-20}$ Fe. This suggests that fine Fe particles, 20 nm calculated from Scherrers equation, in the Fe$_3$O$_{4-10}$ Fe become large particles with the increasing of the Fe content due to coarsening.

Fig. 2 shows the normalized electric resistance versus the external magnetic fields (H) for Fe$_3$O$_{4-x}$ Fe samples. For Fe$_3$O$_4$ and Fe$_3$O$_{4-10}$ Fe samples, the electric resistances decrease with increasing H. These MR-H loops are expected for negative MR by tunneling transport through the interparticle barrier. The largest room temperature MR, 3.3% at 10 kOe, was obtained for the Fe$_3$O$_{4-10}$ Fe sample. However, for the Fe$_3$O$_{4-20}$ Fe sample, the resistance firstly increases in the low field, and then decreases under the high magnetic field. This behavior suggests that there is a positive MR and negative MR. The positive MR may be related to the coarsening of Fe particles which exhibits the ferromagnetism, that is, anisotropy MR. As a result, the partial cancellation of the negative and positive MR effects would give rise to a reduction of the MR ratio.

To clarify the mechanism of electric transport of the sintered Fe$_3$O$_{4-x}$ Fe samples, we have investigated the temperature dependence of ρ. Fig. 3 shows the ρ-T relation of sintered Fe$_3$O$_{4-x}$ Fe ($x=0$, 10, 20 wt.%) samples. ρ of the Fe$_3$O$_4$ and Fe$_3$O$_{4-10}$ Fe samples exhibited negative temperature dependence, while ρ of the Fe$_3$O$_{4-20}$ Fe sample exhibited positive temperature dependence. It can be also shown...