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Author

Tsunekawa, H.

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MICROSTRUCTURE AND PROPERTIES
OF COMMERCIAL GRADE MANGANESE ZINC FERRITES

H. Tsunekawa, A. Nakata, T. Kamijo, and K. Okutani
TDK Electronics Co., Research and Development Laboratory
Ichikawa, Chiba, Japan

and

R.K. Mishra and G. Thomas
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

ABSTRACT

The microstructures of differently processed Commercial grade MnZn soft ferrites have been studied using transmission electron microscopy and microanalysis, and the microstructural features correlated with the magnetic properties. Special emphasis has been placed on the grain boundaries. The permeabilities range from 1200 to 18,000 and loss factors ($\tan\delta/\mu$) from 1.0×10^{-6} to 13.7×10^{-6} at 50 kHz. The pore distribution in these ferrites was quite diverse although the total porosities are nearly the same. In specimens of low μ either the defect density was high or varying amounts of amorphous phase were observed at the grain boundaries. In these samples STEM X-ray analyses revealed the presence of Ca and Si in the thin grain boundary phase. Also, in some specimens the presence of Fe_2O_3 and/or MnO_2 precipitates at some grain junctions was observed. In the high μ ferrites, few defects and no intergranular phases were observed, and Ca could not be detected. It is suggested that the lattice distortion associated with the amorphous phase and the boundary segregation reduces the permeability.

I. INTRODUCTION

It has now been established by detailed microstructural analyses that the magnetic properties of ferrites depend strongly on lattice defects, second phases, etc., as well as on porosity and grain size (e.g. Refs. 1-3). This is in addition to the fact that permeability is a strong function of composition. From a practical viewpoint therefore, considerable interest exists in improving the properties of ferrites by controlling the composition and microstructure through processing. In the present study, particular attention has been paid to try to identify the significant parameters affecting properties in some commercial grade Mn/Zn ferrites. The compositions and properties of the ferrites are listed in Tables 1, 2. These ferrites were sintered from calcined green compacts of initial particle sizes of $0.9\mu-1.1\mu$. Sample 1 was sintered in air to a maximum temperature of 1140°C whilst Sample 3 was taken to 1350°C . Sample 6 was treated a little differently in that during the initial heating cycle the oxygen partial pressure was reduced and a nitrogen atmosphere applied. The finishing temperature was again 1350°C .

II. MATERIALS CHARACTERIZATION

The sintered compacts were examined by transmission electron microscopy including utilization of high voltage, high resolution and STEM analytical techniques. The particular advantages of these methods for analysis of material have been recently summarized.⁽⁴⁾ The micro-analytical capabilities of STEM allow X-ray analysis to be done on very small areas ($\approx 100\text{\AA}$ diameter) at spectroscopic resolutions of order 10^{-3}

for elements with atomic number > 11 . Defect characterization was carried out through using appropriate contrast analyses.

III. EXPERIMENTAL RESULTS AND DISCUSSION

It is convenient to group the experimental results into the various categories of microstructures that are thought to influence the properties. Below, the features that are discussed are lattice defects (not point defects), grain size, porosity, grain boundary segregates and local lattice distortions at the boundaries.

Lattice Defects - Dislocations and stacking faults were observed in almost every grain of Sample 1, but none in Sample 3, and only occasionally (about one grain in ten) in Sample 6. Annealing subsequent to processing has been shown to remove stacking faults in both lithium and nickel ferrites.⁽²⁾ The lowest finishing temperature of Sample 1 is probably one of the reasons for these residual defects and the low values of μ (Table 2) are due in part to these defects. Since the effects of such lattice defects have already been considered previously⁽¹⁾, no further discussion of them will be given here.

Grain Size, Porosity - Due to the different processing conditions, the grain sizes were different, increasing from about 7μ (Sample 1) to $\approx 35\mu$ (Sample 6). The densities of all samples were about the same and thus so is the total porosity. However, pore distribution varies considerably, as seen in Fig. 1. Except for Sample 6, pores exist only at grain boundaries (Fig. 1a), indicating good boundary mobility was achieved by the treatment afforded Sample 6, i.e. grain boundaries can move away from pores leaving a mixture of intra- and intergranular porosity. (Fig. 1b).

In Samples 3 and 6, grain size doubles, but μ increases more than fourfold. Attempts to explain these variations in μ by pore distribution following the method of Jain et. al.⁽⁵⁾ have failed. In this model, pores are regarded as pinning sites for the domain walls and the reversible motion of the domain walls determines the initial μ when the composition is constant. For Samples 3 and 6, where the composition is almost constant, the effective distance between pores is almost the same, but the permeabilities are widely different, due in part to grain size⁽⁶⁾, pore distribution⁽⁷⁾, as well as other microstructural features.

Grain Boundaries - In samples of low μ , fine precipitates⁽⁸⁾ of $\alpha\text{-Fe}_2\text{O}_3$ or MnO_2 (as detected by electron diffraction) were found associated with intergranular pores (Fig. 2). In Sample 3 dark field and lattice imaging analyses⁽⁹⁾ near grain boundaries revealed the presence of a non-crystalline phase 30-50 Å wide and forming pockets at grain boundary junctions (Figs. 3,4). These were not detected in Sample 6. (See Fig. 5).

X-ray microanalysis by STEM showed Ca and some Si segregation at the boundaries⁽¹⁰⁾ in Sample 3 (Fig. 6a), indicating that the glassy phase is probably a calcium silicate. This would be expected also from the chemical composition (Table 1). Fig. 6b shows little variation in Zn, Mn or Fe. In Sample 6 where no glassy phase could be seen, X-ray microanalysis (Fig. 7) failed to detect any Ca or Si.

Since no Ca is detected in Sample 6, either at the grain boundaries or in the grain interiors, one can conclude that Ca is distributed uniformly in the grains. In any case, the Ca concentration is below the detection

limit of STEM.

Lattice Distortion - Lattice imaging in conjunction with optical microdiffraction⁽¹¹⁾ reveals that the lattice parameter is larger near the grain boundaries in the case of Sample 3 and not so in the case of Sample 6. An example of measurements for Sample 3 is shown in Fig. 8. The results indicate that the segregation of calcium is responsible for this effect. Such a change in lattice parameter introduces strain and hence stresses near the boundaries, which in turn affects magnetostriction and magnetocrystalline anisotropy and hence reduces μ . In the present case, lattice distortion due to Ca segregation and the presence of the glassy phase at the grain boundaries is thought to be responsible⁽¹²⁾, in part, for the decreased value of μ in the case of Sample 3. Thus, the large values of μ obtained in Sample 6 through processing control and use of higher purity powders can be attributed partly to the elimination of glassy phases and stress/strain gradients at grain boundaries.

In conclusion, μ depends on the composition of impurities at grain boundaries and grain interiors as well as on internal strains. To lend credence to this, Fig. 9 shows the results of the effect of compression stressing on the temperature dependence of permeability. Etching the sintered compacts to remove surface layers (where chemical segregation and strain are expected) raises the value of μ (Fig. 9).

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REFERENCES

1. R.K. Mishra and G. Thomas, AIP Conf. Proc., Vol. 34, (Eds. J.J. Becker and G.H. Lander) pp. 66-68 (1976).
2. R.K. Mishra and G. Thomas, IEEE Trans. Magnetism, Vol. MAG-13(5), 1354 (1977).
3. P. Haasen, Mat. Sci. Eng., Vol. 9, 191-196 (1972).
4. G. Thomas, IX Int. Conf. Electron Microscopy, Toronto, Canada, 1978; Vol. 3, pp. 392-401 (1978). (Mic. Soc. Canada).
5. G.C. Jain, B.K. Das, R.S. Khanduja and S.C. Gupta, J. Mat. Sc., Vol. 11, 1335 (1976).
6. D.J. Perduijn and H.P. Peloschek, Proc. Ceram. Soc., 10, 263, (1968).
7. E. Röss and J. Hanke, Z. Angew. Phys., 29, 225, (1970).
8. P.K. Gallagher, E.M. Gyorgy and D.J. Johnson, Jr., Cer. Bull. 57, 812, (1978).
9. O.L. Krivanek, T.M. Shaw and G. Thomas, J. Appl. Phys. (in press), LBL Report #7696.
10. P.E.C. Franken, N. Van Doveren, Ber. Dt. Keram. Ges. 55, 287, (1978).
11. R. Sinclair, R. Gronsky and G. Thomas, Acta Met., Vol. 24, pp. 789-796 (1976).
12. B. Hoekstra, et. al., J. Appl. Phys., 49, 4902, (1978).

FIGURE CAPTIONS

- Fig. 1 Microstructure of the sintered materials a) Sample 3, b) Sample 6; notice the inter and intragranular porosity in (b).
- Fig. 2 Transmission electron microscopy a) bright field, b) dark field, showing the presence of small particles of either $\alpha\text{-Fe}_2\text{O}_3$ or MnO; Figure (b) is a dark field image using the precipitate reflections indexed as fcc MnO in the insert.
- Fig. 3 Bright field - dark field transmission electron micrographs of Sample 3. The dark field image of diffuse reflections reveals a glassy phase along the grain boundary A-A.
- Fig. 4 Lattice image using 111 reflections simultaneously in two grains of Sample 3. The absence of fringe patterns at the edge-on grain boundary along A-A confirms the result of Figure 3 that a non-crystalline phase exists at this boundary.
- Fig. 5 Lattice image formed simultaneously using 220 and 111 reflections in two grains, across a grain boundary in Sample 6. No evidence for the presence of a glassy phase could be found at the grain boundary (compare to Figure 4).
- Fig. 6(a) X-ray microanalysis using a STEM instrument across a grain boundary such as shown in Figure 3 showing the presence and microsegregation of calcium and to some extent silicon.
- Fig. 6(b) As for Figure 6(a) but for the elements Fe, Mn, Zn showing no detectable segregation.
- Fig. 7 X-ray STEM microanalysis across the grain boundary shown above for Sample 6. There is no glassy phase and no Ca nor Si could be detected. This is typical of Sample 6.

Fig. 8 Microdensitometer traces across the (111) lattice fringes shown in Figure 4. Notice the large increase in lattice parameter as the glassy phase is approached, indicating a concentration gradient and strain exists in these regions. Comparison to Figure 6(a) indicates this effect is due to calcium segregation.

Fig. 9 Temperature dependence of the permeability of Sample 6. Notice how the application of a compressive stress greatly reduces μ . Highest values of μ are obtained after etching to remove surface layers.

Table 1 Composition & Impurity Content of Specimens			
Sample No.	1	3	6
Material	H ₆ H _x	H ₅ A	H ₅ E
Composition			
Fe ₂ O ₃ (mol %)	54.25	53.30	53.10
MnO	33.15	26.90	25.30
ZnO	12.60	19.80	21.60
Impurity (ppm)	typical value		
CaCO ₃	2927	2543	443
SiO ₂	407	224	200
Na ₂ CO ₃	125	173	150
CoO	87	91	103
NiO	207	242	311
CuO	20	60	24
PbO	32	39	44
Cr ₂ O ₃	306	161	-
TiO ₂	22	22	22

Table 2 Properties of Specimens			
Sample No.	1	3	6
Material	H ₆ H _X	H ₅ A	H ₅ E
Applied freq. (MHz)	0.01-1	0.2	0.05
Initial Permeability	1180	3590	18500
Loss factor $\tan\delta/\mu_i \times 10^{-6}$	1.0*	6.0*	13.7**
Density (g/cm ³)	4.8	4.8	5.0

*100 kHz, ** 10kHz

XBB 780 15842

Fig. 1

Bright field (a), dark field and diffraction pattern (b) showing MnO precipitates at a grain junction of Mn-Zn ferrite (Sample No. 3)
100 KV

XBB 795 7453

Fig. 2

XBB 798 10658

Fig. 3

High resolution lattice fringe image showing the crystalline grains and the noncrystalline intergranular phase near a grain boundary of Mn-Zn ferrite (Sample No.3) 100 KV

XBB 795 7452

Fig. 4

High resolution lattice fringe image showing the crystalline grains near a grain boundary of Mn-Zn ferrite (Sample No.6) 100 KV

XBB 795 7451

Fig. 5

XBL 794-6140

Fig. 6(a)

XBL 795-6375

Fig. 6(b)

XBB 795 7386

Fig. 7

XBL 794-6141

Fig. 8

XBL795-6374

Fig. 9

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