EM STUDY OF THE STRUCTURE AND COMPOSITION OF GRAIN

BOUNDARIES IN (Mn,Zn)Fe₂O₄

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ABSTRACT

Electron diffraction and microscopy studies supplemented by electron spectroscopic techniques such as Auger electron spectroscopy and energy dispersive x-ray spectroscopy were used to characterize the nature of grain boundary segregation in commercial grade (Mn,Zn)Fe₂O₄ samples containing small quantities of CaO. Chemical analyses by AES and EDAX show an enrichment of Ca near the grain boundary region. Convergent beam electron diffraction experiments show that the crystal symmetry of the spinel structure is distorted in the vicinity of the grain boundary. In situ heating experiments in HVEM show the existence of a disordered phase at the sintering temperature. Lorentz microscopy in TEM shows the interaction of magnetic domain wall motion with grain boundaries. These chemical and structural features are correlated with electrical resistivity and magnetic permeability of the ferrites.

INTRODUCTION

The presence of any second phases at grain boundaries in polycrystalline ceramics has been of great interest for their effects on the mechanical or electronic properties. In the case of high temperature structural ceramics, such as Si₃N₄, the amorphous boundary phase is responsible for low temperature creep. In the case of electronic materials, such as PZT, ZnO varistors and soft ferrites, the presence of a thin grain boundary layer drastically affects the electrical and magnetic properties. The formation of the second phase at grain boundaries in ceramic materials is very common and a complete characterisation of these second phases can be done only by modern techniques, such as transmission electron microscopy (TEM), analytical electron microscopy (AEM) and Auger electron
spectroscopy (AES). In the present work, the physical and chemical characterization of an amorphous grain boundary phase in (Mn,Zn)Fe$_2$O$_4$ using the above-mentioned techniques and the effects of this phase on the electrical and magnetic properties of the material will be discussed.

The (Mn,Zn)Fe$_2$O$_4$ is a soft ferrite with high initial permeability ($\mu_i$). Small amounts of CaO are added in commercial (MnZn)Fe$_2$O$_4$ to increase the electrical resistivity through the formation of an insulating layer along the grain boundaries. The existence of a thin intergranular amorphous phase has been observed by Mishra et al. using lattice fringe image microscopy and also by Lin et al. using high resolution dark field microscopy. It has been shown that the grain boundary phase is enriched in Ca. A complete characterization of the grain boundary and its effects upon the magnetic properties and sintering mechanism has not been ascertained, but will be discussed in this work.

EXPERIMENTAL

Sintered specimens of MnZn ferrite with the nominal composition of MnO:ZnO:Fe$_2$O$_3$ = 26.9:19.8:53.3 (mole %) and with the major additive of CaO (2543 ppm) were supplied by TOK Electronics Co. of Japan. A 1mm x 5mm x 10mm slice of sintered material was fractured in situ in a Physical Electronics 590 scanning Auger electron microscopy and the chemical composition was determined from Auger electron spectra. Electron transparent thin foils were prepared from the bulk sample by an ion milling technique. The magnetic domain wall structure and its interaction with grain boundaries were studied in a Philips EM301 microscope using Lorentz microscopy (LM). The symmetry of the crystal structure was studied in a Philips EM400 microscope using convergent beam electron diffraction (CBD). The behavior of Ca-doped grain boundaries at high temperature was studied by heating a thin foil in the hot stage of the Osaka University 3MeV high voltage electron microscope (HVEM) to a temperature of 1400°C.

RESULTS

A typical AES spectrum from a fractured surface of MnZn ferrite (Fig. 1b) clearly shows the existence of Ca. Careful experiments show that the Ca signal comes from those regions of the surface that are intergranular fracture. The Ca-signal completely disappears after the fractured surface is sputtered in-situ by argon ions for six minutes. Since the escape depth of the Auger electrons is less than 20Å and the sputtering rate is only about 10Å/min., the thickness of the Ca containing phase is about 60Å. Besides the Ca signal indicated in Fig. 1b, the spectra from intergranular fracture surfaces also have Fe and Mn signals. This implies that the Ca-containing phase is not a pure CaO phase as proposed by other authors. Although the chemical composition is very difficult to determine quantitatively, it can be concluded that the Ca-containing phase is an intermediate compound of CaO and MnZn ferrite. The existence of the intermediate compound has also been confirmed by Lin et al. by SEM hot