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CaO SEGREGATION IN MnZn FERRITE

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ABSTRACT

The reaction between CaO and MnZn-ferrite is investigated by in-situ heating in a scanning electron microscope. The existence of an intermediate phase and a eutectic liquid at about 1300°C is observed. The CaO segregation behavior of low loss MnZn ferrite is studied by in-situ heating in transmission electron microscope and Auger electron spectroscopy. The Ca is observed to stay at the grain boundaries in the form of amorphous intermediate phase at low temperatures and in a liquid phase at the sintering temperature.

INTRODUCTION

In low loss MnZn ferrites, CaO is added to form a high resistivity layer along grain boundaries so that the electrical resistance of the material increases significantly(1).

There exist two different views on the formation of this high resistivity layer; namely, i) an amorphous phase containing CaO forms at the sintering temperature (1) and ii) grain boundary oxidation as a result of Ca segregation during cooling of the sample from high temperature leads to high resistivity layer (2,3).

Recent study on CaO doped MnZn ferrite has favored the model of the formation of an amorphous phase; Tsunekawa et.al.(4) have shown the existence of an amorphous intergranular phase in Ca doped MnZn Fe_2O_4 .

The equilibrium phase diagram in the CaO- Fe_3O_4 system shows the existence of an intermediate phase with the composition $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ and a eutectic temperature at about 1220°C (5,6). In this investigation, the existence of any intermediate phase between CaO and Mn-Zn ferrite is further investigated and mechanism of the formation of the CaO rich intergranular layer is further explored. In-situ heating in a scanning electron microscope and a high voltage transmission electron microscope is used to examine the formation of the liquid phase at high temperature. Auger electron spectroscopy of fractured surfaces is used to determine the chemical composition of the intergranular phase.

EXPERIMENT

Sintered specimens of MnZn ferrite with a nominal composition of $\text{MnO}:\text{ZnO}:\text{Fe}_2\text{O}_3 = 26.9:19.8:53.3$ (mole %) and with the major impurity of CaO (2543 ppm) were supplied by TDK Electronics Co. of Japan. A 1mm x 4mm x 4mm slice of the sintered specimen was coated with 99.99% pure CaO powder in a platinum crucible and was heated in the hot stage of a JSM-U3 scanning electron microscope in high vacuum to a temperature of 1320°C at a rate of 10°C/minute above 1100°C. A 2.3mm electron transparent thin foil was prepared from the bulk sample by ion milling technique and was heated in the hot stage of the Osaka University 3MeV high voltage electron microscope (7) to a temperature of 1400°C. The grain boundary composition was determined by Auger electron spectroscopy of freshly fractured surfaces and surfaces fractured at high temperature.

RESULTS AND DISCUSSION

The SEM hot stage experiment shows that any reaction between the CaO powder and the ferrite matrix is noticeable only when the specimen is heated above 1250°C. At about 1250°C all the phases are still in the solid state. At about 1320°C, a liquid phase is seen to wet the ferrite substrate and, as shown in figure 1.a) the liquid and the solid phases coexist in some regions. If the sample is cooled slightly from 1320°C, a secondary phase nucleates as shown in figure 1.b). When the sample is further cooled to room temperature, a two phase material, characteristic of solidification of a eutectic liquid is obtained as shown in figure 2. The chemical composition of the two phases, as analysed using x-ray microprobe, shows that in region I (figure 2), the matrix contains negligible amounts of Ca and the elongated precipitates are rich in Ca. On the other hand, in region II, the reverse is the case. In region I, which is coated with a thin layer of CaO, the eutectic liquid is in equilibrium with the ferrite matrix. During cooling, the decomposition of the eutectic liquid results in a Ca-deficient matrix and a Ca-rich precipitate, assumed to be an intermediate compound of ferrite and CaO (fig.2.a). In region II, coated with a thick layer of CaO, the liquid phase is rich in Ca and as it cools, a Ca-deficient phase precipitates out leaving behind the Ca-rich matrix (figure 2.b).

If the heating experiments of CaO embedded MnZn ferrite samples are carried out in air or at 2400 ppm oxygen, then all these features are observed around 1250°C. These results show that CaO can react with MnZn ferrite and form a liquid phase at the sintering temperature which, when cooled, will solidify to crystalline phases.

The existence of the liquid phase and/or the solid phase in commercial low loss MnZn ferrites for which the Ca content is only of the order of 3000 ppm needs to be verified. For this purpose, two experiments were designed: i) in-situ heating of a thin foil in a high voltage electron microscope and ii) determination of the grain boundary composition by Auger electron spectroscopy (AES) in heat treated samples.

In the hot stage experiments in the HVEM, for temperatures below 1300°C , there is no noticeable reaction, neither the sublimation of the bulk material nor the migration of the grain boundaries, observed. However, when the temperature reaches 1300°C , the sublimation of the material near the periphery of the pores and at the edge of the specimen is observed. The sublimation continues at higher temperatures. Besides the acceleration of the sublimation rate, the following three observations are made when the specimen is heated from 1300°C to 1400°C . i) The image of the grain boundary changes from a sharp line (or fringes) to a diffuse line when the temperature reaches 1400°C (figure 3). The existence of a disordered phase at the grain boundary at 1400°C is inferred from this observation. ii) The positions of the three grain junctions are shifted due to grain boundary migration. The migration is more prominent in the junctions where the angle between the grain boundaries originally deviated considerably from 120° . (e.g. junctions a, b and c in figure 3). The tendency of the grain boundaries to make equal angles with each other implies that the grain boundary surface energy is isotropic at high temperature. This also is evidence for the existence of a disordered phase or a liquid phase at the grain boundary. The solid-liquid interfacial energy is known to be less anisotropic than the solid-solid interfacial energy. It should be noted that most of the grain boundary migration occurs when the temperature is rising. The shape and the size of the grains hardly change when the specimen is held at 1400°C . iii) The sublimation of the material at three grain junctions is observed to begin when the specimen temperature reaches 1400°C , and the sublimation continues at that temperature (junction d in figure 3). The sublimation also occurs from the grain boundaries. In view of the above observations, it is suspected that the grain boundary region first melts and then evaporates.

In short, both the preferential sublimation at the grain boundaries and the grain boundary migration can be correlated to the existence of a disordered phase at the grain boundaries at high temperatures. The observations suggest that a rapid rise in the temperature aids in the mass transport.

A typical AES spectrum from a freshly fractured sample of MnZn ferrite (figure 4) clearly shows the existence of Ca. This Ca signal completely disappears after the fractured surface is sputtered by Argon ions for only six minutes. Since the escape depth of the Auger electrons is about 20 Å and the sputtering rate is about 10 Å/min., the thickness of the Ca containing phase is about 60 Å. The Ca signal is observed only when the electron probe, 500 Å in diameter, is placed at intergranular fracture surfaces. No peak is observed when the electron probe is placed at a transgranular fracture surface. Besides the Ca signal in figure 4.a), there exist also the Fe and Mn signal. This implies that the grain boundary phase definitely does not contain CaO alone as proposed by other authors (1,2,3). Although the chemical composition is very difficult to be quantitatively determined, it can be concluded that the grain boundary phase is an intermediate compound of CaO and MnZn ferrite. This is in accord with the result of the SEM hot stage experiment discussed earlier. The high resolution dark field micrograph (figure 5) shows that the grain boundary phase exists as a 50 Å thick amorphous layer. The existence of the grain boundary phase in an amorphous state has been shown in other systems. It occurs due to the difficulties of crystallization of thin layers of liquid trapped between grains (8,9).

The hot stage experiments in the SEM and the HVEM thus establish that a liquid phase exists in the CaO-Mn,ZnFe₂O₄ system at the sintering temperature and such a phase remains as an intergranular phase after the sample has been cooled.

To establish if Ca segregates at the grain boundary region during cooling from the sintering temperature, an experiment was performed in which specimens were fractured at high temperatures or at room temperature and subsequently studied by the AES. In both cases, Ca distribution is similar, viz. Ca exists only at the intergranular fracture surfaces and no Ca is detected at transgranular fracture surfaces. In other words, Ca stays at the grain boundaries, as is shown in the Ca map and the fracture micrograph of a fractured specimen in figures 4.b and 4.c.

If Ca dissolves into the matrix at high temperature and reseggregates upon cooling, it should be distributed uniformly over the fracture surface of a specimen which was fractured at 1300 °C and then cooled. On the other hand, if the amorphous phase only melts upon cooling but stays at the grain boundaries, the Ca distribution will be the same no matter whether it is fractured at high temperature or at room temperature. From the above argument and the experimental data, it is concluded that Ca stays at the grain boundary forming a liquid phase at the sintering temperature. The liquid phase is a eutectic liquid which is in equilibrium with MnZn ferrite.

CONCLUSION

The formation of a Ca- rich liquid phase and/or a solid phase at 1250°C - 1320°C in the CaO-Mn,ZnFe₂O₄ system is confirmed from in-situ SEM observations and other annealing studies. In the case of sintered MnZn ferrite samples containing small quantities of CaO, existence of a liquid phase at the grain boundaries at high temperatures is confirmed from in-situ HVEM observations. Chemical analyses of fractured surfaces (fractured both at high temperature and at room temperature) of MnZn ferrite show that Ca is present only in the grain boundary regions in both cases. Thus the Ca must be present in the liquid phase at the sintering temperature in stead of segregating at the grain boundaries during cooling.

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- Figure 1 a) The eutectic liquid (dark) coexists with solid intermediate phase (white particles). b) A secondary phase is nucleated from the supersaturated liquid at the solid-liquid interface. c) remelting of the secondary phase by electron beam heating.
- Figure 2 Room temperature microstructure of the same specimen as in figure 1 : a) thin CaO coating region, the Ca rich precipitates are distributed in the Ca deficient matrix. b) thick CaO coating region, the round shaped Ca deficient precipitates are distributed in the Ca rich matrix.
- Figure 3 HVEM images of the specimen heated to A) 1300 C B) 1400 C respectively. i) the grain boundary images become diffuse at higher temperatures, ii) grain boundary migration occurs at 3-grain junctions a,b,c. iii) preferential sublimation occurs at grain junction d and grain boundary region.
- Figure 4 a) Auger electron spectrum of freshly fractured surface of MnZn ferrite, b) Ca map of high temperature fracture specimen, c) fracture micrograph corresponding to Ca map in b).
- Figure 5 Bright field (a) and diffuse scattering dark field (b) images of MnZn ferrite showing an amorphous phase at grain boundary.

Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

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