Microstructure Dependence of AC Magnetic Properties in Mn–Zn Ferrites

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***Abstract*—A correlation between microstructure and frequency dependent magnetic properties of Mn–Zn ferrites was established using the inductance spectroscopy method. Several atmosphere conditions and dwell times and temperatures were used during sintering to obtain a variety of microstructures in samples of different compositions. Results show that initial permeability (μ_i) strongly depends on the atmosphere composition during sintering, it increases, while relaxation frequency (f_r) slightly decreases as oxygen content decreases. On the other hand, dwell times longer than three hours led to a slight decrease in permeability (μ) and an increase in f_r. For the compositions prepared, a systematic decrease in μ was observed as zinc content decreases, regardless of the sintering conditions used. For each composition a maximum in μ was obtained for the same sintering conditions, which also correspond to the highest density values.**

***Index Terms*—AC magnetic properties, inductance spectroscopy, microstructure, soft ferrites.**

I. Introduction

THE ELECTROCERAMIC industry is a high-technology industry characterized by rapid innovation and technological change. Several of the electronic ceramic market segments are mature but growing steadily as magnetic ferrites, piezoelectric, insulators and substrates [1].

Soft ferrites are used as magnetic materials in power, pulse and wide band transformers, inductors, recording heads, memory devices, electric motors, temperature sensors and transducers. The application dictates the desirable material characteristics, which in turn defines the chemical composition of the ferrite material. It is clear that not one composition can fulfill all design objectives.

Mn–Zn ferrite is generally preferred at frequencies below a few megahertz because it has low coercivity, high permeability, and high saturation induction [2], [3]. High purity raw materials are needed to manufacture manganese–zinc ferrites cores having good magnetic properties and low losses needed for power transformer application. In order to reduce the losses many parameters, as density, porosity and grain size must be controlled [4].

The preparation of high permeability Mn–Zn ferrites is a very complicated task where not only the overall composition but also homogeneity must be carefully controlled. This homogeneity refers to both compositional as well as grain size distribution throughout the whole specimen [4]. Microstructure is, of course, another key parameter to watch out for.

Because of their importance, magnetic materials have been investigated for a long time from both basic and applied research points of view. In this work we studied the effect of the sintering conditions on the microstructure of several compositions and hence the effect of the microstructure on the final AC magnetic properties.

TABLE I
COMPOSITIONS PREPARED

Identification	Mol % of MnO	Mol % of Fe_2O_3	Mol % of ZnO
A	25	52.5	22.5
B	27.7	53	19.3
C	30.5	53.5	16
D	33	54	13
E	34.5	54.3	11.2

II. Experimental

Reagent grade oxide of the corresponding metals (MnO 99.6%, ZnO 99.9% and Fe_2O_3 99.8%) were used to prepared Mn–Zn ferrites. Five different compositions were selected from a line composition into the ternary diagram, from those having high permeability to those of high saturation [2]. These compositions are shown in Table I.

Raw materials were mixed and milled in an attritor mill (Union Process 01HD) using 1/8 inch stainless steel balls as grinding media. The resulting powder was calcined in air at 950 °C for one hour in a muffle furnace. After calcining, materials were again wet milled, plasticized with 1.5% of polyvinyl alcohol and formed into a toroidal shape by applying a pressure of 2 Ton/cm^2 in a Carver CMG-30-15 press.

Sintering conditions of samples included different dwell time and temperature and atmosphere compositions, as shown in Table II. These heat treatments were performed in a programmable Thermolyne 46 100 furnace.

X-ray powder diffraction was used to established the phase composition in the calcined material using a Siemens D-5000 diffractometer. Laser diffraction technique was used to determined the particle size distribution of calcined powders after milling by a Malvern Mastersizer 2000. Density was evaluated as the relation of weight to volume.

For Curie temperature (T_C) determination, sintered samples were coiled as a transformer and placed in a muffle furnace according to the experimental setup described elsewhere [5].

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TABLE II
SINTERING CONDITIONS

No. of sinter	Dwell Temperature	Dwell time	Atmosphere
Sinter 1	1350 °C	3 h	Air
Sinter 2	1350 °C	3 h	4% O_2 - 96% N_2
Sinter 3	1350 °C	3 h	2% O_2 - 98% N_2
Sinter 4	1300 °C	3 h	2% O_2 - 98% N_2
Sinter 5	1300 °C	4 h	2% O_2 - 98% N_2

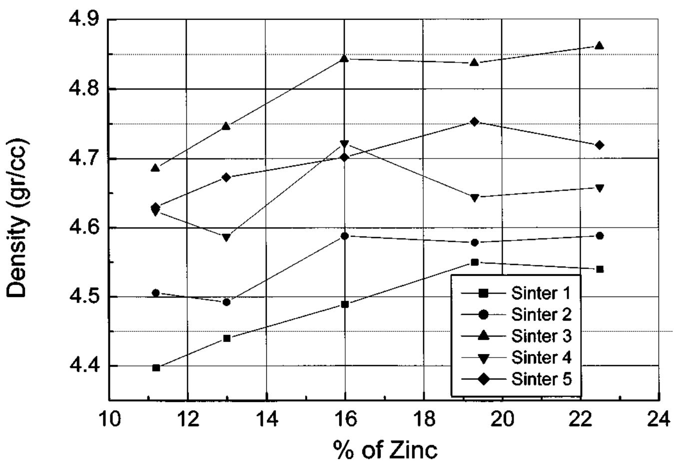

Fig. 1. Density values versus % of zinc oxide.

AC magnetic properties were evaluated in an HP 4192 impedance analyzer in the 10 Hz–13 MHz frequency range. For these measurements an applied voltage of 5 mV was used in samples wired with a 10 turn low inductive coil.

Microstructure studies were made on as-sintered and polished surface of samples as well as in fractures of the specimens. EDS microanalysis or point composition were established in the grain and grain boundaries. These studies and analysis were performed in a Cambridge Leica Stereoscan 440 microscope and in a Oxford Pentafet analyzer.

III. RESULTS AND DISCUSSION

Phase composition of the calcined powder was established for all formulations. It was observed that the higher the content of zinc, the higher the percent of spinel ferrite present. However, for all cases hematite is always present. It may be due to the low calcining temperature used for this treatment (950 °C). In this stage, the presence of hematite is not a critical parameter, because it is expected that spinel phase transformation should be completed during the sintering process. Average particle size of roasting powders was 2 micrometers after milling.

Density values of sintered samples are shown in Fig. 1. In this figure it can be observed that no matter the composition the highest densities were obtained for the thermal treatment identified as "sinter 3"; on the other side the lowest values of density were observed in samples sintered according to the sinter 1. For all the other sintering conditions intermediate values were obtained. Also, a systematic increase of density is observed for all compositions as Zn content increases.

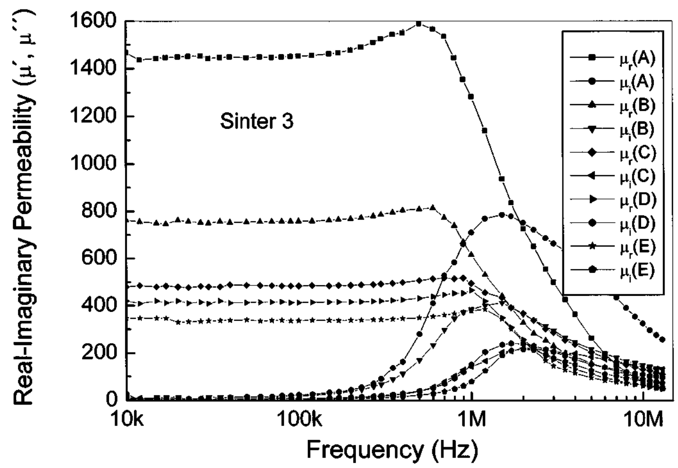

Fig. 2. Real and imaginary permeability versus frequency (sinter 3).

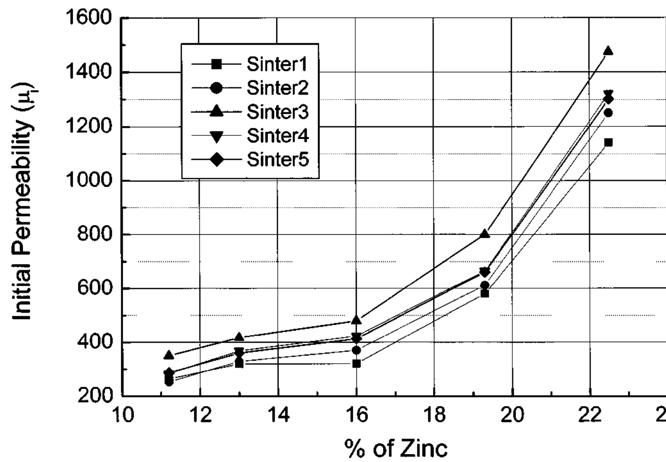

Fig. 3. Initial permeability as a function of Zn content.

To evaluate T_C, the behavior of induction (or μ) as a function of temperature was obtained. Results showed a sharp drop of permeability at the T_C. The sharpness of the induction drop has been associated to the compositional homogeneity of the sample [6], [7]. As it would be expected, results show a clear decrease of T_C for all samples, no matter the sintering conditions, as zinc content increases. For each composition, almost constant values of T_C were obtained.

From the inductance spectroscopy analysis, real and imaginary permeability (μ', μ'') values as a function of frequency were determined for each composition and sintering conditions. Initial permeability was established from the plateau (10 kHz–100 kHz) of the real permeability (μ') curve, while relaxation frequency was obtained from the maximum of imaginary permeability (μ'') plots. Fig. 2 shows the real and imaginary permeability variation as a function of frequency for all compositions and sinter conditions 3.

As can be seen, a systematic decrease in permeability is observed as zinc content decreases. Similar behavior was observed for all thermal treatments. Also, for each composition higher values of permeability were obtained for samples sintered at 1300 °C under low oxygen content atmosphere, i.e., sinter 3.

Fig. 3 shows initial permeability values for all compositions prepared and all thermal treatments. For all samples, in the

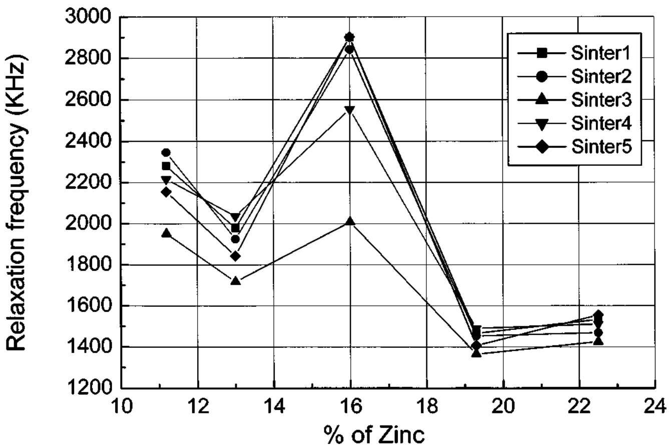

Fig. 4. Relaxation frequency as a function of Zn content.

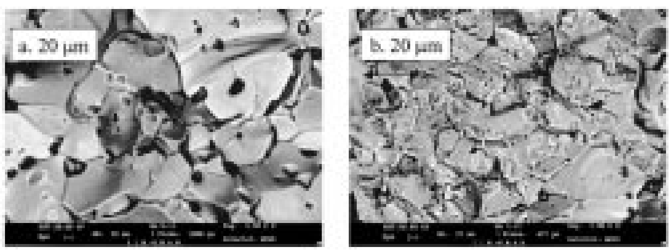

Fig. 5. Microstructure of composition E.

composition range investigated, there exists a systematic decrease in permeability as zinc percent decreases, regardless of the sintering conditions. Hence again, it is clear that the highest values of permeability correspond to sinter conditions 3, while lowest values correspond to samples of sinter 1.

It must be noticed that the only difference for both treatments (sinter 1 and 3) is the atmosphere composition, air and 2% O_2–98% N_2, respectively. So higher permeability values are favored by low oxygen content.

Relaxation frequency (f_r), as determined from the maximum of imaginary permeability, shows an irregular performance for composition having 16% of Zn. Values for this composition are higher than those expected according to the tendency showed for the other compositions. However, in general the lowest relaxation frequencies correspond to samples sintered under conditions of sinter 3, which also present the highest permeabilities. These results are presented in Fig. 4. Indeed, no matter the sintering treatment for compositions studied, those having high zinc content show lower relaxation frequencies. We think additional investigation must be done to explain the relaxation frequency behavior for composition C.

An inverse dependence of Curie temperature and permeability can be established from these results. T_C decreases and μ_i increases as zinc content increases. A similar performance was observed for all thermal treatments.

Fig. 5 shows the microstructure exhibit for the composition E, having 11.2% of Zn. These a and b microstructures correspond to samples sintered according to sinter 1 and 3, respectively. From these microstructure studies it has been established that samples sintered in air atmosphere (sinter 1) exhibit higher intragranular porosity [Fig. 5(a)] compared to samples processed under a low oxygen content ambient, i.e., sinter 3 [Fig. 5(b)]. These observations are in agreement with the density values determined for these two groups of samples.

Also grain size distribution is wider for samples sintered in air, and it is more homogeneous and finer as oxygen content decreases.

Variation of treatment temperature is indeed reflected in variations of porosity. Specimens sintered at 1300 °C (sinter 4) show higher intergranular porosity (may be due to an incomplete sintering) than those samples treated at 1350 °C (sinter 3) under the same dwell times and atmosphere conditions. These behavior is again in agreement with the values of density determined for these samples.

From these results, it is important to notice that intragranular porosity due to sintering conditions in air atmosphere has a higher negative effect in density values, than intergranular porosity due to a low sintering temperature. This behavior was observed in all compositions.

Although a small amount of hematite was detected by x-ray diffraction, especially in compositions D and E, point microanalysis on the grain and on the grain boundaries did not show evidence of a noticeable compositional heterogeneity. Also a compositional scanning on the surface and fracture of samples showed relatively homogeneous specimens for all compositions. These results are in agreement with the sharpness of drop of permeability (or induction) at the Curie point.

For all samples and compositions, obtained values of density and permeability are well correlated with the microstructure observed in each sample. Also there exists a correspondence between higher permeability and density values, in this case the best result corresponds to sinter condition 3.

IV. Conclusions

Samples sintered in a high oxygen atmosphere present mainly intragranular porosity while low dwell temperature produce intergranular porosity.

Intragranular porosity due to sintering conditions in air atmosphere has a more pronounced effect on density and permeability values than intergranular porosity due to lower sintering temperatures, i.e., the sintering atmosphere effect is greater than the sintering temperature effect on the magnetic properties of the compositions investigated.

For the range of compositions studied, the initial permeability increases as the zinc content increases and oxygen content used in the sintering process decreases, i.e., when intragranular porosity decreases. On the other hand, the relaxation frequency decreases as zinc content increases and these lowered values coincide with higher values in permeability. The narrow grain size distribution and lowest porosity obtained with sinter 3 also correspond to the highest values of permeability.

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