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Effect of sintering conditions on microstructure and magnetic properties of Mn–Zn ferrites

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Commercial and specially-prepared Mn–Zn ferrites were characterized, in terms of magnetic performance, microstructure and local composition, by various techniques. The results show the relevance of the structure of the interfaces between grains, the importance of uniform grain size and, finally, the role of composition homogeneity throughout the sample and the atmosphere utilized. The practical relevance of these findings is also discussed.

1. Introduction

Ferrites have been studied for several years due to their wide use as magnetic materials for telecommunications, audio and video, power transformers and many other applications involving electrical signals with frequencies normally not exceeding a few megacycles per second [1–10]. It is already known that the desired, technologically speaking, properties of ferrites depend strongly on the stoichiometry and the adequate control of the corresponding microstructures [1]. Indeed, the influence of segregation, deviations from stoichiometry [2] and grain size [3–7] on properties such as initial permeability, losses, magneto-elastic energies and others have been reported in the last 20 years by groups studing several ferrite-like ceramic systems. Most of those studies, however, are occupied by basic physical and chemical mechanisms governing the performance of ferrites and much less attention has been dedicated to the evolution of properties and microstructures from a manufacturing standpoint, i.e. aiming to have real control of industrial processes for producing ferrite materials. In this work, we reported studies of the dependence of magnetic performance of Mn–Zn ferrites prepared under different conditions, where a number of parameters can be monitored during the preparation procedure. The specimens analysed in this present article were of two types: three samples obtained from commercial sources and another three samples prepared in the authors' laboratories.

2. Experimental Procedure

2.1. Sample preparation

Two sets of three samples each were analysed. Three samples were purchased from Philips Components México (catalog numbers 846T500–3E2A, 846T500–3C81 and 846T500–3C85, respectively). These specimens are industrially utilized as transformer components and have different magnetic permeabilities, according to the manufacturer. Henceforth these samples are identified as 1, 2 and 3.

Another three samples, named 4, 5 and 6, were prepared in the authors' laboratories using Fe_2O_3 (NB Sidmar, 99.05% purity with small amounts of SiO_2, MnO, CuO, Na_2O and K_2O as impurities), ZnO (Industrias Mogar, 99.38% purity with impurities of SiO_2, CaO, Fe_2O_3 and PbO) and MnO (Chemetals, 99.45% purity with small amounts of BaO, CaO and Na_2O). These three samples were subjected to the following procedure

1. Mixing in a ball mill for 4 h along with a 35 wt % water. The mill was charged with 1.27 cm stainless steel balls.
2. Drying in a stove for 8 h at 70 °C.
3. Calcining in a Lindberg furnace for 4 h at 1050 °C.
4. Milling in a ball mill with 20 wt % water for 4 h.
5. Drying in a stove for 8 h at 70 °C.
6. Mixing for 3 h with 3 wt% poly-vinyl alcohol (PVA, 217 IMP from Química Mexibras S.A.). The PVA was added at this stage as a plasticizer for sintering purposes.
7. Drying in the stove for 8 h at 70 °C with constant agitation.
8. Milling without water for 2 h in a ball mill.
9. Pressing to a toroidal shape (outer diameter 3.75 cm, inner diameter 2.3 cm and weight 25 g) in a 7 tons press.
10. Finally, the sintering was different for each sample. Sample 4 was sintered at 1360 °C for 6 h under a nitrogen–oxygen atmosphere ($283\,l\,h^{-1}$ for N_2 and $12.17\,l\,h^{-1}$ for O_2). Sample 5 was sintered at 1300 °C for 5 h under nitrogen at $204\,l\,h^{-1}$ flow. Sample 6 was sintered at 1290 °C for 8 h in air.

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2.2. Characterization techniques

The permeability, loss factor and quality factor, Q, of all six specimens were determined by winding a 24 caliber Cu wire onto the toroidal samples and by using a Hewlett Packard inductance bridge (HP-4192A) from 1 to 1000 kHz. X-ray powder diffractometry was done in a Siemens D-5000 machine equipped with a Cu source. Scanning electron microscopy (SEM) and Energy dispersive analytical X-rays (EDAX) analysis were performed in a Jeol 6400 microscope. Optical microscopy observations were carried out in a Vickers M-171 167 microscope on sections included in polyester resin and polished down to 0.5 μm Al_2O_3 powder grade.

3. Results and Discussion

Fig. 1 shows X-ray diffractograms of samples 1 and 4, two samples corresponding to each of the two different sets utilized in this study. As can be noticed, the diffractograms are very similar, showing the same main phases identified therein and little presence of unexpected phases or components. Only these two spectra are presented because all the others are basically the same. The first observation is then that, on the basis of X-ray analysis, all the samples present the same overall composition, which is not surprising since good care was taken to try to preserve the general stoichiometry.

The magnetic measurements, however, present a completely different picture, as can be observed from the set of plots of Figs 2 and 3. Each figure contains six graphs as a function of frequency, one corresponding to the permeability and the other to the loss factor, for each of the six samples analysed. In every case, the frequency range covered from 1 to 1000 kHz. The corresponding quality factors, Q, for the same frequency range, are presented in Fig. 4.

All the permeability curves present a similar behaviour with a constant value up to a given frequency value, then increase and finally drop rather sharply at around 1 MHz in all cases. The first plateau, corresponding to the working range, provides the permeability figure provided by the manufacturer and gives a good idea of the quality of the material. Accordingly, the best sample is number 1, having a permeability

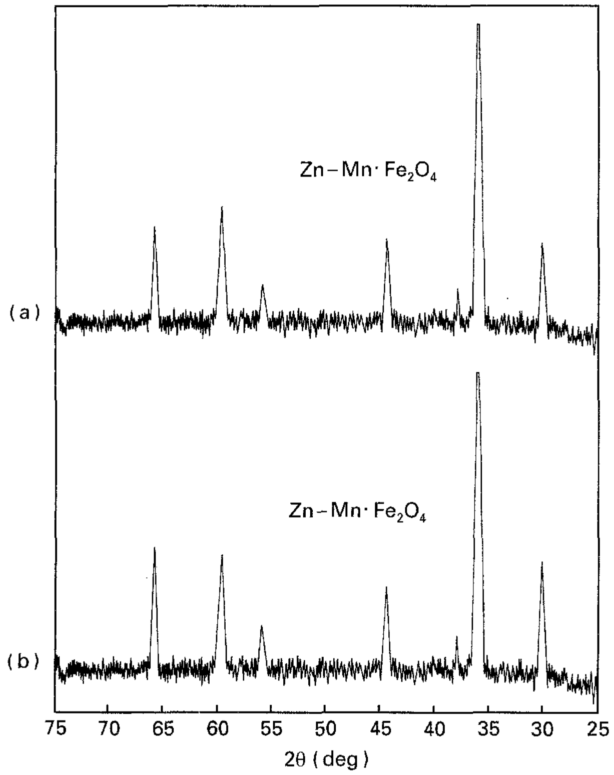

Figure 1 X-ray powder diffractograms of (a) sample 1 and (b) sample 4.

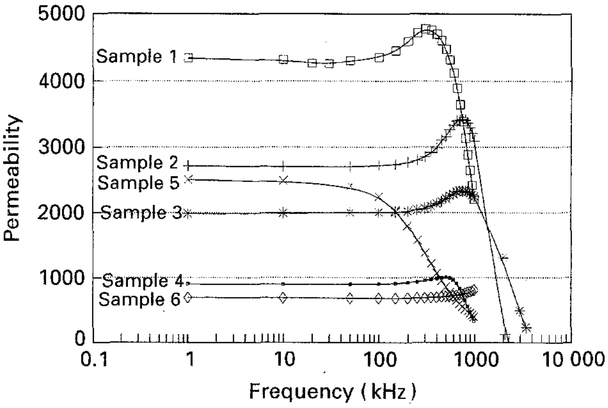

Figure 2 Permeability versus frequency for samples 1–6.

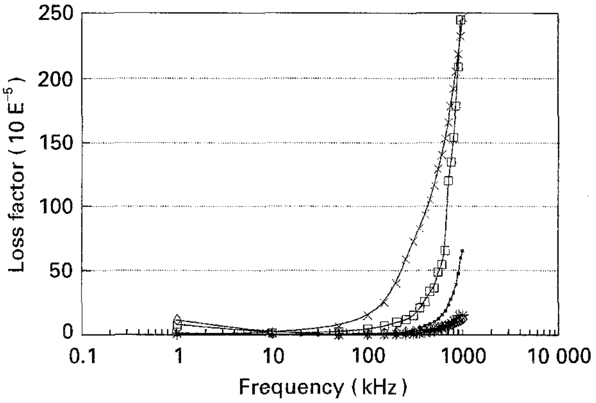

Figure 3 Loss factor versus frequency for samples 1–6: (⊖) sample 1, (+) sample 2, (∗) sample 3, (⊟) sample 4, (×) sample 5, and (◇) sample 6.

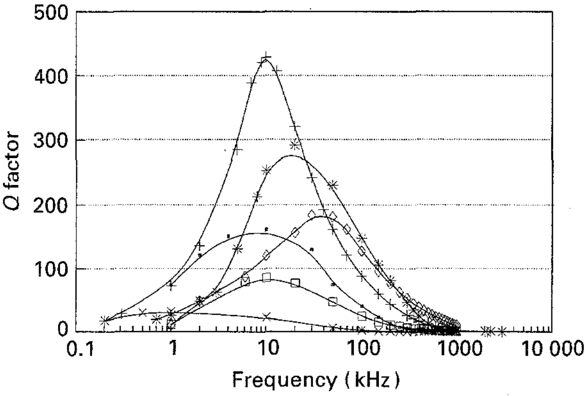

Figure 4 Quality factor, Q, versus frequency for the six ferrite samples: (⊖) sample 1, (+) sample 2, (∗) sample 3, (⊟) sample 4, (×) sample 5, and (◇) sample 6.

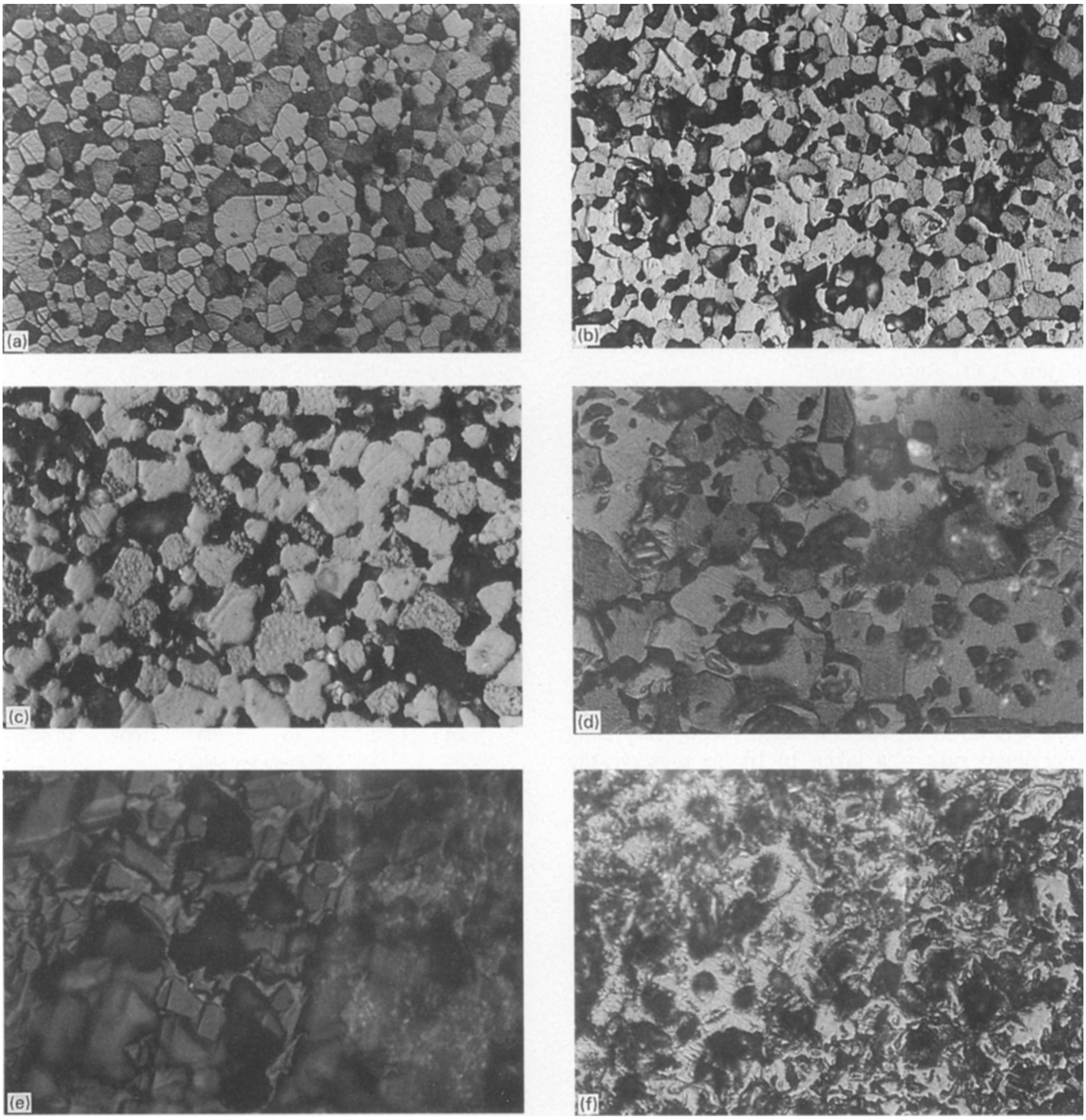

Figure 5 (a–f). Optical micrographs of samples 1–6, respectively.

value of 5000, then sample 2 with 2700, sample 5 with 2500, sample 3 with 2000, sample 4 with 900 and, finally, sample 6 with 700. That is, despite the equivalent overall stoichiometry, the samples present quite different magnetic properties.

To study further this, optical microscopy was performed on polished sections of each sample. Fig. 5a–f corresponds to the reflection images of those sections. As can be observed there, the better specimens tend to have well defined grains, sharp interfaces and fewer phases. Also, it is interesting to notice that the samples with better magnetic properties show polyhedral grains, indicating crystalline phases; whereas the poor quality specimens have an amorphous contrast in some grains and at the interfaces, which tend to be broader than those of the best performing samples.

These observations are supported by the SEM results, which also show polyhedra for the better samples and an amorphous contrast for the poor specimens, as can be seen in Fig. 6a–b for samples 1 and 6, respectively. These differences in the structure of the interfaces have been observed in the past, but deserved little attention. It is important, nevertheless, to point out that electrical conductivity and magnetic domains will be influenced surely by a glassy interface as compared to a narrow boundary.

Another important parameter seems to be the grain size. For instance, sample 3, which has good polyhedral grain structure, also shows a large amount of smaller grains of the order of 1 μm or smaller. This result is in agreement with earlier reports [1–4] which described the role of grain size on the initial permeability of these materials. What the present results indicate is that, perhaps more importantly than the specific value of the grain diameter, is the mixing of grains of different sizes in the samples.

On the other hand, most reports have studied the effect of the overall stoichiometry on magnetic and

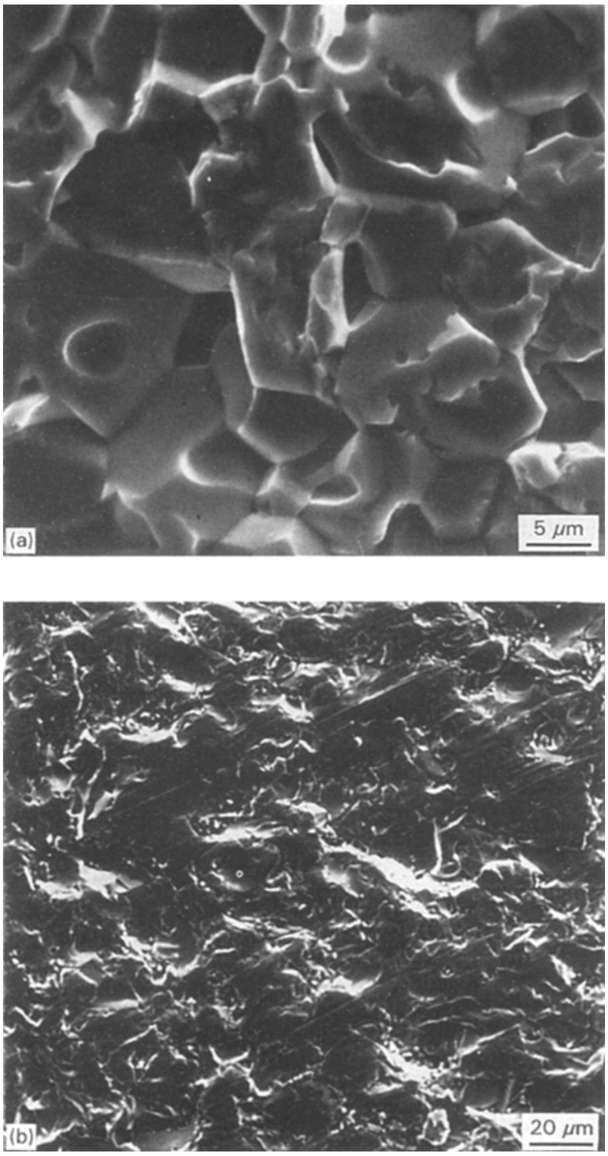

Figure 6 SEM micrographs of (a) sample 1 and (b) sample 6.

related electrical properties of these ferrites. However, since, as shown before, these samples have basically the same stoichiometry and yet quite different permeability, the need for more detailed analysis is stressed.

Accordingly, Fig. 7 shows the results of microanalysis on the samples. Due to the capabilities of the microscope used, it was possible to determine the composition of practically each different grain in all the specimens with several measurements carried out in each case to assure reproducibility and good statistical representation. For example, the best performing sample (number 1) presents always two phases, one with a light contrast and the other having a dark contrast. The microanalysis showedthat the content of Mn, Fe and Zn in both zones is basically the same, being then the impurity content the only difference detected.

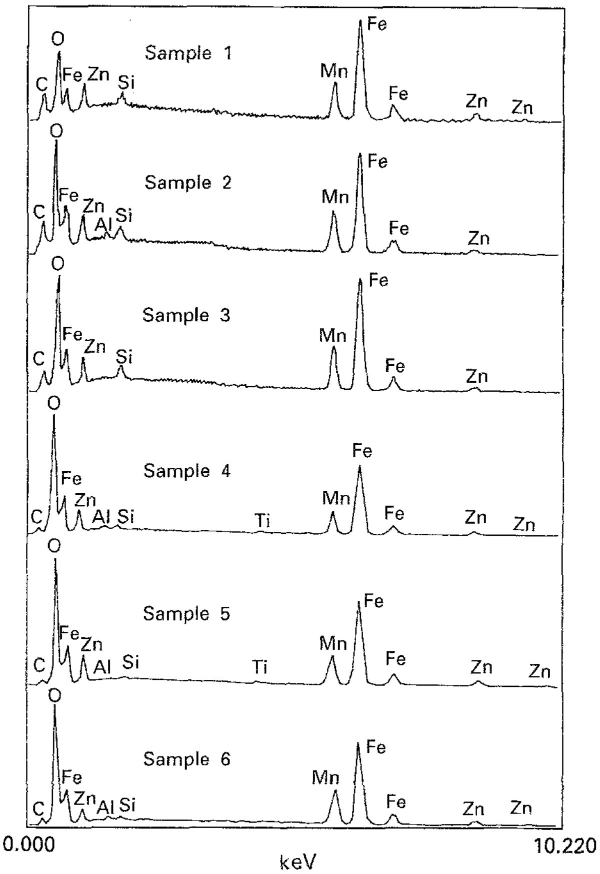

Figure 7 (a–f). Results of microanalysis of samples 1–6, respectively.

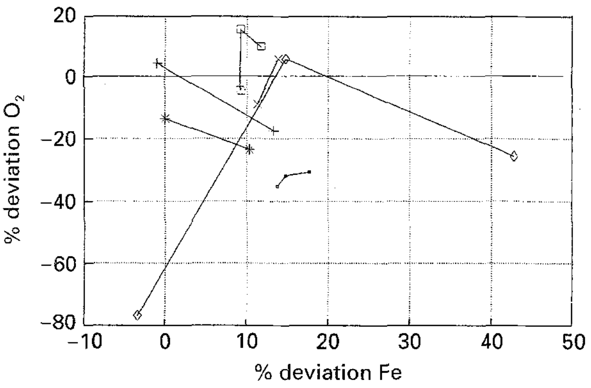

Figure 8 Per cent deviation from stoichiometry of iron versus per cent deviation from stoichiometry of oxygen for the six samples. The results in two different points in each sample are shown: (⊖) sample 1, (+) sample 2, (∗) sample 3, (⊟) sample 4, (×) sample 5, and (◈) sample 6.

An interesting finding is shown in Fig. 8, which shows the behaviour of permeability as a function of deviation from the stoichiometry values for Fe and for the whole set of samples. As observed, for each sample two values of such deviation are depicted taken at different points in the sample, to illustrate the relevance of homogeneity rather than the precise stoichiometry. Indeed, the better samples tend to be more homogeneous; despite that, they show a rather large deviation from stoichiometry. Thus, the role of impurities as controllers of segregation is stressed. Also, the effect of the different sintering conditions, atmosphere and temperature, in samples 4 through 6 (see the Experimental section), is strongly reflected on the homogeneity and then the magnetic properties achieved. In fact, samples prepared in air and at lower temperatures (number 6) showed the lowest figure in permeability, whereas samples maintained at higher temperatures in a nitrogen atmosphere (number 5) showed much better behaviour. This is an important result in the authors' opinion, since most reports in the field stress the relevance of composition as the key parameter to control, without paying much attention to the detailed final homogeneity of the specimens, and to the effect of the sintering atmosphere.

4. Conclusions

The controlled preparation of high permeability Mn–Zn ferrites is a very complicated task where not only the overall composition but also homogeneity must be carefully monitored. This homogeneity refers to both grain size distribution as well as stoichiometry throughout the whole specimen. Microstructure is, of course, another key parameter to watch out for, especially at the level of the structure of the interfaces; since, as the optical micrographs show, flat thin interfaces tend to favour magnetic and electrical properties, whereas thick glassy interfaces are detrimental. These observations show the convenience of studying the important role of manufacturing procedures and sintering aids if good quality magnetic materials are to be prepared.

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