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# INITIAL SUSCEPTIBILITY AND MICROSTRUCTURE OF NON-STOICHIOMETRIC Ni-Zn FERRITES *

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ABSTRACT

The effect of non-stoichiometry on microstructure of ceramic Ni ferrites is analyzed, on the basis of Globus'model for initial susce bility. It is shown that the model proposed by Globus can be genera ed to non-stoichiometric Ni-Zn ferrites, in order to take into accou microstructural changes. Besides, experimental results herein repor exhibit clear evidence of ionic structure changes.

RESUMEN

El efecto de las desviaciones a la estequiometría sobre la micr tructura de ferritas Ni-Zn es analizado en base al modelo Globus de susceptibilidad inicial. Se demuestra que el modelo propuesto por G bus puede ser generalizado a las ferritas Ni-Zn no estequiométricas, ra evaluar los cambios en la microestructura. Por otra parte, los r tados experimentales obtenidos exhiben una evidencia clara de cambio la estructura iónica.

## 1. INTRODUCTION

Polycrystalline ferrites are usually prepared by normal ceramic methods. The high sensitivity of structure to technical conditions, t great number of parameters involved, and the complexity of magnetic nomena made difficult the interpretation of experimental results, sp ly initial susceptibility mechanism.

By separating microstructure factors like porosity character, g growth and impurities with a proper technology, Globus[1] showed tha the initial susceptibility varies linearly with mean grain diameter, constant temperature and for stoichiometric compounds, if porosity,

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crystallite defects in general (inclusions, precipitates, etc) had an intergranular character. Similar results[2] have been obtained for several types of ferrimagnetic compounds. All these results indicate that Bloch wall movements are the main susceptibility mechanism, and spin rotation contributes only for a small extent.

One of the most important factors in sintering and magnetic properties is stoichiometry. Reijnen[3] has shown the influence of deviations to stoichiometric composition in sintering and explained some results. Guillaud[4] and Stuijts[5] have shown initial susceptibility variations in non-stoichiometric ferrites; however, the origin of these important variations has not been elucidated.

In this paper, initial susceptibility variations produced by deviations to stoichiometric composition in the initial mixture of oxydes are examinated. An interpretation of this phenomena is proposed on the basis of Globus'model, as far as microstructure is concerned.

## 2. SAMPLE PREPARATION

The Ni-Zn ferrite system was chosen, since there is no ambiguity in cation distribution on tetrahedral and octahedral spinel sites. In order to set Curie temperature of stoichiometric compound, $\frac{NiO}{ZnO}$ ratio was fixed, for one sample series, at $\frac{18}{32}$. For this series, reagent grade oxydes (NiO, ZnO, $Fe_2O_3$) were employed. Experimental results were significant, but a more systematic behavior was obtained in another series, prepared with very pure** oxydes. In these series, $\frac{NiO}{ZnO}$ ratio was fixed at $\frac{15}{35}$.

Classical ceramic method was used for preparing samples. Deviations from stoichiometry were introduced in the initial oxydes mixture, varying $Fe_2O_3$ content in the formulae:

$$\alpha\ NiO \cdot (50-\alpha)\ ZnO \cdot X\ Fe_2O_3$$

$\alpha$ was maintained constant and equal to 18 for the first series, and 15 for the second. The X values went from X = 45 to X = 55; stoichiometric compound corresponds to X = 50. For X > 50, there is a $Fe_2O_3$ excess in

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** J.M. Specpure.

oxydes mixture; for X < 50, bivalent NiO·ZnO oxydes are in excess. Iron content correction was not necessary by milling with a special method[6], that introduce no impurities even in long milling time. After pressing, the toroidal samples were sintered in an oxydant atmosphere. Except for sintering temperature and time, all technical conditions where the same for all the samples.

## 3. EXPERIMENTAL RESULTS

Density measurements of several series, sintered at different temperatures, showed a maximum near X = 49, Fig. 1. The effect of non-stoichiometry seems to be less important, as far as densification is concerned at high sintering temperatures.

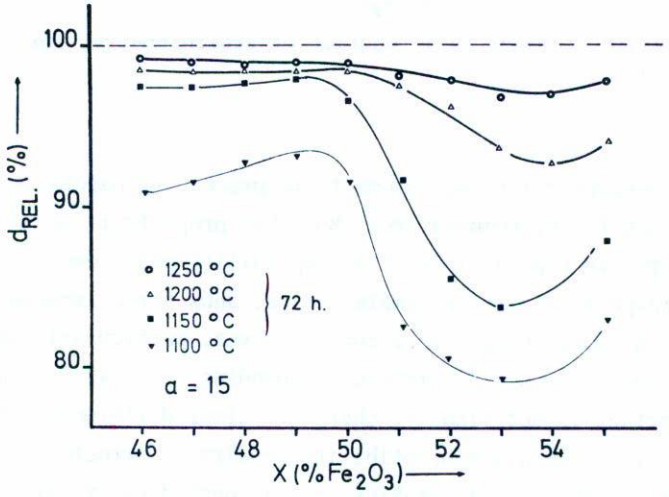
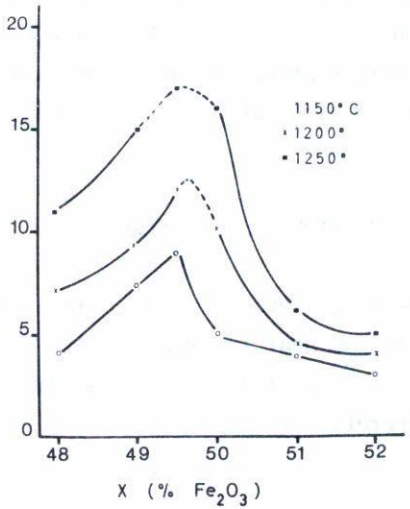



Fig. 1. Relative density (actual density/theoretical density of stoichiometric compound, %) as a function of deviation to stoichiometry, for several heat treatments.

Mean grain diameter measurements exhibited also a maximum for bivalent oxydes excess compositions, but sintering temperature does not seem to affect the form of the curves, Fig. 2.




**2. Mean grain diameter as a function of stoichiometry, for three treatments.**

Initial susceptibility measurements in preceeding papers were only at constant (room) temperature. But this property is very tempera- dependent. In Fig. 3, initial susceptibility measurements, as a - ion of temperature, for a sample series, show three important fea-- there is a spectacular dispersion of curves, particularly near Curie rature; initial susceptibility corresponding to X ∿49.5 seems to have ost important value; finally, there are clear differences in Curie - rature value. In all susceptibility results, "corrected susceptibi- ' concept is employed, for taking into account density effect:

$$(\mu-1)_c = (\mu-1)\frac{dx}{d}$$

e:

$)_c$ = corrected initial susceptibility.

$)$ = actual initial susceptibility.

= theoretical (Rx) density of stoichiometric compound.

= actual density.

Absolute value of initial susceptibility were changed, but relative values remained similar to other heat treatments in both $\frac{NiO}{ZnO}$ series ratio. In this sense, this is a systematic behavior.

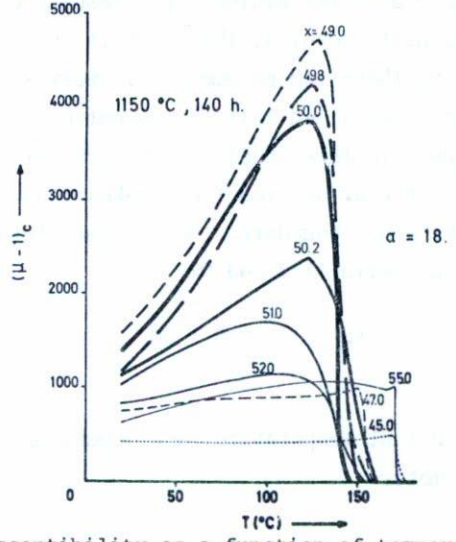



Fig. 3. Initial susceptibility as a function of temperature. x indicates deviation to stoichiometry.

The lattice parameter was determined for several series. Systematically, a maximum appeared for stoichiometric compound (Fig. 4). For -- $NiO \cdot ZnO$ excess, lattice parameter becomes constant around X = 49; for -- $Fe_2O_3$ excess, lattice parameter does not stabilize, even for high (X=55) stoichiometry deviations.

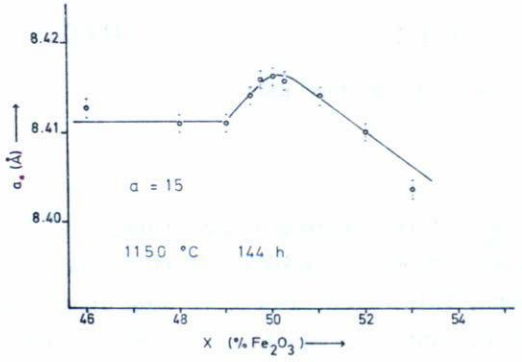



Fig. 4. Lattice parameter and stoichiometry for a sample series.

## 4. DISCUSSION

Density results agree with Reijnen's theory of sintering in non-stoichiometric compounds. The grain growth results exhibited some similarities with the density results; therefore it may be assumed that the mechanism controlling these two parameters is very similar.

Globus'model has explained initial susceptibility results in stoichiometric compounds. In this model, a spherical grain is divided by a Bloch wall, Fig. 5. A weak applied field makes the wall bulge while it remains fixed to the grain boundary. Such a curvature leads to a linear relations between susceptibility and Dm:

$$(\mu - 1)_c = A \cdot Dm$$

where:

A = constant at constant temperature, and depending on ionic structure.

Dm = mean grain diameter.

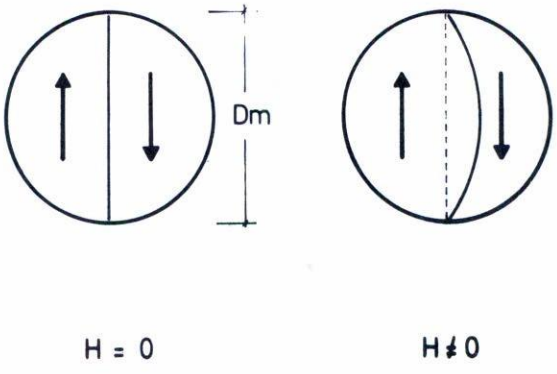



Fig. 5. Globus'model

Drawing $(\mu-1)_c = f(Dm)$ at room temperature, Fig. 6, a straight line appears for each deviation from stoichiometry. Some dispersion affects X > 50 compositions; this effect is due to some inhomogeneity. As density results showed, sintering was lower for these samples.

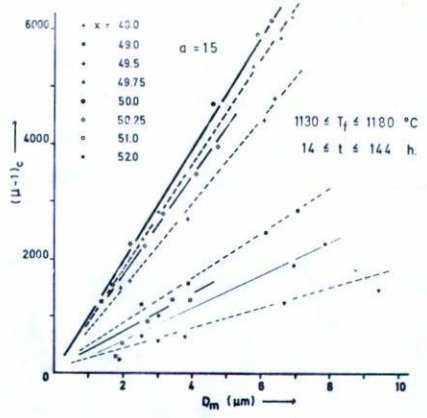



Fig. 6. Linear dependence between initial susceptibility and mean grain diameter. Time and temperature of sintering are indicated.

An important feature in Fig. 6 is that the stoichiometric composition has the most important susceptibility value. Therefore, the high value of X = 49 composition in Fig. 3 is only the effect of mean grain diameter. This fact appears clearly in Fig. 7, where slope A vs. composition is drawn. As shown in this figure, several samples showed no -

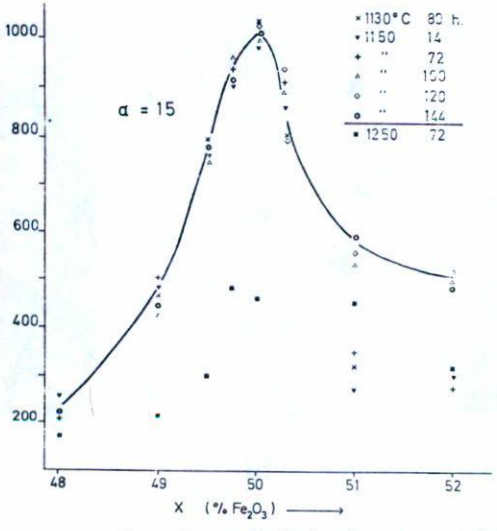
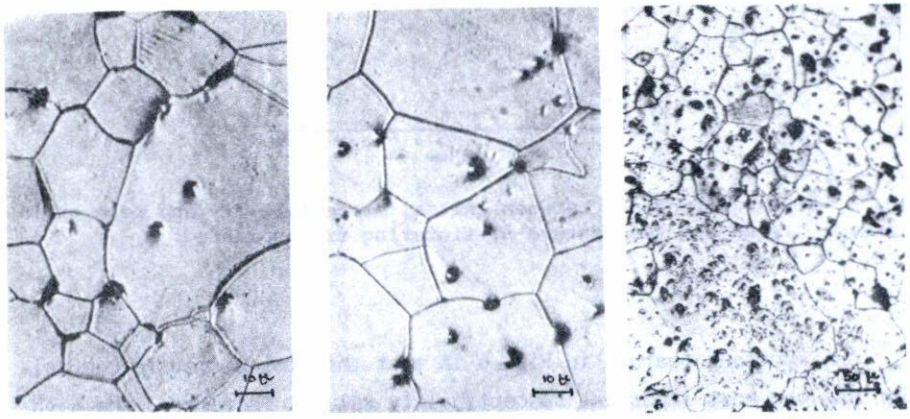


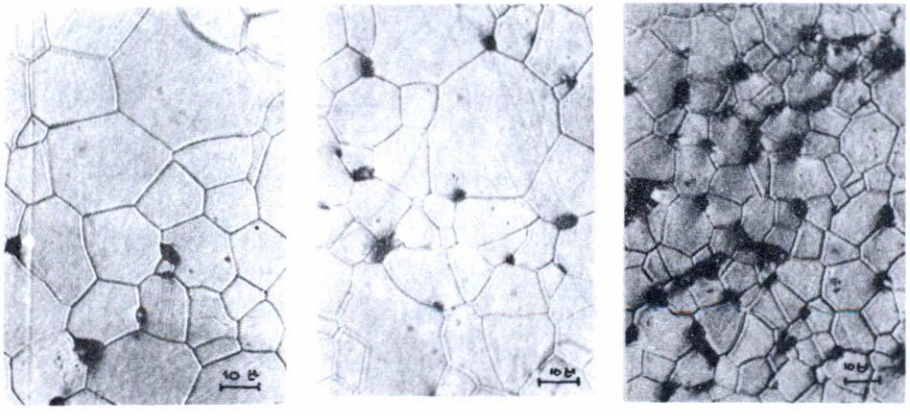

Fig. 7. The slope A as a function of deviation to stoichiometry. Low values of A appear for high sintering (1200°C) temperature.

agreement with linear relation. Optical microscope observations revealed that, in all the cases, these samples had an intra-granular distribution of defects, Fig. 7. The samples following the linear relation, exhibited less defects, and localized only in the grain boundary regions, Fig. 8. Schematically, this fact can be explained by Fig. 9. Any imperfections behave like an obstacle to wall bulging; if there exist defects in intra-



X = 48 50 52

Fig. 8. Samples that did not follow linear relation. Intra-granular porosity and defects.



X = 48 50 52

Fig. 9. Polished and thermally attacked surfaces of samples following the linear relation. Inter-granular porosity.

granular position, wall bulging is troubled, and the observed mean grain diameter does not correspond to the defect-free mean diameter.

As shown in slope A (Fig. 6), curie temperature differences (Fig. 3) and lattice parameter differences (Fig. 4), the problem of non-stoichiometry is not the simple one where bivalent oxydes excess, or $Fe_2O_3$ excess, remains in the form of a second phase. For both sides of stoichiometry, there is, at least for a small excess, some dilution of this excess in the ferrite phase. The introduction of this excess affects not only granular microstructure, but also ionic structure. Therefore the important variations detected in initial susceptibility can not be explained by the only microstructural changes. In order to elucidate these phenomena, the parameters contributing to slope A have to be analyzed, as discussed in reference[8].

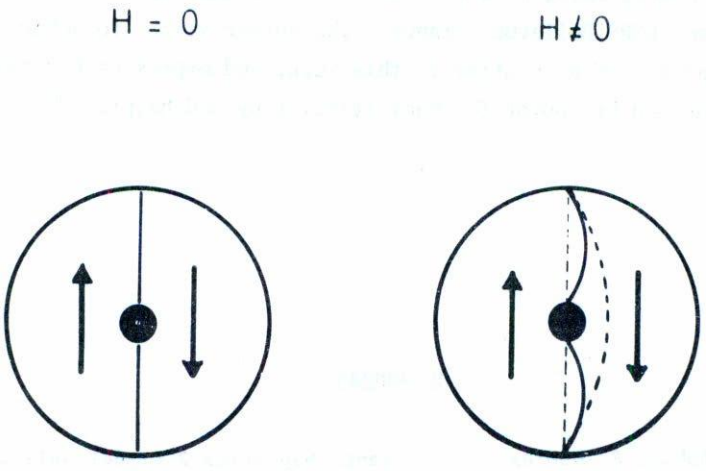



Fig. 10. Schematic representation of intra-granular defect effect on Globus' model.

Initial susceptibility is a very sensitive property. A comparison between lattice parameter variations and initial susceptibility differences(corrected by mean grain diameter), shows that while the biggest difference measured in $a_o$ is $\sim 2\%$, the biggest variation in $\frac{(\mu-1)c}{Dm}$ is around 5 times.

## 5. CONCLUSIONS

1) The stoichiometry deviations produce important changes in sintering, microstructure and ionic structure.

2) Small excess of divalent oxydes in sintering spinel Ni-Zn ferrite promotes densification and grain growth.

3) Globus'model can be generalized to non-stoichiometric ferrite compounds, provided defects distribution has an intergranular character.

4) Initial susceptibility measurements are a very sensitive instrument in ferrimagnetic materials characterization.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. A. Globus, P. Duplex. IEEE Trans. Magnetics 2 (1966) 441-445.
2. E. Roess. Proc. Int. Conf. in Ferrites Kyoto (1970) 203-209.
3. P.J.L. Reijnen, Problems of Non-stoichiometry, North-Holland, (1970), 219-238.
4. C. Guillaud et al. Sol. St. Phys. in Elect. and Comm. Academic Press., (1958) 71-98.
5. A.L. Stuijts. Proc. Brit. Ceram. Soc. 2 (1964) 73.
6. A. Globus, P. Duplex, R. Vautier. Franch Patent. 15.97.435.
7. R. Valenzuela (to be published).