CORRELATION BETWEEN MICROSTRUCTURE AND MAGNETIC PROPERTIES OF Co-NiZn FERRITES

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JOURNAL DE PHYSIQUE
Colloque C6, supplément au n°9, Tome 46, septembre 1985

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Résumé - Les propriétés magnétiques des ferrites NiZn sont influencées par plusieurs paramètres dont la microstructure qui est de première importance. La technique de pression à chaud a été utilisée afin d'obtenir un matériau à grain fin. Les analyses d'images d'échantillons comprimés à chaud d'une part, frittés de manière classique d'autre part, ont été réalisées par microscopie optique. De plus, les propriétés de la microstructure à l'échelle locale ont été étudiées par spectroscopie Mössbauer du Fe^{57} à température ambiante. Les paramètres de champs hyperfins ont été reliés aux propriétés magnétiques, aux variations de structure et à la répartition des cations sur les sites tétrahédriques et octahédriques de la structure spinelle. Un comportement très semblable a été observé entre les ferrites Co-NiZn comprimées à chaud et celles préparées par la technique habituelle des céramiques avec l'addition de BaO.

Abstract — Magnetic properties of NiZn ferrites are influenced by several variables of which microstructure is of prime importance. The hot pressing technique was applied to obtain a fine grain sized material. Stereological analyses of hot pressed and conventionally sintered samples were performed by optical microscopy. In addition microstructural properties on a local scale were studied by Mössbauer spectra of ^{57}Fe at room temperature. The hyperfine parameters were correlated with magnetic properties, structural variations and the distribution of cations over tetrahedral and octahedral sites in the spinel structure. A close similarity in the behaviour of hot pressed Co-NiZn ferrites and those prepared by usual ceramic techniques with the additions of BaO was found.

I — INTRODUCTION

Because of their high electrical resistivity and low magnetic losses NiZn ferrites are considered to be technically very important materials. Different applications require a small change in permeability with temperature over a range dedicated by these applications. Besides, low magnetic losses at high frequencies are necessary. Magnetic losses can be reduced either with the substitution of Fe^{2+} ions on the octahedral positions in the spinel lattice with highly anisotropic Co^{2+} ions or with a fine grained microstructure [1].

The addition of Co^{2+} ions effectively reduces magnetic losses at high frequencies but, on the other hand, its contribution to magnetic anisotropy causes an undesirable permeability maximum at room temperature, the secondary permeability maximum.

This negative influence of Co^{2+} ions can be avoided with the addition of small amounts Ba^{2+} ions which improves the linearity of the temperature coefficient of permeability simultaneously with the low magnetic losses at high frequencies [2].

Recently we demonstrated how the addition of BaO reacts with CoNiZn ferrite forming the

$BaCo_2Fe_{16}O_{27}$ phase which grows topotactically on the (111) faces of the spinel grains. Subsequently it was proposed that a thin layer of the BaO rich phase concentrated on the grain surface during growth retards the growth rate and thus essentially improves the temperature stability of BaO doped Co-NiZn ferrites [3].

The second way to reduce magnetic losses is a fine grained microstructure which can be obtained with the hot pressing technique. The purpose of the present work was to prepare samples with small grains and an appropriately sintered density in order to attain low magnetic losses and a linear temperature coefficient of permeability for CoNiZn ferrites with a permeability of 40 and to compare them with conventionally prepared samples with and without the addition of BaO.

II – EXPERIMENTAL METHODS

Co-NiZn ferrites with the composition $Ni_{0.49}Zn_{0.245}Co_{0.017}Fe_2O_{4-\delta}$ were prepared by the conventional ceramic process and the hot pressing technique. The raw material was obtained by prefiring a mixture of NiO, ZnO, Co_3O_4 and Fe_2O_3 and, in one case, $Ba(OH)_2.8H_2O$ at 1150°C in air. The milled slurry was dried and granulated with a camphor as a binder. The mean particle size of milled powder was $\bar{d}$ = 1.25 μm measured by the Fisher Sub Sieve Size method. Samples in the form of discs and toroids were pressed from these granulated powders. Samples in the form of discs were hot pressed in alumina dies and sintered at 1150°C for 5 – 15 minutes. The pressure applied during sintering was 50 MPa. After sintering samples were subjected to a thermal after treatment at 900°C in order to remove residual stresses from the material. Toroids for magnetic measurements were cut out of the hot pressed discs. In addition green samples with and without 0.05 at % of BaO in the form of toroids were also conventionally sintered at 1230°C for 3 hours.

Samples were magnetically and microstructurally characterized. The dependence of magnetic permeability on the temperature was measured with a simple apparatus in which the sample in the form of toroid was used as a transformer core [4]. The permeability was measured using an impedance admittance bridge at 1 MHz with a field of 0.25 mT. Magnetic losses were measured in the frequency range of 5 – 50 MHz ([1]). Microstructural investigations were carried out on polished surfaces using optical microscopy ([2]). The average grain size was estimated from the photomicrographs of samples by a linear intercept method [5]. The intercept lengths were measured using the modular system for semiautomatic quantitative evaluation of images ([3]). Microstructural properties on the local scale were studied by Mössbauer spectra of ^{57}Fe at room temperature ([4]). The source was ^{57}Co in Rhodium matrix and the velocity scale was calibrated by the spectra of metallic iron. The spectra were analyzed by using a least squares computer program assuming Lorentzian lines.

III – RESULTS AND DISCUSSION

Fig. 1 presents the difference in microstructure between conventionally prepared and pressure sintered samples. The raw material was the same powder with the average particle size of $\bar{d}_{FSSS}$ = 1.25 μm. Table I contains the results of sintered density, permeability and measurements of grain size (mean intercept length) and their distribution for normally sintered samples without additives (C), sintered samples with 0.05 at % of BaO (B) and hot pressed samples without BaO addition (A).

([1]) 4192 A LF Impedance Analyzer, Hewlett Packard

([2]) Leitz–Amray 1600 T

([3]) MOP/AMO 2, Kontron Messgerate, West Germany

([4]) Elscint constant acceleration Spectrometer with Promeda Data Acquisition System.

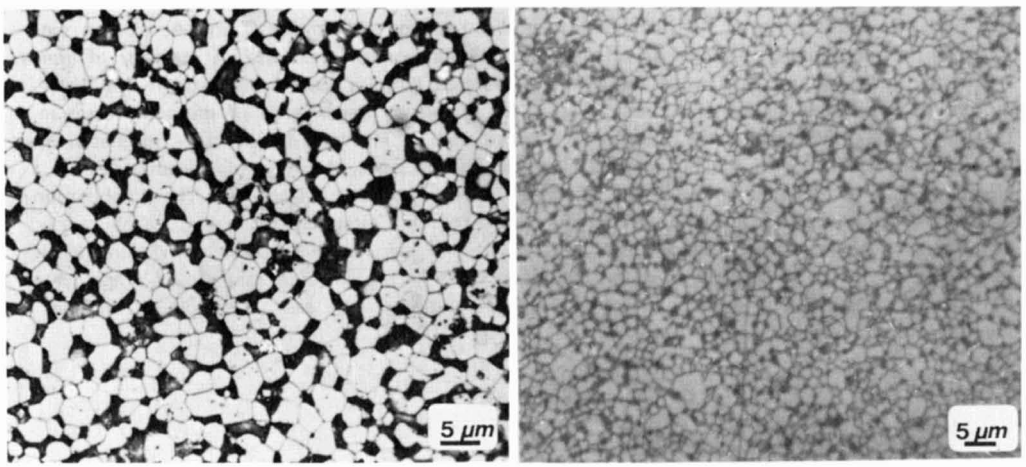

Fig. 1 — Microstructure of conventionally sintered (C) and hot pressed (A) Co-NiZn ferrite samples.

Table I

Sample	ρ_s (g/cm^3)	μ_i (1 MHz)	Mean intercept length (μm)	Standard deviation (μm)
C	3.95	45	2.5	1.2
B	4.24	45	—	—
A	4.23	41	1.5	0.7

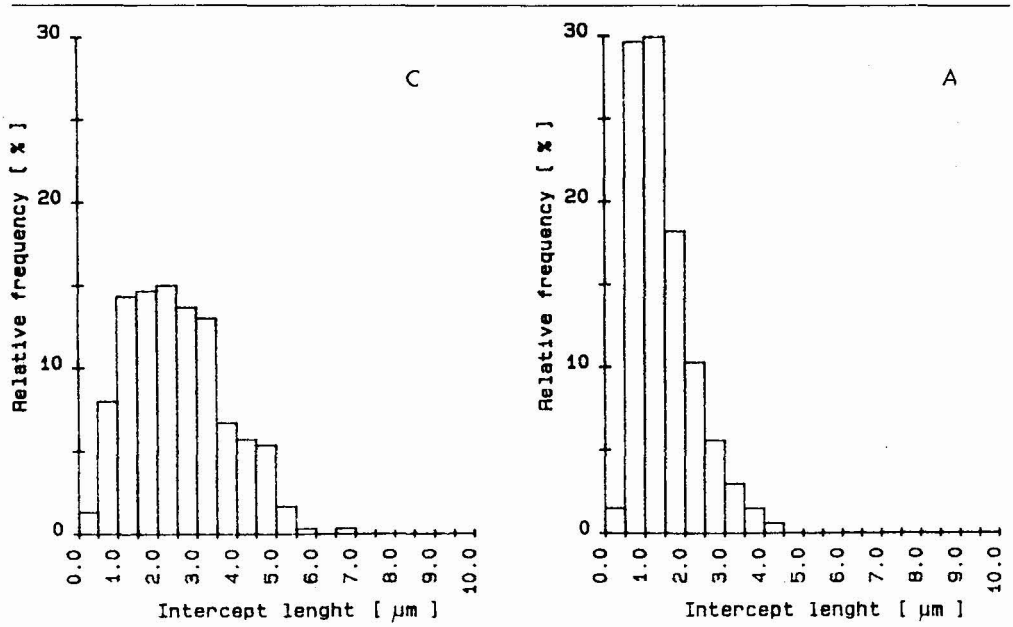

Fig. 2 — Histograms of conventionally sintered (C) and hot pressed (A) Co-NiZn ferrite samples.

From Fig. 2, which presents the histograms of microstructures of samples C and A, we can see that the pressure sintered samples have a narrower distribution of grain size. A majority of grains are in the 1 to 1,5 μm class while the normally sintered samples have a broad grain size distribution. In Fig. 3 the family of curves represent the frequency dependence of magnetic losses in the range of 5 – 50 MHz of the three samples A, B and C. The best frequency – magnetic losses relation was attained with the hot pressed samples. The presence of many grain boundaries effectively pin up the domain walls and improve the high frequency properties. The combination of many grain boundaries and the additional presence of Co^{2+} ions created a material with a linear temperature coefficient of permeability (Fig. 4) and low magnetic losses at high frequencies simultaneously. We also suppose that the inhomogeneities in the structure, the Co_2W phase (3) in the case of sample B and defects induced during preparation in the case of sample A, improve the temperature stability of Co–NiZn ferrites.

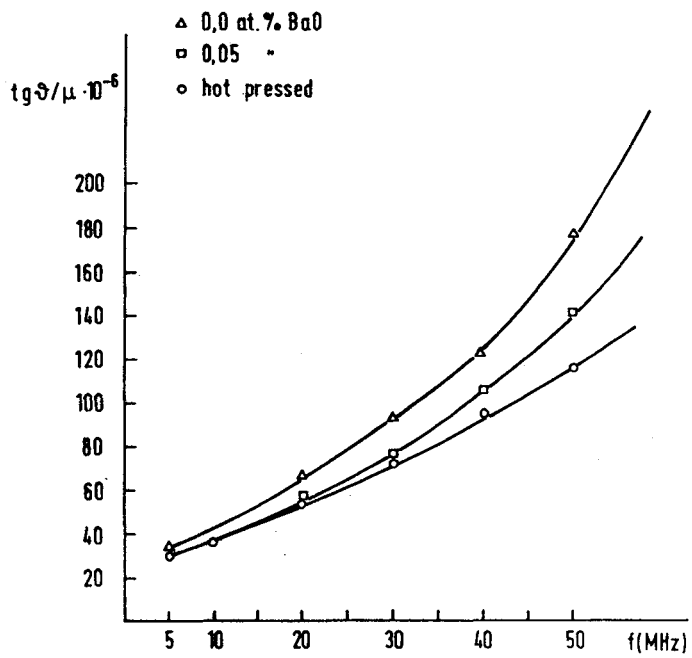

Fig. 3. – Frequency dependence of magnetic losses of different Co–NiZn ferrite samples.

These nonstoichiometric NiZn ferrites were also characterized by Mössbauer spectra of ^{57}Fe in order to obtain further information on the internal magnetic fields at different iron sites. Some typical Mössbauer spectra measured at R.T. are shown in Fig. 5.

Samples belonging to category A and B experience very similar Mössbauer spectra which are characterized by well resolved sextet patterns of broadened resonance lines. However these spectra could not be satisfactorily fitted by assuming single sextet patterns with resonance lines of Lorentzian shape. The asymmetry in amplitudes and widths of resonance lines gave evidence that at least two sets of strongly overlaped six line patterns are necessary for acceptable least squares fit. In analysis some constraints regarding the widths and intensities of resonance lines were made. The results of such analysis can be interpreted on the basis of the existence of two distinct forms of oxygen environments around Fe^{3+} ions with effective magnetic fields: H_{eff}(oct) = 480 kG, H_{eff}(tet) = 476 kG and average line widths of 0.36 mms^{-1}. The subspectra with lower values of

effective magnetic field were ascribed to tetrahedral Fe^{3+} sites due to an increased degree of covalency proposed for these sites.

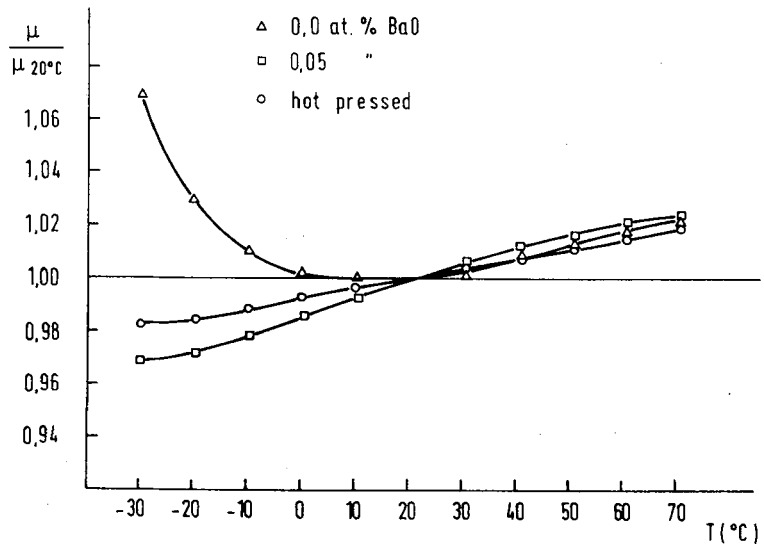

Fig. 4 — Effect of BaO addition and preparation methods on normalized change in permeability.

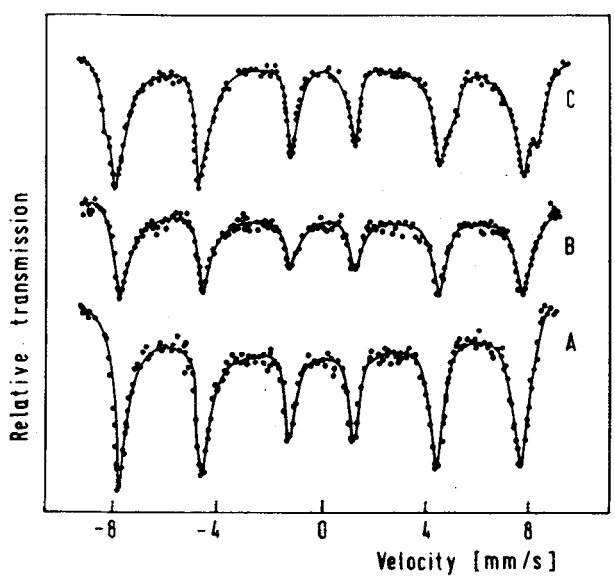

Fig. 5 — Mössbauer spectra at RT of the samples of conventionally sintered without BaO addition (C), with 0.05 at % BaO addition (B) and hot pressed (A) series.

Although the fitting procedures with two hyperfine subspectra gave good agreement with the experimental spectra, some residual broadening of the resonance lines in both subspectra still exist. This means that in spite of the fact that magnetic ions interact with one another via super-exchange antiferromagnetic interaction constituting two main magnetic sublattices, there also exist variations in hyperfine parameters which influence the long range and short range ordering due to clustering, local distorsions and defect configurations. Thus sintering at high pressure and/or sintering with BaO affect not only the morphology and grain sizes but also complicate the two sublattice pictures of long range ordering by creating various magnetic intrinsic properties. Most previous Mössbauer studies have been caried out on stoichiometric samples where the relation of the broadening of the resonance lines with relaxations [6] due to near neighbour cations environments and noncollinear spin structures [7] at iron sites have been considered. It is quite likely that these might be considered in the nonstoichiometric NiZn compounds studied here, too.

The samples belonging to category C had broader resonance lines in Mossbauer subspectra (the average line widths of 0.56 mms^{-1}) and broader distribution of grain sizes (Fig. 2) than samples A and B. However, there are differencies in the values of the hyperfine magnetic fields, too. Namely, the subspectra of sample C are characterised with effective magnetic fields: $H_{eff}(oct)$ = 494 kG, $H_{eff}(tet)$ = 478 kG. Thus, the effective magnetic fields at the octahedral Fe^{3+} sites are larger than in the samples belonging to the groups A and B indicating different co-valencies. It is known that covalency reduces the effective magnetic field but it could not be the only reason for such a reduction. Therefore it is necessary to include another mechanisms such as supertransferred hyperfine fields [8] and changes in lattice parameters.

The analysis of Mössbauer data gave evidence that distribution of cations in the samples from category C are different from those in samples A and B. There is also evidence that the distribution of grain size is related to the widths of resonance lines. It is interesting to note that samples with sharper resonance lines and smaller grains (samples A and B) reveal technologically better bulk magnetic properties (low magnetic losses and T–stable permeability) than samples C with broader resonance lines and larger grain sizes.

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