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Improved Mechanical Properties in Nb_2O_5/V_2O_5 Doped Spinel Ferrites

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Ceramic Zn ferrites have been obtained from powder synthesized by solidification of a liquid solution technique. Typical dopants used by the ceramic ferrites industry, such as SiO_2, CaO, V_2O_5, and Nb_2O_5, have been added. From porosity, fractographic, and indentation studies, differences in mechanical properties have been observed. Vickers hardness and fracture toughness improve with the addition of V_2O_5 and Nb_2O_5 when compared with undoped and with SiO_2–CaO ferrites. In order to explain the behavior of our ferrites, two different mechanisms on a grain boundary are proposed. © 1999 Academic Press

1. INTRODUCTION

In the past 50 years, ferrites have been known as one of the most important materials with a wide range of applications and have also contributed to advances in electronics (1–3). Except in the cases of recording media, copier powders, or ferrofluids, ferrite powders are not generally the finished products. In most cases the powders must be conformed into a body with a microstructure appropriate for the application (4). For this purpose, two processing steps must be carefully controlled: powder preparation and sintering.

In general, the main drawback of ceramic materials is their poor mechanical properties when compared with metals. These materials often show catastrophic brittle fractures, with very low absorption energy. This is one of the most important problems in the ceramic ferrite industry. These materials are usually exposed to many operations such as tumbling, grinding, winding, clamping, and handling, causing them to break or chip.

As it is well known, the mechanical strength is related to porosity, with the more porous materials having lower strength. In the ceramic method, the porosity is almost removed during sintering. However, the pore elimination is often incomplete. Any residual porosity leads to a decrease of the elastic properties and toughness. Another cause of weakness is the effect of some grain boundary modifiers. The formation of structures with some very large grains, called duplex structures, is often due to the segregation of a particular impurity (such as SiO_2) which locally produces rapid grain growth, while other undoped areas are unaffected (5). The formation of a $CaSiO_3$ glassy phase surrounding grains when CaO and SiO_2 are present has been reported (6). This phase leads to an enhancement of the strains in the material.

In this work, we study the effect on the mechanical properties of some additives, such as SiO_2, CaO, Nb_2O_5, and V_2O_5, used in ferrite processing. These additives are often used in order to improve the electrical properties by means of a highly resistive layer in the grain boundary region. The effect of these dopants on the mechanical parameters has been determined taking into account the topics mentioned above.

2. EXPERIMENTAL

Zinc ferrites ($ZnFe_2O_4$) were synthesized by solidification of a liquid solution technique as described in Pechini's patent (7). A solution of Fe^{3+} and Zn^{2+} was obtained from 73.75 wt% $Fe(NO_3)_3{\cdot}9H_2O$ and 23.25 wt.% $ZnSO_4{\cdot}7H_2O$, dissolved in a saturated citric acid–water solution. All reagents were Aldrich products. This synthesis method allows us to obtain ferrites without the SiO_2 impurities often present in Fe_2O_3 when the classical solid state method is used.

Thermal treatments of 723 K for 12 h and 973 K for 4 h were carried out in order to remove organic, nitrogen, and sulphur residues. We denominated the product of this processing step "presintered powder." Water suspensions of this powder were formed. For this purpose, 1 wt.% Noramer™ and 5 wt.% Primal™ were added as dispersing and binder agents, respectively.

Four different groups have been established:

Group A: no additives.
Group B: with SiO_2 (0.3 wt.%) and CaO (0.1 wt.%).
Group C: with Nb_2O_5 (0.02 wt.%) and V_2O_5 (0.04 wt%).
Group D: with SiO_2 (0.3 wt.%), CaO (0.1 wt.%), Nb_2O_5 (0.02 wt.%) and V_2O_5 (0.04 wt.%).

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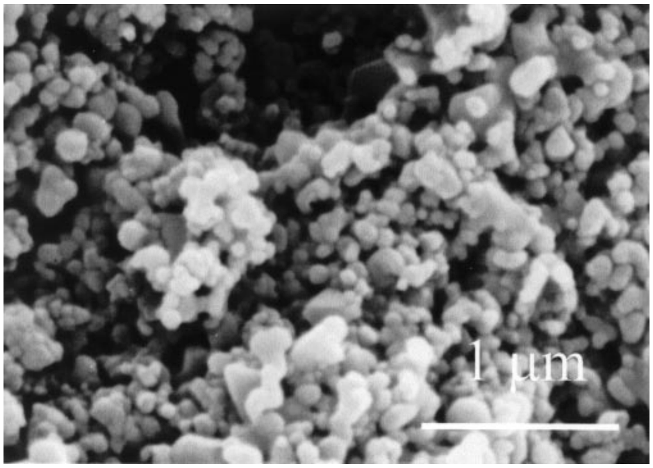

FIG. 1. Scanning electron micrograph obtained from presintered powder.

After drying, the powder was pressed into disks of 10 mm diameter and 2 mm height. The samples were heated at a rate of 180 K h^{-1} to 1073 K and a rate of 300 K h^{-1} to 1623 K, kept at this temperature for 2 h under air atmosphere and then cooled at a rate of 180 K h^{-1} to room temperature. Scanning electron micrographs (SEM) and fractographic studies were carried out on a scanning electron microscope JEOL 6400, coupled with an energy dispersive X-ray (EDX) analyzer.

X-ray diffraction patterns were collected using a Philips X'Pert MPD diffractometer with Cu$K\alpha$ radiation.

The Hg porosimetry study was carried out in a Micromeritics Autopore III 9410 porosimeter. Ferrites were analyzed in the pressure range from 0.007 to 415 MPa. Pore volume, percent porosity, and pore volume distributions in the mesopore to macropore ranges were obtained.

The indentation test was performed in a Matzuzawa microhardness tester at 4.9 N and 0.9, with Vickers and Knoop indenters.

3. RESULTS AND DISCUSSION

Figure 1 shows the micrograph obtained for presintered powder. In this step, the material consists of small particles of about 100 nm. No nitrogen or sulfur were found by EDX, indicating that the presintering temperature of 973 K was sufficient to obtain powders free of residues from the raw materials.

XRD patterns for the presintered powder (Fig. 2a) show a single spinel phase without any other maxima attributable to other residual phases.

XRD patterns for sintered samples (Fig. 2b) show a single spinel phase with a high degree of crystallinity. No significant differences were observed in lattice parameters among the groups. Values of about 8.4365 Å were calculated for the four groups of ferrites.

Micrographs obtained over the fracture surfaces are shown in Fig. 3. Groups A and C show clear differences with respect to groups B and D. Groups A and C have a grain size between 2 and 8 µm, with grain boundaries well

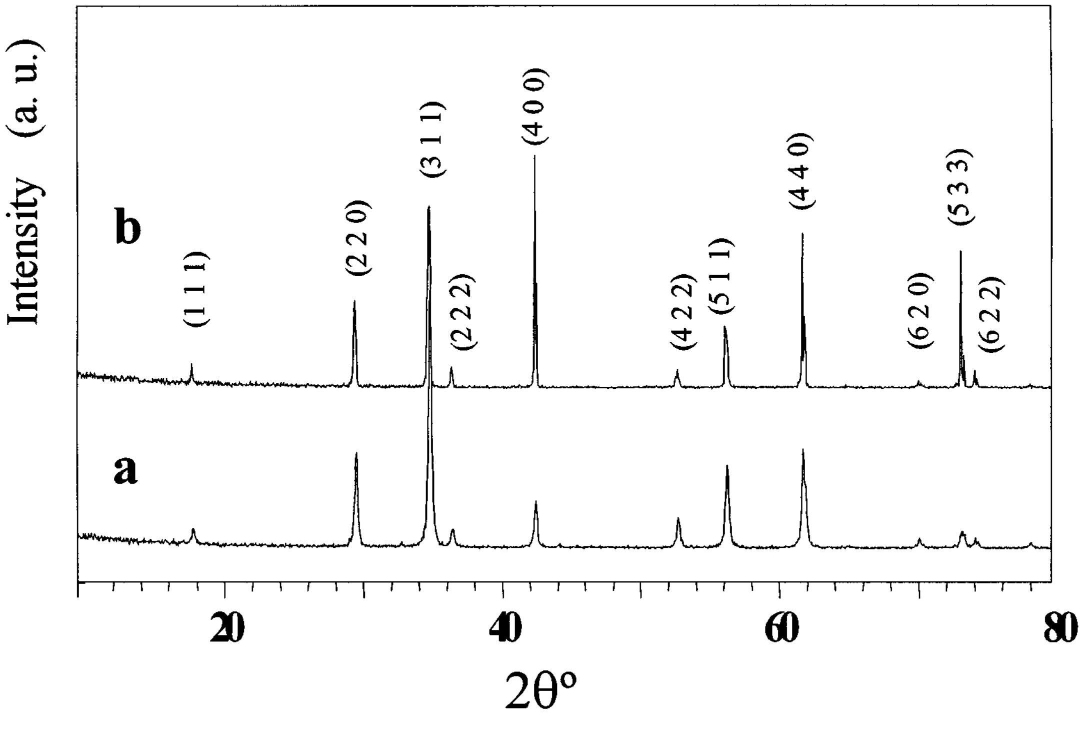

FIG. 2. XRD patterns for (a) presintered powder and (b) sintered ferrite. Ferrites of the four groups showed similar patterns.

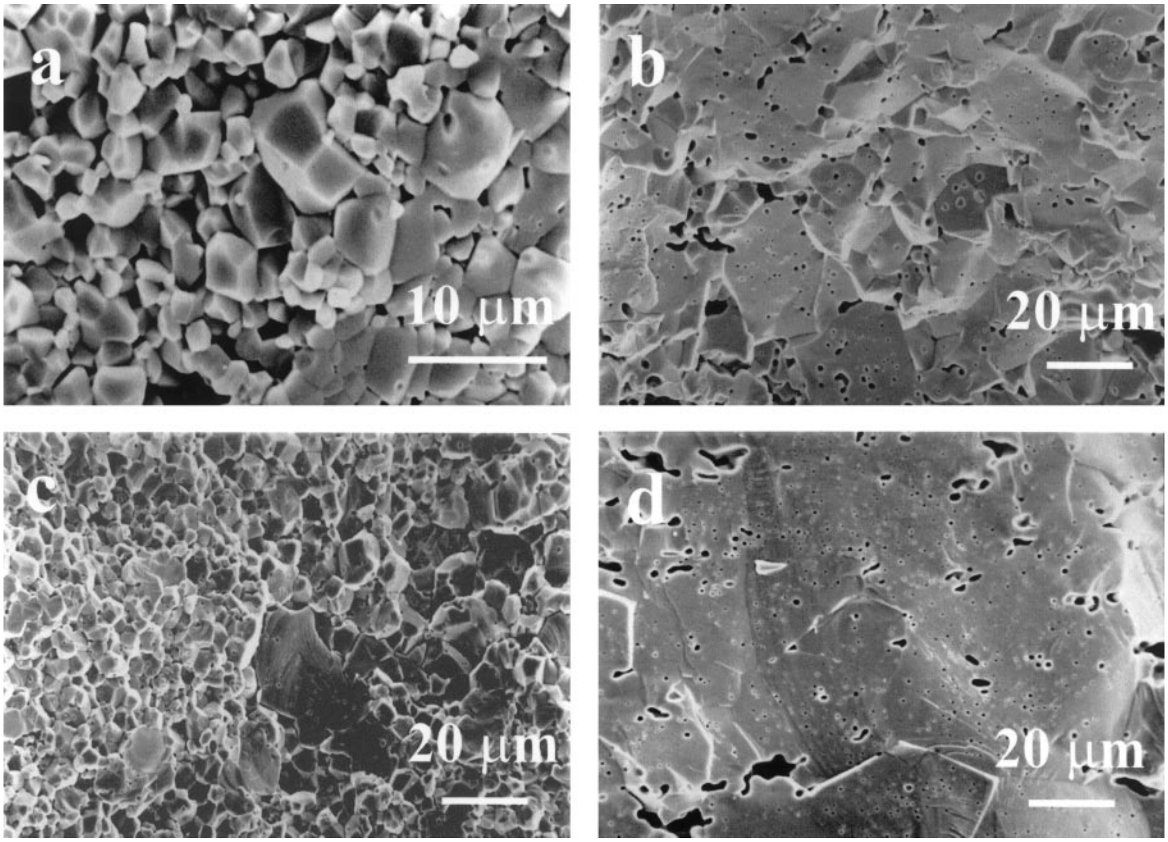

FIG. 3. Scanning electron micrograph obtained from fracture side of ferrites corresponding to Groups A, B, C, and D. Porosity, grain size, and fracture differences are clearly observed.

delimited. Moreover, these groups show a mixed kind of fracture surfaces, with two kinds of fracture propagation, that is, inter- and transgranular.

Groups B and D show the formation of a glassy phase surrounding the grains, with a single transgranular propagation of the fracture. Since grain boundaries are not clearly seen, SEM could not determine the grain size. In addition, a higher degree of porosity is observed in these groups which contain SiO_2/CaO in their composition.

Density and porosity data are presented in Table 1. Skeletal density refers to that excluding pores and interparticle spaces while bulk density includes both pore and interparticle spaces. Also, some porosity cannot be detected by Hg porosimetry, i.e., closed pores inside the material grains. Therefore, taking into account the crystallographic density for $ZnFe_2O_4$ ($5.32\,g\,cm^{-3}$), intragranular porosity can be estimated. Porosity percentages were calculated between 0.2 and 30 μm. Bimodal distribution was observed for Groups B, C, and D, with maxima at 5.3 and 15.1 μm. Pore diameter for Group A was unavailable due to the low degree of porosity.

These data point out that the addition of any considered additives leads to an enhancement of the porosity. Therefore, the bulk and skeletal density values of the material decrease.

Skeletal density for Groups B, C, and D decreases as a consequence of the intragranular porosity. This effect is clearer in samples with only SiO_2/CaO (Group B). The formation of a $CaSiO_3$ glassy phase, which induces strain in grain boundaries, and the segregation of SiO_2 leads to an irregular and faster growth of some grains, at the cost of the smaller ones, occluding pores into themselves. Porosity between grains is also enhanced with SiO_2 and CaO, reaching values of 25.7 and 12% for Groups B and D, respectively.

Nb_2O_5/V_2O_5 together with SiO_2/CaO (Group D) decrease the intragranular porosity with respect to Group B. An explanation would be the control that, in the grain

TABLE 1
Density and Porosity Data Obtained by Hg Intrusion

	Density ($g \cdot cm^{-3}$)		Porosity (%)	
	Skeletal	Bulk	Intergranular	Intragranular
Group A	5.25	5.24	0.3	1
Group B	4.81	3.44	25.7	9.6
Group C	5.02	4.54	9	5.6
Group D	5.01	4.37	12	5.8

Note. Crystallographic density for $ZnFe_2O_4 = 5.32\,g\,cm^{-3}$.

TABLE 2
Mechanical Properties Data Obtained by Indentation Test

	H_V (Kp/mm^2)	K_{Ic} Radial (MPa m^2)	K_{Ic} Palmquist (MPa m^2)
Group A	594.45	0.97	1.23
	(± 39.04)	(± 0.08)	(± 0.18)
Group B	486.74	0.70	0.57
	(± 35.76)	(± 0.03)	(± 0.12)
Group C	650.24	1.16	1.55
	(± 34.94)	(± 0.17)	(± 0.16)
Group D	545.30	0.91	1.03
	(± 28.99)	(± 0.10)	(± 0.14)

boundary region, Nb_2O_5 and V_2O_5 exercise on the grain growth, although differences in grain size could not be confirmed by SEM.

Data obtained by indentation tests are shown in Table 2. We have considered two different models corresponding to radial (8) and Palmquist-type cracks (9). These data point out that Vickers hardness (H_V) and fracture toughness (K_{Ic}) decrease when SiO_2 and CaO are present (Group B). However, an improvement in these parameters is observed when Nb_2O_5/V_2O_5 are added (Group C). In this way, a compensatory effect takes place where all four additives are present in the composition.

The presence of SiO_2/CaO in the ferrites leads to a higher porosity and the formation of a glassy phase, as could be seen by SEM. Moreover, Ca^{2+} is incorporated into the spinel structure (10) producing an enhancement in structural stressing due to its higher volume. The higher porosity and the stressing would lead to the higher brittleness in ferrites.

It has been reported that Nb_2O_5 and V_2O_5 are retained on the grain boundaries of spinel ferrites (11). These additives form a highly resistive layer in the grain boundary by forming bonds such as Fe^{2+}–Nb^{5+} and Fe^{2+}–V^{5+} (12). Similarly, Ca^{+}–Nb^{5+} and Ca^{2+}–V^{5+} bonds are formed preventing the incorporation of Ca^{2+} into the spinel structure. On the other hand, similar additives such as Ta_2O_5 inhibit the grain growth by segregating at the grain boundary (13). Our data point out that Nb_2O_5 and V_2O_5 inhibit the extremely high porosity caused by SiO_2 and CaO by controlling the grain growth. However, the improvement of mechanical parameters in Group C with respect to Group A (without additives), indicates that Nb_2O_5 and V_2O_5 also play a reinforcing role on grain boundary. Differences in the kind of fracture surface were not found. Moreover, the porosity in Group C is higher than in Group A. The data obtained of Vickers hardness and fracture toughness point out that the presence of these additives in grain boundary prevents the intergranular crack propagation. However, we have no experimental evidence of this fact. This point is currently under study by the authors.

The presence of V_2O_5 and Nb_2O_5 leads to an improvement of the mechanical parameters in spinel ferrites through the control of the porosity and also avoiding the incorporation of Ca^{2+} by means of its fixation on grain boundary.

4. CONCLUSIONS

1. Pieces of ceramic ferrites have been obtained from zinc ferrite powders synthesized by solidification of a liquid solution technique.
2. Four different groups have been prepared differing in the additives incorporated:
   Group A: no additives.
   Group B: with SiO_2 and CaO
   Group C: with Nb_2O_5 and V_2O_5
   Group D: with SiO_2, CaO, Nb_2O_5 and V_2O_5.
3. Additives are critical regarding the porosity and the grain structure of the material. SiO_2 and CaO lead to an enhancement of inter- and intragranular porosity, as well as the formation of a glassy phase that induces strains in the structure. The presence of Nb_2O_5 and V_2O_5 in samples with SiO_2 and CaO exercise a clear control on the porosity.
4. The addition of Nb_2O_5/V_2O_5 leads to the improvement of hardness and fracture toughness in ceramic ferrites.

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