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Influence of iron oxide reactivity on microstructure development in MnZn ferrites

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The reactive sintering of manganese zinc ferrite has been studied using powders prereacted at 600 °C, 900 °C, and 1200 °C. The results show that the calcination temperature has a pronounced influence on the microstructure evolution during sintering. The selfsintering of iron oxide during the heating of MnZn ferrite compacts prepared from prereacted mixtures, shifts the chemical reaction of MnZn ferrite formation to higher temperatures where the final microstructure is developed.

1. Introduction

One of the most important steps during the processing of MnZn ferrites is the sintering of the powder compact into the final product. During this process evolution of the microstructure occurs, which to a great extent determines its final magnetic properties. On the other hand, the discontinuous grain growth which often accompanies sintering of MnZn ferrites and degrades their essential magnetic properties, is the most unfavourable process which can occur during microstructural development of powder ferrites. Grains with large grain size and trapped porosity, which are formed during discontinuous grain growth, make the ferrite cores susceptible to eddy currents. Such a microstructure strongly increases the high-frequency power loss of MnZn ferrites.

The microstructural development of ferrites depends on many parameters; however, the reactivity of the raw oxides, the morphology of ferrite powders, and the proportions of the ingredients are of prime importance. Besides, chemical heterogeneity, i.e. the presence of free Fe_2O_3, which accompanies the grain growth and densification of MnZn ferrite, usually leads to its reactive sintering [1]. During reactive sintering, the chemical reaction of MnZn ferrite and the densification of the sample occur during the same firing cycle. Depending on the raw oxide reactivity and processing parameters, i.e. powder morphology, heating rate and temperature of sintering, the chemical reaction and the densification/grain growth can occur in separate steps or simultaneously [2].

During the preparation of MnZn ferrite via the conventional ceramic route, the uncalcined powder is prereacted at temperatures around 900 °C. At this temperature, a relatively high amount of iron oxide remains in the calcined ferrite powder depending on the atmosphere and temperature during the calcination and the reactivity of the raw oxides. The reaction products accumulating on the grain boundary during sintering may slow down the grain-boundary mobility. Therefore, the presence of Fe_2O_3 and other reaction products during sintering hinders the grain growth of MnZn ferrite during sintering. Also, the additional pore growth induced during reactive sintering [1], and consequently the presence of large pores, pins the grain boundaries and prevents discontinuous grain growth as well.

It was repeatedly found that less-presintered ferrite powders suffer less from exaggerated grain growth [1,3]. Therefore, discontinuous grain growth in MnZn ferrites can be successfully suppressed and a smaller average grain-size microstructure can be achieved when the degree of calcination is decreased. In the extreme case when the uncalcined powder is sintered, discontinuous grain growth is practically unobserved. On the other hand, in that limiting case when the uncalcined powder is sintered, the low compressibility of the starting raw oxides and, consequently, the large shrinkage of the sintered ferrite, induce inhomogeneities during compacting and deformation after sintering, which decreases the reproducibility and reliability of ferrite core preparation.

In general, uncalcined powders or less-calcined ferrite powders are resistant towards discontinuous grain growth, while calcined and milled powders often show a great tendency to anomalous grain growth. Particularly when intensive milling is used in order to decrease the starting grain size of the ferrite grains, which readily causes inhomogeneities in grain-size distribution and introduces the impurities which induce the liquid phase during sintering, the probability of developing discontinuous grain growth becomes very high.

A compromise should be achieved in order to provide a high resistance of the MnZn ferrite powder to discontinuous grain growth, to improve the starting

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powder compressibility and to decrease the shrinkage after sintering. Such a compromise could be maintained when iron oxide is added, causing the densification, grain growth and the chemical reaction, i.e. the formation of MnZn ferrite, to occur simultaneously. In that case the accumulation of reaction products on the grain boundary will slow down the grain growth and will govern the evolution of the final ferrite microstructure.

If iron oxide is used, which exhibits selfsintering (the sintering of Fe_2O_3 prior to its reaction) at lower temperatures, the ferrite formation will be delayed [4]. The selfsintering (compression and deactivation of Fe_2O_3) of iron oxides prepared at lower decomposition temperatures starts at lower temperatures. This is in accordance with the general observation that the lower the decomposition temperature of the basic salt, the lower is the temperature region where the decomposition product reaches its optimal reactivity. The free surface of Fe_2O_3 in the starting mixture will strongly decrease during heating, thus impeding the solid-state reaction between the starting raw oxides, so that ferrite formation will be displaced to higher temperatures and will thereby accompany the final microstructure formation. In addition, the compressibility of the starting powder can be modified by a proper calcination temperature. Such a ferrite powder will be resistant to discontinuous grain growth even when calcined at relative high temperatures, and will exhibit relatively low specific surface area and a relatively high compressibility, which will ensure the fabrication of homogeneous and dense ferrite compacts.

2. Experimental procedure

Conventional powder processing techniques were employed to prepare the powders. Chemically pure Fe_2O_3, ZnO (Zinc White Harzsiegel CF, purity 99.8 wt %, $A_s(\mathrm{BET}) = 5.0\,\mathrm{m^2\,g^{-1}}$) and Mn_3O_4 (Fermac, purity 98.9 wt %, $A_S(\mathrm{BET}) = 10.0\,\mathrm{m^2\,g^{-1}}$) were weighed in definite proportions and ball milled in deionized water. The chemical composition of the MnZn ferrite studied was $Mn_{0.4}Zn_{0.6}Fe_2O_4$. The iron oxide used (Iron-NKK Co. Ltd, Fukuyama Works; (NK-α) SH, lot 4-2010) is a typical raw oxide obtained directly from iron chloride solution at a reactor temperature around 500 °C by spray roasting, with a purity of 99.44 wt %, $A_s(\mathrm{BET}) = 5.63\,\mathrm{m^2\,g^{-1}}$, $\bar{d}$ (Fisher Sub-Sieve Sizer) = 0.90 μm. The dried powders were calcined at 600 °C (A), 900 °C (B) and 1200 °C (C) for 2 h and afterwards milled in a planetary ball mill. The uncalcined powders were denoted powder D. The relative shrinkage rate spectra of the powders were measured by a dilatometer, heating rate $10\,°\mathrm{C\,min^{-1}}$ (Bähr-Gerätebau GmBh), the specific surface area was determined by the BET method, and the average particle size was determined by an HR 850-Cilas/Alcatel Granulometer. X-ray powder diffraction patterns were determined by a Philips PW-1710 diffractometer and magnetization was determined by suscepto/magnetometer (DSM-8 Manics 67120 Ernalsheim/B). Powders A, B, C and D were granulated with addition of 1 wt % PVA (polyvinyl alcohol). Toroids with dimensions i.d. 5 mm, o.d. 15 mm and height 10 mm were pressed from the granulated powders. The compacting pressure was varied from 200–500 MPa in order to obtain the same "green" density in all the samples, which was about $3.0\,\mathrm{g\,cm^{-3}}$. The compacts were then sintered at 1250 °C and 1400 °C in a computerized tube furnace, which regulates the O_2/N_2 atmosphere during sintering and cooling. The density of the sintered samples was determined by Archimedes' method. From enlarged micrographs of polished and etched samples, the average grain cross-sectional area was determined. The average grain radius, $r = D/2$, was related to the radius, R, of the average grain cross-section of the equation $r = (4/\pi)R$.

3. Results and discussion

In Fig. 1 the relative shrinkage rate spectra of samples A, B, C and D, including the shrinkage curve of Fe_2O_3, are shown. The iron oxide and the uncalcined powder exhibit a pronounced peak in the relative shrinkage rate at about 950 °C. This peak is a characteristic of the Fe_2O_3 used and in sample D demonstrates its ability for selfsintering. This peak is also clearly visible in calcined samples A and B, indicating that selfsintering was not complete during calcination

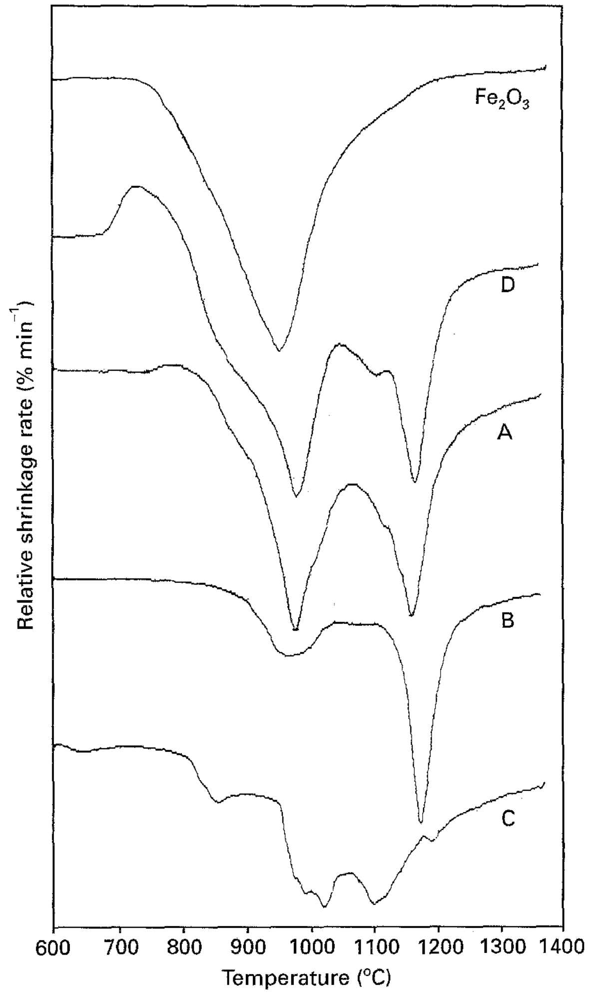

Figure 1 The relative shrinkage rate of pure Fe_2O_3, green powder D and powders calcined at 600 °C (A), 900 °C (B) and 1200 °C (C).

and is continued during dilatometric analysis. In addition, samples D, A and B exhibit an additional peak at about 1150 °C which represents the shrinkage of MnZn ferrite during sintering. In sample C calcined at 1200 °C, instead of two peaks, one broad peak is observed indicating that both dominant processes, i.e. the selfsintering of Fe_2O_3 and the densification–ferrite formation occur in close steps. The formation of the ferrite at that calcination temperature is more intensive and the ability of "free" Fe_2O_3 to selfsinter decreases after heat treatment.

Figs 2 and 3 show the X-ray diffraction pattern of powders D, A, B and C and their magnetization. The X-ray pattern and the room-temperature magnetization measurements indicate a relatively low amount of MnZn ferrite present in the calcined powder. The magnetization, σ, of prereacted powders cooled in nitrogen shown in Fig. 3 is proportional to the content of MnZn ferrite. The difference in the magnetization between the two curves is proportional to the amount of MnZn ferrite which disintegrates, and to the amount of haematite which simultaneously appears during cooling of the prereacted powders in air.

The magnetization measurements and the X-ray powder diffraction pattern of powders D, A, B and C indicate a relatively large amount of iron oxide present in the calcined powder, Figs 2 and 3. A remarkable finding during examination of the X-ray diffraction pattern is the fact that the first reaction product at 600 °C (sample A) is $ZnMn_2O_4$, indicating that Fe_2O_3 does not take part in the chemical reaction at lower temperatures. However, of essential importance is not so much the relatively large amount of α-Fe_2O_3 present in the prereacted samples as the ability of the iron oxide to selfsinter (Fig. 1).

The selfsintering of iron oxide during sintering will strongly delay the formation of MnZn ferrite and will cause the final chemical reaction to accompany sintering and the final microstructural development. The reaction products accumulating on the grain surface during grain growth, as well as the growth of large pores which accompanies reactive sintering, hinder the ferrite grain growth. This can be noted when the average grain sizes of samples sintered at 1250 and 1400 °C are compared, Table I. In samples B and C, prereacted at higher temperatures (900 and 1200 °C), where the ability of Fe_2O_3 to selfsinter strongly diminishes (Fig. 1), the grains grow faster and the increase in average grain size is noticeably large compared to samples D and A. This is in accordance with the basic assumption of this paper that the iron oxide used in the MnZn ferrite preparation strongly impedes grain growth and thereby prevents discontinuous grain growth. The microstructure of sintered samples and related parameters are shown in Fig. 4 and in Table I.

A homogeneous microstructure is obtained with an overall average grain size of 6 μm for samples sintered at 1250 °C and around 10 μm for samples sintered at 1400 °C with relatively large intergranular pores. Whereas the average grain size of samples sintered at 1400 °C increases by about 60% compared to those sintered at 1250 °C, the average density increases by about 2%, which implies that the average pore size

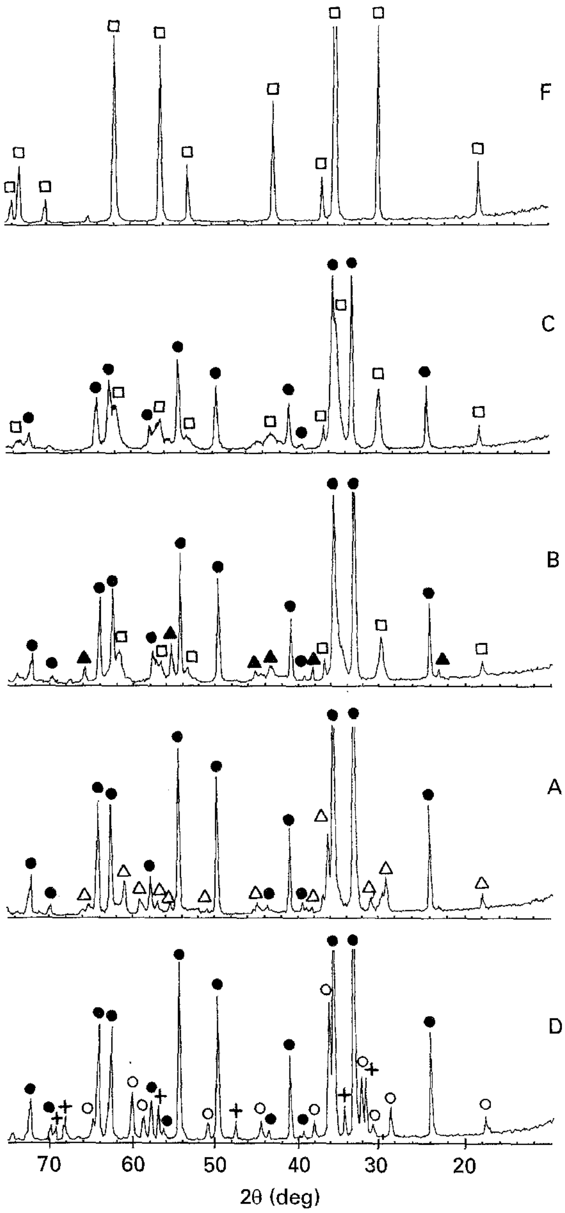

Figure 2 The X-ray powder diffraction pattern of "green" powder (D) and of powders calcined at 600 °C (A), 900 °C (B) and 1200 °C (C). The diffraction pattern of sintered MnZn ferrite (F) is also shown (□). (▲) Mn_2O_3, (●) Fe_2O_3, (+) ZnO, (○) Mn_3O_4, (△) $ZnMn_2O_4$.

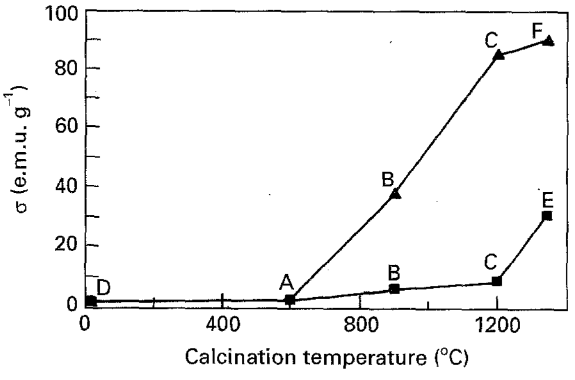

Figure 3 The magnetization of uncalcined powder D and of powders calcined at 600 °C (A), 900 °C (B) and 1200 °C (C). The magnetization of sintered MnZn ferrite (F) and ferrite powder calcined at 1350 °C (E) are also shown; (▲) magnetization of powders calcined in air and cooled in nitrogen (■) magnetization of powders calcined and cooled in air.

TABLE I Properties of starting ferrite powders and of sintered samples; specific surface A_S, the median particle size $\bar{d}$, sintered density ρ, relative density TD, and the average grain size $\bar{D}$, of samples sintered at 1250 and 1400 °C

			1250 °C			1400 °C		
Samples	A_S (m^2 g^{-1})	$\bar{d}$ (μm)	ρ(g cm^{-3})	TD (%)	$\bar{D}$(μm)	ρ(g cm^{-3})	TD (%)	$\bar{D}$(μm)
D	6.7	0.70	4.70	92	5.60	4.85	95	8.50
A	4.1	0.80	4.84	95	5.78	4.89	96	8.80
B	2.3	1.56	4.80	94	6.31	4.85	95	10.80
C	2.6	1.99	4.75	93	6.25	4.88	96	11.00
Overall average values			4.77	93.5	5.98	4.87	95.5	9.77

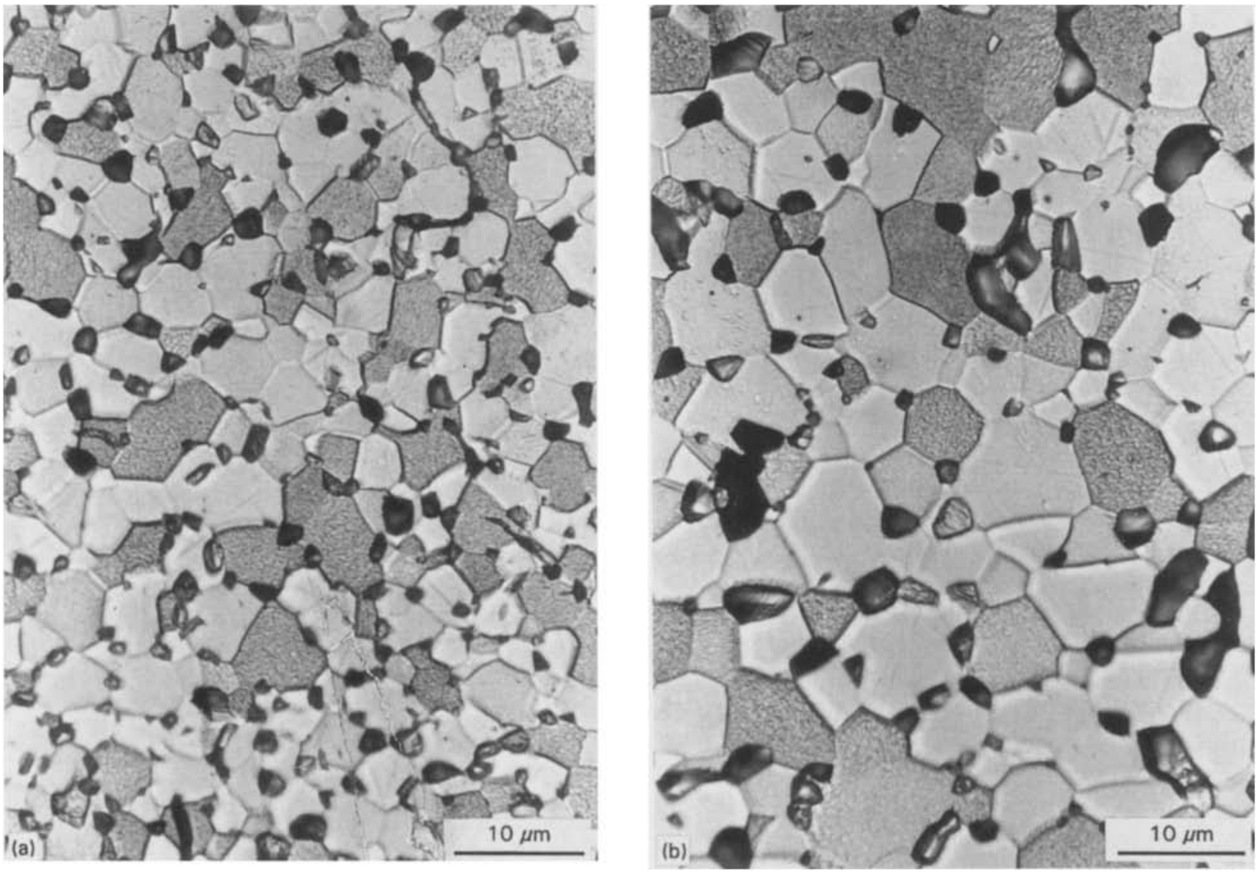

Figure 4 Microstructure of MnZn ferrite prepared from powder B sintered at (a) 1250 °C and (b) 1400 °C.

increases during grain growth. Using the elementary topological relation $n_0 - n_1 + n_2 - n_3 = 1$ where n_0, n_1, n_2 and n_3 are the numbers of 0, 1, 2 and 3 dimensional features, i.e. points, lines, polygons and polyhedra [5] one can derive the relation between the number of pores and grains and their sizes as $n_g \propto 1/D_g^2$ and $n_p \propto 1/D_p^2$, Fig. 5, where D_g and D_p are the equivalent grain and pore diameters. From these relations and the equation $n_g = 2Rn_p$, which is a consequence of the topological relation, one can obtain the final relation between the pore size and grain size $D_p \propto D_g$. Thus, during normal grain growth, the pore size increases proportionally to the grain size increase, provided that the fraction of corners occupied by pores, R, stays constant, as well as the sintered density.

In Fig. 6a and b the grain-size distribution as a function of sintering temperature is shown. The distribution remains more or less similar when the sintering

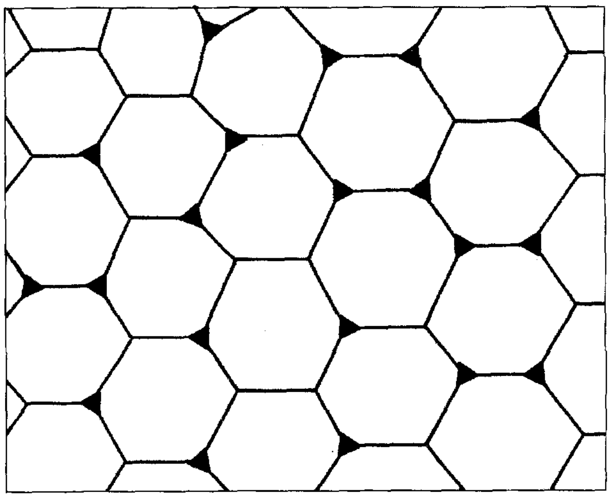

Figure 5 The idealized microstructure of a MnZn ferrite with $A = n_g \pi D_g^2/4$, where A is the area considered, n_g is the number of grains per area, A, and D_g is the average equivalent grain diameter.

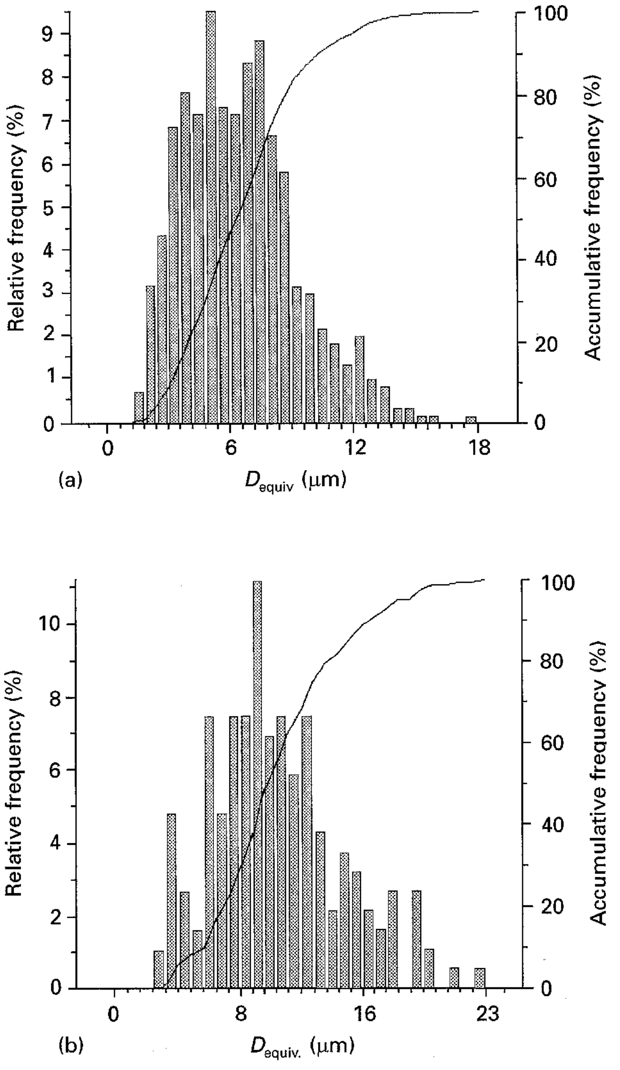

Figure 6 The grain-size distribution of sample B sintered at (a) 1250 °C and (b) 1400 °C, respectively.

temperature is increased, only the average grain size is shifted to higher values. No grains with exaggerated grain size can be observed. This tendency, i.e. resistance to exaggerated grain growth during sintering, is equally well observed in high-temperature-calcined powders (C) as in green compacts (D) or low-temperature-calcined samples (A and B). On the other hand, however, the microstructure of sintered samples shows exaggerated pore growth. The exaggerated pore growth during the initial stage of sintering occurs via surface diffusion, particle-size distribution effects and particle coalescence [6]. During sintering of MnZn ferrites in an oxygen-rich atmosphere, the pore mobility is high [7], and pores move along the grain boundaries, leading to exaggerated pore growth. Beside this, Kirkendall porosity can also be formed due to unequal mutual diffusion of the reactants, particularly when the chemical reaction, and consequently the participating reaction products, accompany grain growth, as is the case during reactive sintering.

These investigations showed that the application of an iron oxide which sinters prior to chemical reaction during sintering increases the resistivity of MnZn ferrite powders against discontinuous grain growth, even when a high calcination temperature and intensive milling is applied. However, the samples prepared from such an Fe_2O_3 usually show a larger final average pore size. Thus, the resistance of MnZn ferrite powders to discontinuous grain growth can be effectively improved at the expense of a larger final average pore size.

4. Conclusion

The results of the present work have shown that the iron oxide exhibiting a "low-temperature reactivity" impedes the grain growth during sintering. A higher calcination temperature promotes the grain growth during sintering. The MnZn ferrites prepared from low-temperature reactivity iron oxides are resistant to the formation of large grains and trapped porosity.

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