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Studies on densification of α-Fe_2O_3 ceramics

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The densification of ceramics of α-Fe_2O_3 depends on the processing parameters. The separate influences of milling, sieving, isostatic pressure and sintering atmosphere were investigated. The maximum density, with a value around 96%, was obtained in a sintering atmosphere of nitrogen.

1. Introduction

The porosity of ceramics affects their electrical behaviour [1]. It is well known that porosity and, consequently, density depends strongly on the fabrication process. In this work, a study of the variation of the density of α-Fe_2O_3 ceramics as a function of milling time, sieving mesh, compaction pressure, sintering time and sintering atmosphere, was performed. The separate influences of milling, sieving and isostatic pressure have been evaluated. The purpose was to obtain the correct combination of process parameters which can lead to a maximum densification of α-Fe_2O_3 ceramics in order to obtain a high dielectric strength.

2. Experimental procedure

The samples were prepared from Fe_2O_3 powders (Fluka) with 98.0% purity. The green specimens were processed through the following sequence of operations [2]: drying, sieving, dry compaction and hydrostatic pressure. Dry compaction was uniaxial and manually done.

The samples (discs 10 mm diameter and 3 mm high) were introduced into a horizontal tubular furnace, the atmosphere of which can be controlled by the independent injection of two gases. To prevent thermal fracture, the samples were introduced and retired through four stages of 5 min each. The samples were heated gradually at a rate of 7.5 °C min^{-1}, from room temperature to 1350 °C. The increase of temperature was stopped several times to allow measurement of the density at different temperatures.

Density was determined from the volume and weight. Above 90% relative density, the volume was determined by Archimedes' principle.

3. Results

3.1. Influence of milling

Fig. 1 shows the variation of relative density in terms of the sintering temperature for three samples whose powders were milled for 0, 1 and 10 h. The other processing parameters were the same, namely no sieving, dry compaction manually done with a uniaxial pressure equal to 0.4 kg mm^{-2}, and no hydrostatic pressure applied. The best relative density, equal to 94.7%, was obtained with the sample whose powder had been milled for 1 h.

3.2. Influence of sieving

The powder of one of the samples was not sieved; powders of the other two samples were sieved through 0.063 and 0.038 mm meshes. The common processing parameters were no milling, dry compaction manually done with a uniaxial pressure equal to 0.4 kg mm^{-2}, and no hydrostatic compaction pressure. The maximum value of density, 94.6%, was obtained for the sample fabricated with the unsieved powder (see Fig. 2).

3.3. Influence of the hydrostatic compaction pressure

The values of the hydrostatic compaction pressure used in fabricating the four samples were 0, 5, 10 and 30 kg mm^{-2}. The common parameters were no milling, no sieving, and dry compaction manually done with a uniaxial pressure of 0.4 kg mm^{-2}. The maximum value of relative density, 94.6%, was obtained for the sample which has not been subjected to hydrostatic pressure (see Fig. 3).

3.4. Influence of sintering atmosphere

Fig. 4 shows the variation of density with atmosphere for two samples with a milling time of 1 h. For one of the samples, the atmosphere was air throughout the sintering process. For the other sample, the sintering atmosphere was air until the relative density reached 85%, after which the atmosphere was changed to nitrogen. For this specimen the maximum value of relative density, equal to 96.2%, was obtained.

4. Discussion

All the curves in Figs 1–4 show that the relative density depends on the sintering temperature. The

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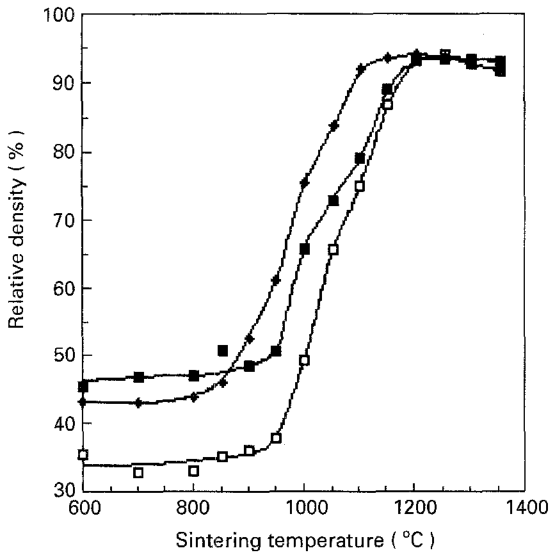

Figure 1 Density versus sintering temperature at milling times of (□) 0 h, (◆) 1 h, and (■) 10 h. $\Delta T/\Delta t = 7.5\,°\mathrm{C\,min^{-1}}$.

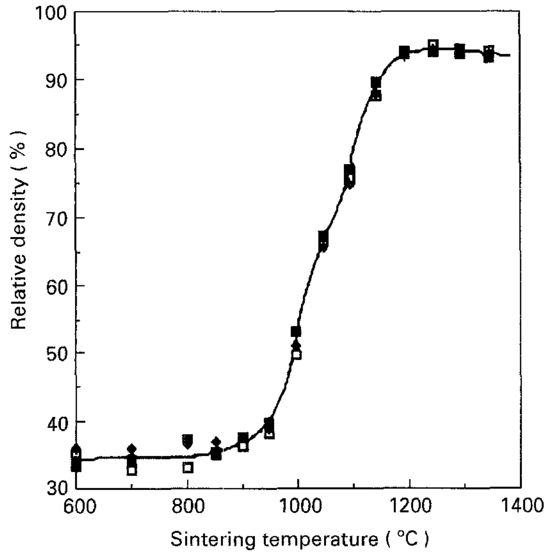

Figure 2 Density versus sintering temperature for various sieve meshes: (□) unsieved, (◆) 0.063 mm, (■) 0.038 mm. $\Delta T/\Delta t = 7.5\,°\mathrm{C\,min^{-1}}$.

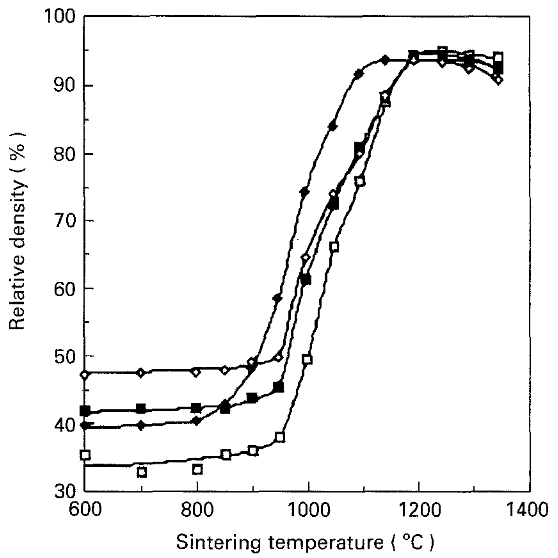

Figure 3 Density versus sintering temperature at powder pressures of (□) $0.4\,\mathrm{kg\,mm^{-2}}$, (◆) $5\,\mathrm{kg\,mm^{-2}}$, (■) $10\,\mathrm{kg\,mm^{-2}}$, and (◇) $30\,\mathrm{kg\,mm^{-2}}$. $\Delta T/\Delta t = 7.5\,°\mathrm{C\,min^{-1}}$.

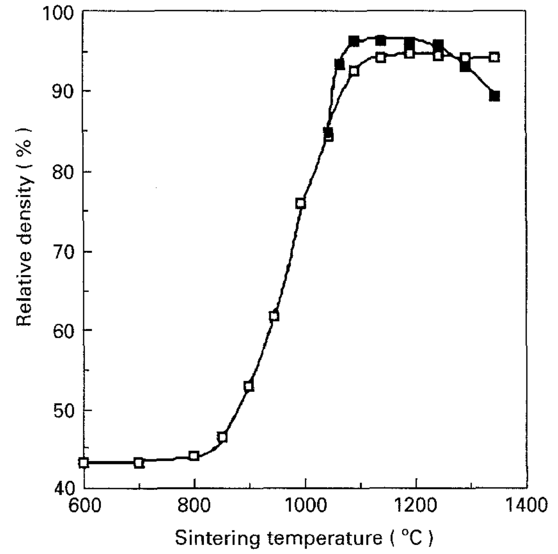

Figure 4 Density versus sintering temperature for various sintering atmospheres: (□) air, (■) nitrogen. $\Delta T/\Delta t = 7.5\,°\mathrm{C\,min^{-1}}$.

temperature, T, acts especially through the diffusion coefficient [3]

$$D = D_0 \exp(-Q/RT) \qquad (1)$$

where Q is the activation energy of the process at work, and R is the gas constant. At low temperatures, up to 800 °C, the surface diffusion mechanism dominates [4] which does not promote significant mass transport. Within the temperature range 800–1100 °C, the density increases quite fast. Here the dominant mass-transport mechanisms are those of volume diffusion and grain-boundary diffusion. For higher temperatures, the density increases a little, slowly up to a maximum around 1200–1250 °C, then starts to decrease slowly. The fact that densification stops in the final stage, for values of relative density greater than 90%, could be due either to abnormal grain growth or to insoluble gases, having a low diffusion coefficient, enclosed inside the closed pores. Observation of the microstructure of the samples sintered at 1350 °C excludes the existence of abnormal grain growth (see Fig. 5). This leaves the existence of nitrogen in the air, which has a low solubility. This nitrogen is certainly responsible for the expansion of the material above 1250 °C [3, 5].

Fig. 1 shows that milling can lower the temperature at which densification takes place, and also can alter the evolution of density with temperature, although the final value of density, for temperatures higher than 1200 °C, does not show any clear dependence in relation to milling times.

Fig. 3 shows that densification starts at 800 °C for those powders compacted with an isostatic pressure of 0 and $5\,\mathrm{kg\,mm^{-2}}$ and at 900 °C with 10 and $30\,\mathrm{kg\,mm^{-2}}$. The increase of isostatic pressure above a given value leads to rupture of the initial aggregates, which does not favour further aggregation of the particles.

Assuming that the size of the primary particles remains unchanged, the observed shift in the relative

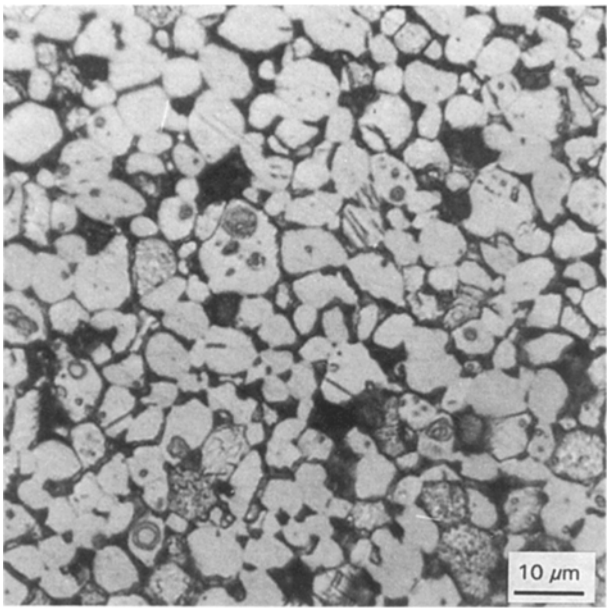

Figure 5 Photomicrograph of an α-Fe_2O_3 sample with a 93.8% density, fired in air gradually from room temperature to 1350 °C, at a rate of 7.5 °C min^{-1}, whose powder was milled for 1 h, not sieved and compacted manually with a uniaxial pressure of 0.4 kg mm^{-2}.

density–temperature curves is directly related to the aggregation state in the powder compacts [4].

The aggregates with large diameters do not play an important role in the sintering process, as can be concluded from Fig. 2, because sieving did not alter significantly the relative density–temperature curves. It is also quite clear, that it is possible to obtain high values of density for lower temperatures, by choosing adequately certain processing parameters. This is the case shown in Fig. 1: the same value of density at 1150 °C for the sample whose powder was milled for 1 h, was attained for the samples with other milling times at 1200 °C. Similarly, it can be seen in Fig. 3 that the same density is obtained either at 1150 °C for 5 kg mm^{-2} or at 1200 °C for the other pressures.

Fig. 4 shows that the relative density increases more when the air atmosphere is substituted by nitrogen for a value of relative density of 85%, i.e. when the open porosity begins to close. Very likely, this is due to the oxygen in the air retained inside some pores which can diffuse more easily to the nitrogen atmosphere, causing, as a consequence, an increase in the density. It is known that the diffusion coefficient of oxygen, D, at low pressures, is inversely proportional to the 1/6th powder of the partial pressure [6], $D \propto P_{O_2}^{-1/6}$. Consequently, the diffusion coefficient for oxygen becomes quite high when the sample is in a sintering atmosphere of nitrogen. The density reaches a maximum at 1100 °C, then decreases slowly up to 1250 °C, after which it decreases quickly. The slow decrease can be attributed to the expansion of the nitrogen included inside the closed pores [3, 5] . The expansion of the sample above 1250 °C is a consequence of the phase change [7] of α-Fe_2O_3 to Fe_3O_4, which causes fracture, as consequence of the large difference between the size of the elementary cell of α-Fe_2O_3 (= 0.5420 nm) [8] and that of Fe_3O_4 (= 0.8390 nm) [9].

5. Conclusion

A better densification can be obtained by choosing the correct combination of processing parameters. This has been achieved with a powder milling time of 1 h and an isostatic compaction pressure of 5 kg mm^{-2}. In our experiments sieving was found to have no influence.

However, the sintering atmosphere can have a decisive influence on the final densification. The greater values of the density were obtained in a nitrogen atmosphere. The density of α-Fe_2O_3 ceramics shows a strong dependence on the aggregation state of the powders.

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