

Investigation in the sintering of Y_2O_3 powders in the temperature range 1000 to 1400° C

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This paper is devoted to a study of the sintering of two Y_2O_3 powders in the temperature range where only minor densification occurs. Two powders have been examined; one powder, Y_2O_3 -A, was obtained by decomposition of hydroxide, because earlier examinations showed [11] that use of this powder resulted in the highest densities of samples in the sintering temperature range from 1300 to 1900° C. The second powder, Y_2O_3 -D, was purchased externally. In order to ensure that the pores in the Y_2O_3 -A compacts closed as late as possible, the heating rates up to the appropriate temperatures (1000 to 1400° C) were varied in the range 0.013 to 6° C sec⁻¹. The results obtained show that the heating rate in this temperature range, for the powder obtained by decomposition of hydroxide, is of primary importance in the densification of the material, and that cessation of shrinkage was not observed in the period of 240 min.

1. Introduction

Yttrium oxide has been widely studied in the ferrite industry, for nuclear and rocket techniques, as well as because of its refractoriness. In order to get as dense Y_2O_3 ceramic as possible, it is important *inter alia* to start with an active powder. Detailed analysis of Y_2O_3 powders obtained by decomposition of various salts is given by Furlong and Domingues [1], who relate the powder sinterability to crystallite size, specific surface area and compact texture of particular powders. However, the works of Ivensen and others on the structure of sinterable powders indicate [2-4, 12] that particle size itself cannot be accepted as a single characteristic parameter of sinterability. The overall defectiveness of material (both surface and inner) present at the temperatures at which the sintering begins, has an essential influence on the course of the densification process.

Marlowe and Wilder's [8] and Scieltz and Wilder's [9] kinetic considerations of the Y_2O_3 densification process indicate that a definite maximum density is reached at any temperature within a wide temperature range (670 to 1600° C) after rather short annealing; they called it the anomalous characteristic of Y_2O_3 sintering.

However, the data on Y_2O_3 densification kinetics, given by Anderson [10], do not confirm this phenomenon.

The present paper is concerned with the study of Y_2O_3 sintering in the temperature range where little densification occurs. In order to obtain pore closure in Y_2O_3 compacts as late as possible, the heating rates up to particular temperatures have been varied.

2. Experimental work

2.1. Obtaining and characterization of powders

Two Y_2O_3 powders, of 99.99% purity, were used. One powder, Y_2O_3 -D, purchased externally (Gosintorg - USSR), was sintered without subsequent processing, while the Y_2O_3 -A powder was made as already described [11]. Previous analysis of this powder, by IR spectrometer, by measurement of refractive index by an optical microscope, and also by harmonic analysis of the diffraction lines [222] and [622], showed that this powder was a very fine one and had a significant extent of defect structure [11]. The electron-microscope analysis showed that the powder Y_2O_3 -A had a crystallite size under 0.1 μ m, with undefined crystal planes, while the

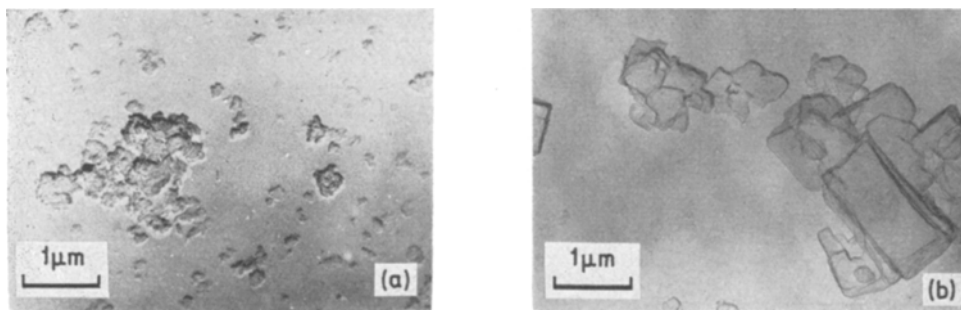


Figure 1 Electron micrographs of Y_2O_3 powders (a) Y_2O_3 -A, (b) Y_2O_3 -D.

powder Y_2O_3 -D had a crystallite size about 10 μm , with developed prism-like planes (Fig. 1). Specific surface areas, obtained by using a modified BET apparatus (AREA meter – “Strölein” production) were 9.2 and 50 $m^2 g^{-1}$ respectively for Y_2O_3 -D and Y_2O_3 -A powders.

2.2. Sample pressing

Both Y_2O_3 powders were pressed using a hydraulic press in a die 9 mm in diameter, the sample height varying from 5 to 7 mm. The powders were formed without binders, and in order to obtain about the same values of density for the compacts of each powder, the pressure used for powder Y_2O_3 -D was 100 $kg cm^{-2}$ and for powder Y_2O_3 -A varied from 200 to 500 $kg cm^{-2}$. With Y_2O_3 -D powder compacts, the density value was 1.80 $g cm^{-3}$, while in Y_2O_3 -A powder it varied as a function of pressure from 1.60 to 1.80 $g cm^{-3}$; deviation from the average value, for all compacts, was $\pm 0.03 g cm^{-3}$.

2.3. Sintering

The sintering was performed in an air atmosphere, in a tube-furnace with SiC heaters. The sintering temperatures varied from 1100 to 1300°C, while the time of the isothermal annealing was increasing from 10 to 240 min. In the course of the isothermal annealing the samples were pushed into the already heated furnace, and after sintering were rapidly removed.

The influence of the heating rates 0.013, 0.027, 0.055, 0.125, 0.270 and 6° sec^{-1} , on the bulk density achieved at 1000, 1100, 1200, 1300 and 1400°C, was examined assuming that the system reached thermal equilibrium after 10 min. The influence on the bulk density of the previous heating rate during the isothermal annealing was examined at 1300°C. The dependence of the bulk density of the sintered samples on the compacting pressure was also examined at 1300°C both

for the pellets pushed into the furnace rapidly and also for the slowest rate.

3. Results and discussion

3.1. Results

The bulk densities of the sintered samples are shown in Figs. 2 to 5 as a factor of various parameters. Dilatometric examinations are given in Fig. 6. The results of the open porosity measurements using a mercury porosimeter, are given in Table I.

3.2. Isothermal sintering

The data on the bulk densities of the sintered samples of Y_2O_3 -A and Y_2O_3 -D powders are

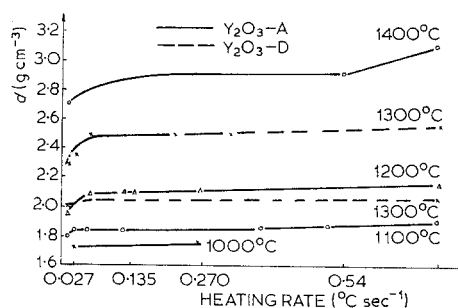


Figure 2 Bulk density change of sintered samples of Y_2O_3 powders in dependence on the heating rate.

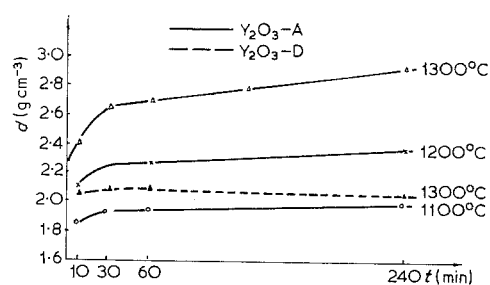
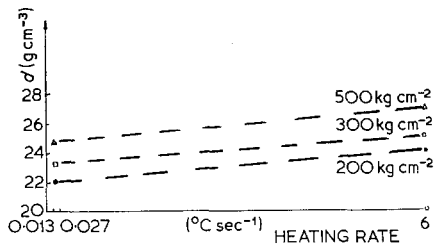
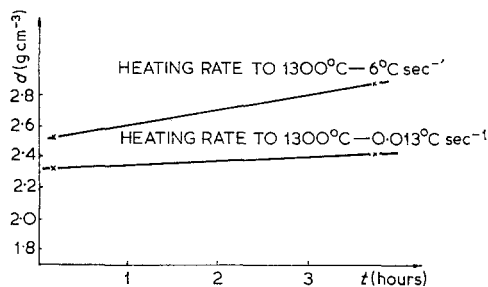


Figure 3 Bulk density change of the sintered Y_2O_3 samples during the isothermal heating.

TABLE I Open porosity results of the sintered Y_2O_3 -A samples (%)

Isothermal time (min)	Temperature ($^{\circ}C$)							
	1100		1200		1300		1400	
	Heating rate ($^{\circ}C\ sec^{-1}$)							
	0.013	6	0.013	6	0.013	6	0.013	6
10	51	48	41	40	34	34	28	20
30		47		37		26		
60		45		34		21		
240		43		33		22		

Figure 4 Pressing pressure influence on the bulk density of Y_2O_3 -A samples sintered at $1300^{\circ}C$.Figure 5 Bulk density change of the Y_2O_3 -A samples sintered at $1300^{\circ}C$ in the function of the heating time.

given in Fig. 3. It is clear that more densification is produced by increasing the temperature than in the course of the isothermal annealing. Although during the heating period considerable densification takes place, the existence of a maximum bulk density for Y_2O_3 -A powder, at particular temperatures, was not observed during the isothermal heating. But, in Y_2O_3 -D powder sintered at $1300^{\circ}C$, besides the fact that it is less sinterable in comparison with Y_2O_3 -A after 30 min there was practically no shrinkage at all.

Starting from the fact that the surface energy content is determined not only by the particle size, but also to a high degree by the particle surface state, it is to be expected that Y_2O_3 -A powder will be more active than Y_2O_3 -D powder. Apart from high surface energy, there is

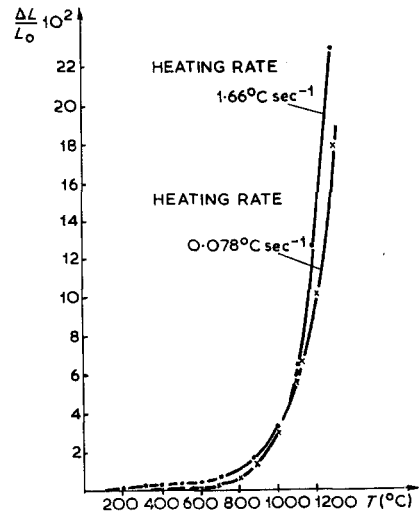


Figure 6 Shrinkage change in the function of temperature.

a further factor that influences the behaviour of the powder during the sintering process, namely the crystallite defect structure. Previous work [11] has shown the existence of defects and a disordered lattice in Y_2O_3 -A powder. The recovery of crystal structure defects, other than surface smoothing, influences retardation of densification during isothermal sintering. In this way Ivensen [3] explains the rapid decrease of densification rate (compared with the values at the beginning of the isothermal sintering) independent of the fact that open porosity may also exist. The present data on the open porosity change during the isothermal heating of samples (Table I) establishes the expected decrease in this parameter with sintering time. However, after annealing for 1 h the porosity change, if any, is very small (within the limits of error, $\pm 5\%$). Asymptotic approach of the open porosity to some limiting value at each temperature, contributes to the thesis that it is the relatively quick recovery of the lattice defects that causes the retardation of the densification process. The

rapid cessation of densification at 1300°C , can probably be explained by the relatively small defect content in Y_2O_3 -D powder.

In the absence of detailed knowledge of the exact effects of individual structural-surface factors, Ivensen's [2] phenomenological sintering theory has been used for the quantitative analysis of the results obtained during the sintering of dispersed Y_2O_3 .

Generally, the sintering kinetics can be described [2] by the equation:

$$K = K_n(qmt + 1)^{-\frac{1}{m}}$$

in which q = relative rate of decrease in pore volume at the beginning of isothermal sintering; m = parameter characterizing "the intensity of densification rate decrease during the sintering" [2]; K = coefficient of the relative pore volume decreases in the course of sintering after the time t ; K_n = coefficient of the relative pore volume decrease at the beginning of the isothermal sintering. The values of the sintering parameters m and q , based on the experimentally obtained data, are given in Table II. Analysing their changes with temperature it can be concluded that the change is in accordance with Ivensen's theoretical postulates. It is evident that the initial densification rate increases with increase of sintering temperature, but the intensity of the densification rate decrease itself decreases. It should be emphasized that, on the basis of this data, the above mentioned investigations of Marlowe and Wilder [8], as well as those of Scieltz and Wilder [9], could never be taken as an anomalous characteristic of Y_2O_3 sintering. On the contrary, bearing in mind that the data given by Anderson [10] also do not confirm this statement, it can be assumed that the abrupt cessation of the Y_2O_3 powder shrinkage may, in their cases, be the consequence of the powder properties. In any case, this suggests that a deeper analysis of the role of structural and geometric factors in the said cases should be undertaken.

TABLE II Values of parameters m and q for Y_2O_3 -A powder

Temperature ($^\circ\text{C}$)	q (1/min)	m
1100	0.0031	26.3030
1200	0.0052	14.5660
1300	0.0084	9.5801

3.3. Heating rate influence on densification

Data on sintering studies [2, 5-7] indicate that the densification rate can reach a maximum even during the non-isothermal heating up to the sintering temperature. Such a state can be explained by the fact that at relatively low temperatures during the heating, the removing of the existing defect structure in the lattice proceeds quite quickly. Hence the sintering shrinkage rate at the beginning of the isothermal heating is not only dependent on the properties of the powder and the sintering temperature, but also on the rate and on the extent of temperature increase prior to isothermal sintering. Some experimental data show [5] that the influence of the structural changes taking place in the sintered body during the previous heating, is sometimes so important that it can mask the influence of other factors affecting the densification process. This is also confirmed by our data on Y_2O_3 -A densification (Fig. 2) (in Y_2O_3 -D powder this phenomenon is less apparent); the heating rates varied from 0.013 to 6°C sec^{-1} and it was observed that the pellet bulk density increased with increase of the heating rate at all temperatures in this range. Such behaviour was more marked at 1300 and 1400°C . It can be seen in Fig. 4, where the data for 1300°C are given that this dependence was not changed with change in the pressing pressure (i.e. the energy introduced during the pressing was not the cause of this phenomenon).

The influence on density of heating time can better be explained by the dilatometric data; this shows (Fig. 6) that slow heating allows the lattice to recover to a high degree before the sintering temperature is reached, so that densification during the isothermal heating is controlled by a relatively small quantity of high-temperature (1100 to 1300°C) defects. In that case, the densification rate will mainly depend on the density of defects present. The data in Fig. 5 show that, as expected, the rapid heating up to 1300°C led to a higher degree of densification for the same heating time.

4. Conclusion

This paper deals with the sintering in the range 1000 to 1400°C of very active Y_2O_3 powder obtained by decomposition of yttrium hydroxide. Differences in the sintering behaviour of this powder as compared with an inactive Y_2O_3 powder have been experimentally demonstrated. These differences point to the importance in sintering such oxides, of the role of structural

and geometric defects. The analysis of the experimentally obtained results, using Ivensen's phenomenological sintering theory, shows that the initial densification rate increases with increase of sintering temperature, but the retarding of the densification process simultaneously decreases.

The role of the heating rate to the required sintering temperature was also studied. The rates were changed in the range of 0.013 to 6°C sec⁻¹. On the basis of dilatometric investigations it was concluded that the crystal lattice recovery is taking place during the slow heating rates, while at the higher rates this recovery was much reduced. This affects both the sintering kinetics and the sintering mechanism leading to densification.

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