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Enhanced Densification of Yttria by Addition of Titanium Oxide

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Abstract

The influence of several additives (ZrO_2, CeO_2, TiO_2, SiO_2) on sintering of conventional yttria powders is investigated. Titanium oxide is the most efficient in promoting densification and in lowering sintering temperatures. Almost full densities can be obtained at 1400–1500°C if a small amount of dopant (0.2 wt% TiO_2) is dispersed homogeneously onto the surface of yttria during powder processing.

Es wird der Einfluß mehrerer Additive (ZrO_2, CeO_2, TiO_2, SiO_2) auf das Sinterverhalten konventioneller Yttriumpulver untersucht. Titanoxid fördert am effektivsten die Verdichtung und senkt am stärksten die Sintertemperaturen. Beinahe vollständige Dichten können bei Temperaturen von 1400– 1500°C erreicht werden, wenn während der Pulverherstellung eine kleine Menge Additiv (0·2 wt% TiO_2) homogen auf der Oberfläche des Yttriumoxids verteilt wird.

On a étudié l'influence de différents additifs (ZrO_2, CeO_2, TiO_2, SiO_2) sur le frittage de poudres conventionnelles d'oxide d'yttrium. L'oxyde de titane est le plus efficace pour favoriser la densification et pour abaisser les températures de frittage. On peut obtenir des densifications pratiquement totales à 1400–1500°C, si une petite quantité de dopant (0.2% en poids de TiO_2) est dispersée de façon homogène à la surface de la poudre d'oxyde yttrium durant la préparation.

Introduction

Inherent qualities of yttrium oxide, such as low reactivity, refractory character and a high melting point (2410°C), combine to make it an attractive ceramic material. In addition, it has been shown that yttria is one of the scarce oxides which can be sintered to full density.[1, 2] Due to a large transmission window in the visible and the infrared, ranging from 0.3 to 8 μm, these materials offer interesting optical properties.[3, 4] A number of authors have investigated sintering of yttria over the past years.[5–22] It seems agreed that sintering of pure, conventional yttria powders requires firing at very high temperatures, in excess of 1800°C.[1, 6] A direct consequence is considerable grain growth during densification, and pore entrapment within the grains once the density has reached 95–97% of the theoretical density, d_{th}.[6] This could be one reason why several groups have investigated the possibilities offered by powders obtained from chemical routes, for instance those from precipitation of yttrium hydrates,[13, 14] or from thermal decomposition of inorganic salts.[17] The main purpose was presumably to get finer, more reactive powders, provided that they are free from agglomeration. It has been shown by Rasmussen *et al.*[13] that, during the synthesis of yttria powder by alkaline precipitation in water, a careful control of the washing and drying steps was highly beneficial for the sintering ability. In the case of oxides, the extent of agglomeration of fine powders depends

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on the technique used to remove water,[23] and this consideration is also expected to apply to yttria. Recently, Dogan *et al.*[16] tested lyophilisation to dry ultrafine yttria powders, which were subsequently calcined at 1000°C before dry-pressing. Densities larger than 99 % of the theoretical density could be obtained after firing at 1450°C.

As emphasized in recent literature,[24, 25] an efficient technique to decrease firing temperatures and limit consequences of grain growth in the final stage of sintering consists of using a suitable additive which promotes the kinetics of densification with respect to grain growth. This additive can help to avoid the entrapment of the porosity located on the surfaces and the grain boundaries. Many compounds have been tested so far in the case of yttrium oxide, including such oxides as Al_2O_3,[1] La_2O_3,[1,3] ThO_2,[6, 19] SrO,[4, 21] CaO,[21] MgO,[21] and fluorides such as AlF_3, MgF_2, CaF_2[26] or LiF.[27] A dopant which proves quite useful is La_2O_3, when sintering is operated in the two phase (cubic + hexagonal) field of the Y_2O_3–La_2O_3 phase diagram, and is by annealing at a lower temperature in the single phase (cubic) field. This technique is often referred to as 'controlled transient solid second-phase sintering' and follows from the work of Rhodes.[1] Full densities can be reached and thus transparent yttria materials can be obtained, but temperatures larger than 2000°C are necessary to enter the two-phase field.

These are the reasons why the authors decided to start a new investigation on the effect of other additives, with the aim to densify conventional yttria powders at lower temperatures. The present work focused on the action of oxides possessing 4+ cations, namely ZrO_2, CeO_2, TiO_2 and SiO_2. This choice covers various ionic sizes and solubilities of the additive in the matrix. Preliminary results are now reported, which indicate that one additive at least, namely titanium oxide, is quite efficient in promoting densification.

Experimental

The preparation of samples is described schematically in Fig. 1. Materials containing a large amount of additive (more than 2 wt%) were prepared by attrition milling of the yttria powder (nominal purity larger than 99.99%, the main impurities being rare earth oxides) and of the selected additive (ZrO_2, CeO_2, TiO_2 or SiO_2) in isopropanol. For samples containing an amount of TiO_2 below 1 wt%, the yttria powder was deagglomerated first in isopropanol, then a titanium alkoxide, $Ti(OBu)_4$, was dissolved at the desired Ti/Y ratio, and a given quantity of water ($H_2O/Ti=4$) added to obtain the hydrolysis of the alkoxide. Samples of yttria without any additive deliberately introduced were also prepared for comparison.

1—Attrition-milling in propan-2-ol
⇓
2—Solvent removal (Rotovac)
⇓
3—Drying (110°C, ½ h)
⇓
4—Granulation
⇓
5—Dry-pressing (140 MPa)
⇓
6—Sintering

Fig. 1. The flow chart of the ceramic process.

The solvent was then removed (Rotovac) and the powders dried at 110°C before granulation. Disk-shaped samples (30 mm in diameter and 5 mm in thickness) were dry-pressed at 140 MPa. Typical green densities ranged from 54–60% d_{th}. Most of the samples were fired in ordinary air atmosphere, but a few of them were fired in a furnace equipped to deliver atmospheres with controlled oxygen potentials. The final densities were measured according to the Archimedes technique with water.

The theoretical density of pure Y_2O_3 was taken as 5.031 g cm^{-3}.[10] In the case of samples containing additives, the procedure adopted to calculate the theoretical density of fired materials depends on the solubility of the additive in the matrix. ZrO_2[28] and CeO_2[29] are known to enter into solid solution with Y_2O_3 over a large composition range. The theoretical density was here calculated under the assumption of a constant lattice parameter. On the other hand, the solubility of TiO_2 is known to be much smaller, although non-negligible at temperatures of 1800–2000°C.[30] Examination of the Y_2O_3–TiO_2 phase diagrams[31] reveals the existence of two ternary oxides, namely $Y_2Ti_2O_7$ and Y_2TiO_5. Therefore the theoretical density of samples containing TiO_2 was calculated on the basis of a diphasic system containing Y_2O_3 and Y_2TiO_5. Owing to the difference in ionic radii ($r_{Y^{3+}}$ = 0.89 Å $r_{Si^{4+}}$ = 0.4 Å),[32] one also expects a very limited solubility of silica into the lattice of yttria. The theoretical density of samples containing SiO_2 was then calculated on the basis of a diphasic system containing Y_2O_3 and Y_2SiO_5.[33] Uncertainties in the estimation of the theoretical densities will induce negligible effects in the conclusions of the present work.

Table 1. The influence of various additives on the shrinkage and relative density of samples fired up to 1600°C, and cooled down immediately.

Additive	*Wt %*	*Green density (%)*	*Shrinkage (%)*	*Final density (%)*
No additive	—	54·8	7·6	69·6
CeO_2	5	59.0	4·6	66·3
ZrO_2	5	58·3	4·9	67·7
SiO_2	2	55·6	13·3	82·2
TiO_2	2	57·4	16·6	98·7

Results and Discussion

The influence of each additive, which was first introduced deliberately in large proportions (2–5 wt%), on the densification behaviour has been examined by measurements of relative densities after firing up to 1600°C. Results are given in Table 1. From inspection of the data, it is obvious that addition of TiO_2 induces the most beneficial effects on the final density. This result was confirmed by the determination of shrinkage curves (Fig. 2), which reveal that the onset of shrinkage occurs at a temperature lowered by about 300°C with respect to pure yttria.

The next step was to determine the minimum amount of titanium oxide which must be incorporated in the powder to produce significant improvements on the densification. As mentioned in the previous section, mixed oxides $Y_2Ti_2O_7$ and/or Y_2TiO_5 are expected to form, at least as transient compounds during firing of doped samples. Attrition milling of yttria and TiO_2-containing compounds, e.g. anatase, $Y_2Ti_2O_7$ or Y_2TiO_5, was used to incorporate the additive in small proportions (1 and 0.2 wt%). However, in the classical example of MgO-doped alumina, where minute amounts of MgO procure the desired effect of limiting grain growth in the final stage of sintering, the nature of the MgO precursor is not essential, but the distribution of dopant in the alumina powder should be as homogeneous as possible on the surface of the grains before firing.[34] This is the reason why a chemical route, described in the previous part and based upon the hydrolysis of an alkoxide, has also been considered to improve the distribution of the additive on the surface of the grains.

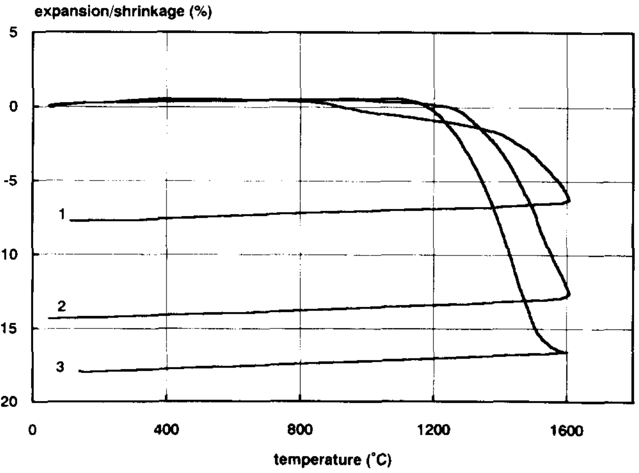
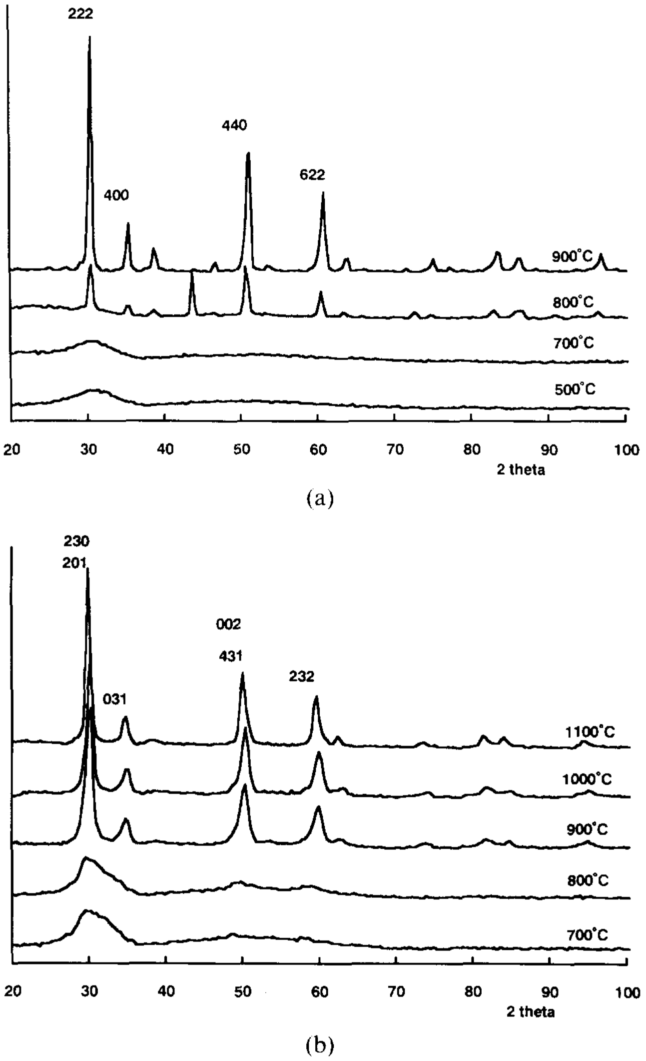


Fig. 2. The shrinkage curves of samples containing 2 wt% SiO_2 (curve 2) or TiO_2 (curve 3) compared to the shrinkage curve of nominally pure yttria (curve 1).

Synthesis of Y_2TiO_5 by the high temperature route involving mixing and firing of mixtures of Y_2O_3 and TiO_2 proved rather unsuccessful. The transient compound $Y_2Ti_2O_7$ is obtained first, and complete reaction with excess yttria requires temperatures higher than 1500°C. This is the reason why a sol-gel type synthesis was adopted to prepare finely divided $Y_2Ti_2O_7$ and Y_2TiO_5. Yttrium nitrate $Y(NO_3)_3$, $6H_2O$ is added to an anhydrous solution of titanium butoxide in isopropanol. Titanium alkoxide is hydrolysed by water issued from the salt, and a gelatinous suspension results within a few minutes. After drying and calcination, the solid phase crystallizes progressively, and by 900°C leads to fine powders of $Y_2Ti_2O_7$ or Y_2TiO_5, according to the initial Ti/Y ratio (Fig. 3).



(a)

(b)

Fig. 3. The evolution of X-ray diffraction patterns of (a) $Y_2Ti_2O_7$, and (b) Y_2TiO_5 after calcination of the gel at various temperatures.

Table 2. The relative densities of samples containing titanium oxide and fired at 1500°C for 3 h.

Additive used	*0·2 wt% additive*	*1 wt% additive*
TiO_2 anatase	—	96·0
$Y_2Ti_2O_7$	84·5	99·0
Y_2TiO_5	90·5	99·6
$Ti(OC_4H_9)_4$	98·8	99·5

These oxides were then used as additives in the first step of the ceramic process.

Relative densities measured on the samples doped with 0.2 and 1 wt% TiO_2 respectively and fired at 1500°C are given in Table 2. Larger relative densities are observed when dispersion of the dopant in the powder is improved. This can be achieved by a preliminary 'dilution' of TiO_2 in intermediate oxides $Y_2Ti_2O_7$ or Y_2TiO_5, but best results are obtained by a chemical route. These features are more or less similar to those published previously on a parent system, TiO_2-doped ceria.[35]

A further improvement is still expected if titania can be deposited uniformly onto the surface of yttria grains. The next step of the present work relied on the propensity of the surface of yttrium oxide to react slowly with water.[36] In order to accelerate the formation of a hydrated layer at the surface of the grains, the yttria powder was attrition-milled in water. TGA experiments indicate larger weight losses for powders milled for extended periods of time and confirm reaction of yttria with water (Fig. 4). The powder, once dried, was introduced into propanol and titanium alkoxide was added to get a final TiO_2 content of 0.2 wt%. The suspension was gently shaken for two days to modify the surface through hydrolysis of the titanium alkoxide by the hydroxyl groups. After drying, the process was then completed without any further modification. Relative densities achieved after a firing of 3 h at 1500°C were repeatedly higher than 99.5% d_{th}. It is noteworthy that larger densities are probably difficult to achieve by normal firing in air atmosphere, because of entrapment of gases other than oxygen in the closed porosity during the final stage of sintering. In the case of oxides, it is commonly admitted for instance[37] that nitrogen cannot be subsequently removed by lattice or grain-boundary diffusion during the final stage of sintering, and that an equilibrium situation is reached when the pressure of residual gases in the pores compensates the driving force for sintering.

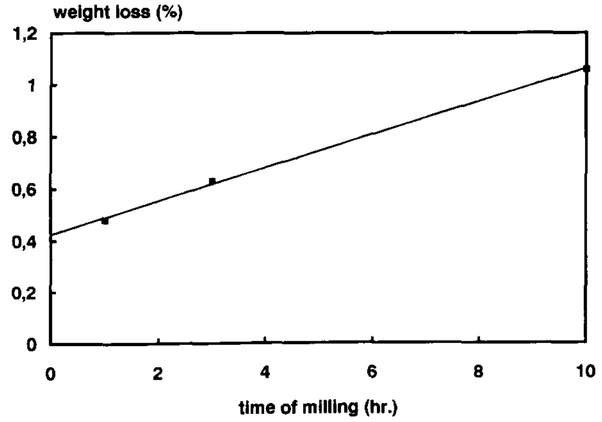


Fig. 4. The weight loss (at 1000°C) of yttria powders after attrition milling in water.

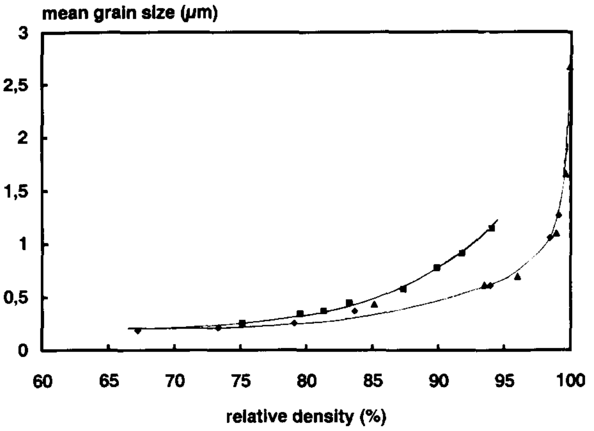


Fig. 5. A plot of grain size versus density for (■), yttria fired at 1500°C; and yttria doped with 0.2 wt% TiO_2 and fired at (♦), 1400°C or (▲), 1500°C.

The effect of the dopant is best illustrated by plotting the grain size versus density after firing at a given temperature for various times and by comparing trajectories observed for both pure and doped materials.[38] This has been done here for

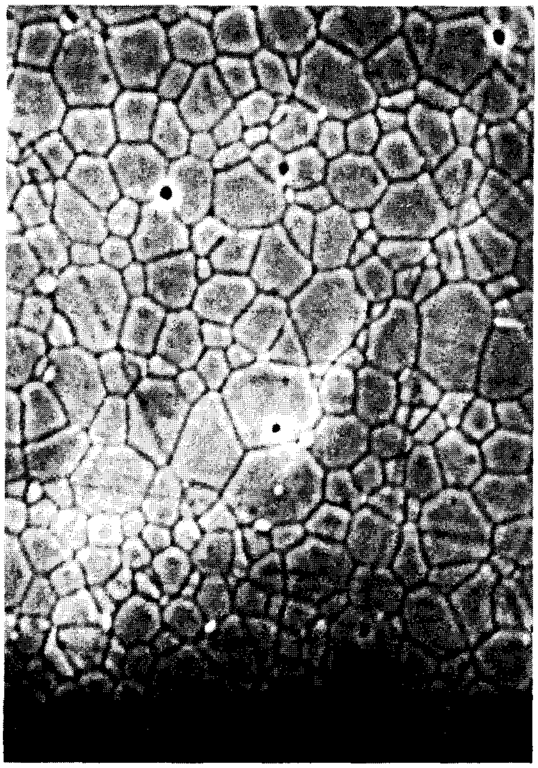


Fig. 6. A typical microstructure of yttria samples containing 0.2 wt% titania and sintered at 1500°C for 3 h.

temperatures of 1400 and 1500°C. Results are plotted in Fig. 5. At a given density, the dopant maintains smaller grain sizes. Thus the densification kinetics are enhanced with respect to grain growth. Quite probably a lower trajectory allows avoidance of the region where the pore–grain boundary attachment is broken, so that densification can proceed towards full density. This situation is basically similar to that encountered in the case of MgO-doped alumina.[38] For comparison, some samples were also fired in pure oxygen at the same temperature. These specimens exhibited pronounced transparency in the visible range. This proves that relative densities close to unity can be achieved by appropriate doping even at moderate temperatures (Fig. 6).

Conclusions

The main conclusions which were obtained during the present work are as follows:

- —titania is an efficient additive to promote densification of yttria, which can be sintered to almost full density at 1500°C.
- —amounts of titania as low as 0.2 wt% can be used if the additive is distributed uniformly onto the surface of the powder.
- —titania addition modifies the grain size–density trajectory, by promoting the densification rate with respect to the kinetics of grain growth.

Further investigations are in progress to clarify the mechanisms through which the additive acts on the matter transport during sintering.

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