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MODIFICATION OF MASS TRANSPORT DURING SINTERING INDUCED BY THERMAL GRADIENT

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ABSTRACT

Due to the developments of the new sintering processes, the thermal cycles duration has been considerably reduced. But it turns out that this cycle time decrease can also conduct to thermal gradients in the sample.

Up to day, the effects of such gradients are not well known. That's why the aim of this study is to contribute to understand phenomena induced by thermal gradients applied during the initial stage of sintering. We will observe the consequences on this stage but also on the further densification. Two important results are brought out :

- For pure alpha-alumina : the comparison between conventional treatments and treatments under thermal gradients has shown that a gradient modifies the specific surface area drop and then accelerates the further densification.

- For alpha-alumina containing impurities : The experiments have revealed that a gradient can modify the impurities' dissolution and change the mass transport. Finally grain growth can be favoured at the expense of densification.

INTRODUCTION

Compared to conventional sintering, sintering under microwaves leads to a better homogeneity and to an improvement of the microstructure with a reduction of porosity and grain size^{1,2}. Moreover, experimental data on spark plasma sintering showed a higher sintering activity^{3,4}. In addition to these advantages, both new processes are based on very fast heating rate. In such processes, the high heating rate inevitably leads to a complex temperature distribution, and possibly to the appearance of temperature gradient in the piece.

The presence of density gradients in samples sintered by field activated sintering processes is mentioned in the literature^{5,6}. This constitutes an indirect evidence of the development of temperature gradient during this sintering process. Moreover, Zavaliangos et al.^{7,8} have recently studied the temperature distribution in the FAST device using the finite elements methods simulation. They have showed the development of temperature gradient in this device.

Although thermal gradients are present in a lot of sintering processes, few experimental studies treat about the consequences induced by thermal gradients^{9,10,11}. This can be explained by the difficulty to dissociate the effect induced by heating rate and the effect induced by the thermal gradient. Then the consequences of a thermal gradient are not well known. Nevertheless, it seems that a thermal gradient can enhance the densification.

Other studies have mentioned that a thermal gradient can induce mass transport which lead to a demixing in multi-component oxides^{12,13}.

The present study deals with the quantification of the effect induced by the existence of a thermal gradient applied during the initial stage of sintering on submicronics aluminas with different purities.

MATERIALS STUDIED AND EXPERIMENTAL METHODS

Powder formulation and processing

The powder used in this study is a submicronic α -alumina powder (named UF powder) generated by ex-alun process. This alumina contains initially 210 ppm of impurities. The main impurities are: Na, K, Si and Ca. To carry out a slurry of 60 wt.% powders, alumina is dispersed in a pH 10 deionised water using polyacrylic acid (Acros Organics, USA) of molecular weight 2000. After 24 hours in a mixer with rollers, attrition using zirconia balls doped with CaO, MgO and SiO₂ has been carried out (830 rpm for 1 h). In these conditions, the contamination in zirconia due to the attrition is quantified at 0.79 weight % (measured by X-ray fluorescence). Then 2.25 wt.% of polyvinyl alcohol 4/125 (Prolabo, France) and 0.75 wt.% of plasticizer polyethylene glycol 4000 (Merck-Schuchardt, Germany) are added. After attrition milling the powders are atomized. Cylindrical samples of 6 cm lengths are obtained by uniaxially compaction at 40 MPa in a steel die of 8 mm diameter and cold isostatically compacted at 400 MPa. Finally, in order to remove the organic phases, green samples are treated during 1 hour at 600°C. The theoretical density of the material takes into account the zirconia contamination coming from attrition milling (measured by X-ray fluorescence). After debinding, the density homogeneity of the green sample is verified (equal to 53.1 % \pm 1% TD).

Furnace with heat gradient

To carry out thermal gradients, a muffle furnace has been used (figure 1). Inside this furnace, different systems of porous refractory masks are introduced to make a thermal barrier. By the modification of the thickness of the masks, thermal gradients can be reached. To study the thermal gradient in the initial stage of sintering, the samples stay under the mask. The temperature regulation of the furnace allows to obtain a temperature difference of 100°C on the 6 cm length sample. The temperature applied on the sample is reported in figure 2. After this pre-treatment the samples are cut in sections of one centimetre length and then undergo various analyses (analyses of specific surface areas, sinterability,...). In these operating conditions, each section do not have the same thermal history. To quantify thermal gradient effects, reference samples (1 cm length) are sintered with a same thermal schedule of each section but without thermal gradient.

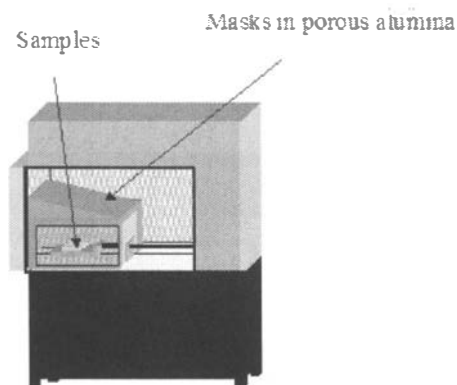


Figure 1. Representation of the thermal furnace.

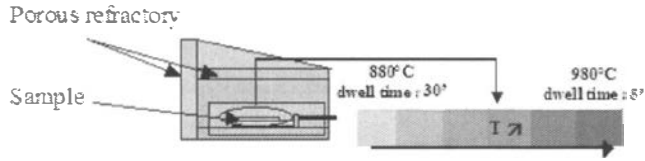


Figure 2. Temperature profile in the thermal furnace

Experimental analysis

Relative densities and porosities are measured by using the water immersion method. The error of measurement on the density is estimated at 0,1 % in the case of the double weighing. This error can reach 0.5 % in the case of triple weighed. To study the influence of the thermal gradient in the initial stage of sintering, the specific surface area of the specimens is evaluated by the Brunauer-Emmet-Teller (BET) method. Microstructural observations are carried out via scanning electron microscopy (model 6500 F, JEOL, Japan).

RESULTS

Influence of a thermal gradient applied in the initial stage of sintering

Analyses of specific surface area measured by the BET method are done on pre-sintered samples (UF alumina) under thermal gradient and without thermal gradient. The specific surface area is measured at both extremities (average temperatures of 880°C and 980°C) of the samples treated under thermal gradient and compared with those obtained in conventional treatment (Table 1). It appears a more important specific surface area decrease for conventional heating than for heating under thermal gradient. This result is valid for an average temperature of 880°C and 980°C. However, this difference is less significant when the temperature increases. These results obtained suggest that a thermal gradient applied in initial stage of sintering leads to neck formation delay.

Table 1. Specific surface area of UF alumina

Green samples	Specific surface area (m ² /g)	
		$\Delta S/S_0$ (%)
Conventional pre-treatment at 880°C	14.2 ± 0,1	- 17.9
Pre-treatment under gradient at 880°C	15.1 ± 0,1	- 12.7
Conventional pre-treatment at 980°C	12.8 ± 0,1	- 26.0
Pre-treatment under gradient at 980°C	13.4 ± 0,1	- 22.5

To see the consequences of a thermal gradient applied in the initial stage of sintering on the future densification of the material, a dilatometric study is realised for each section. A relatively low temperature of sintering is chosen (1450°C) in order not to be nearby to the theoretical density and then to mask the effects of gradient. Besides, the heating rate used is fast (20°C/min), in order to avoid the screening of the initial treatment effects.

The dilatometric results (Figure 3) show a densification gain (compared to conventional sintering) when the sample is first pre-treated under thermal gradient. This gain is more important for a pre-treatment at lower temperature.

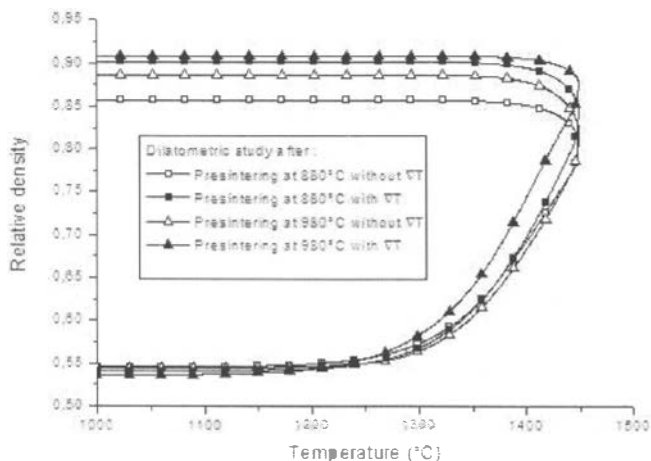


Figure 3. Dilatometric behaviour of UF alumina after different pre-treatment .

Effect thermal gradient and impurities on sintering

To enhance the level of impurities present in the alumina powder, the attrition time has been increased. Thus the contamination in zirconia measured by X-ray fluorescence in this new powder (noticed UF*) is 1,81 weight %.

A same pre-treatment under thermal gradient is applied on the UF* alumina. After cutting up the pre-treated samples, measures of specific surface areas have been carried out (Table 2). For a same pre-treatment under gradient, it appears a strongest specific surface area decrease for UF * samples (i.e. sample with more impurities) than for UF samples.

Table 2. Specific surface area of UF and UF* alumina after pre-treatment under gradient.

	UF alumina			UF* alumina		
	S_{BET} (m ² /g)	$\Delta S/S_0$ (%)	Final density (1450°C)	S_{BET} (m ² /g)	$\Delta S/S_0$ (%)	Final density (1450°C)
Green samples	17.3 ± 0,1			18.2 ± 0,1		
Pre-treatment at 880°C	15.1	- 12.7	90.1%TD	15.0	- 17.6	77.1%TD
Pre-treatment at 980°C	13.4	- 22.5	90.9%TD	13.2	- 27.4	84.8%TD

Nevertheless, after sintering cycle (20°C/min up to 1450°C), the densification rate of samples with impurities (UF*) are lower than those recorded for pure alumina UF (Table 2). This phenomenon is the more pronounced if the pre-treatment is realized at low temperatures.

Sintering with high heating rate

UF* sample (without pre-treatment) has been sintered at 1450°C with a heating rate of 20°C/min in a muffle furnace and in a dilatometer. The obtained densification is 87.3 ± 0.3 %TD in the case of the muffle furnace. For the sintering in the dilatometer the final density is only $63.3 \% \pm 0.8$ %. The microstructure obtain in this two cases are presented in figure 4. For sintering in the muffle furnace, the grain size is smaller in spite of a better densification.

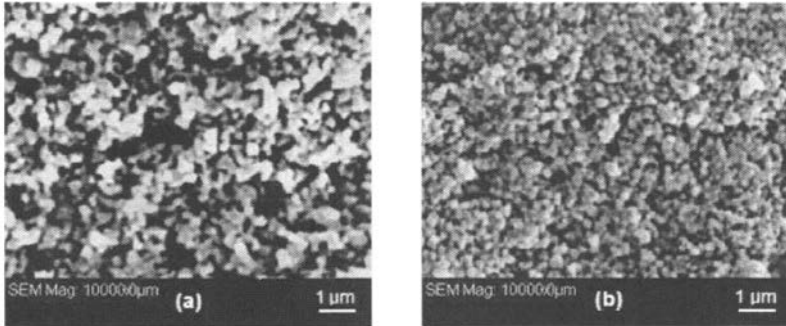


Figure 4. Microstructural observations after sintering with a heating rate of 20°C/min in a dilatometer (a) and in a muffle furnace (b).

For an identical thermal cycle (heating rate and sintering temperature), the behaviour of UF* is totally different according to the furnace type (muffle and dilatometer). Nevertheless, the temperature field is more uniform in the muffle furnace than in the dilatometer. Thus, reactivity difference experimentally observed are linked with the existence of thermal gradient in the dilatometer. Besides, in the next part, we are going to study the effects of technological parameters of the dilatometer affecting the thermal gradient value.

Various parameters can affect the thermal gradient value which can be developed in the dilatometer:

- the gas flow;
- the sample height;
- the heating rate.

The influences of these parameters on the alumina UF* sintering without presintering are summarised in table 3.

Increasing the heating rate or the gas flow or the sample heights leads to a significant decrease in final densification. In addition, analysis of microstructure fracture show an increase of the grains size and a faceted aspect when the gas flow, the heating rate or the sample heights increase (Figure 5).

Table 3. Effect of technological parameters on the final density.

	Heating rate (°C/min)	Gas flow (L/h)	Sample height (mm)	Final density (% TD)
	5	1,8	7	92,4
	20	1,8	7	63,3
(a)	20	0	7	76,2
	20	0,5	7	64,1
	20	1,8	7	63,3
(b)	20	3	7	62,4
(c)	20	1,8	2	68,1
	20	1,8	7	63,3
(d)	20	1,8	15	59,5

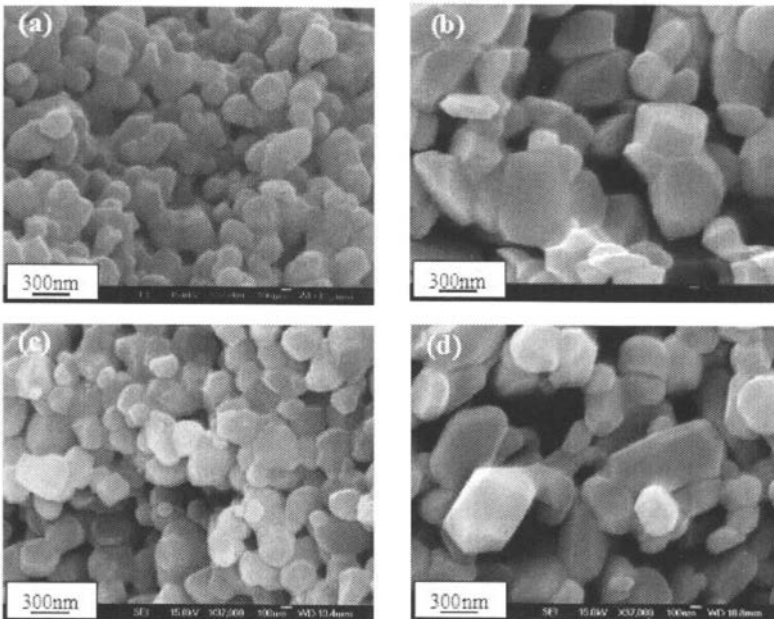


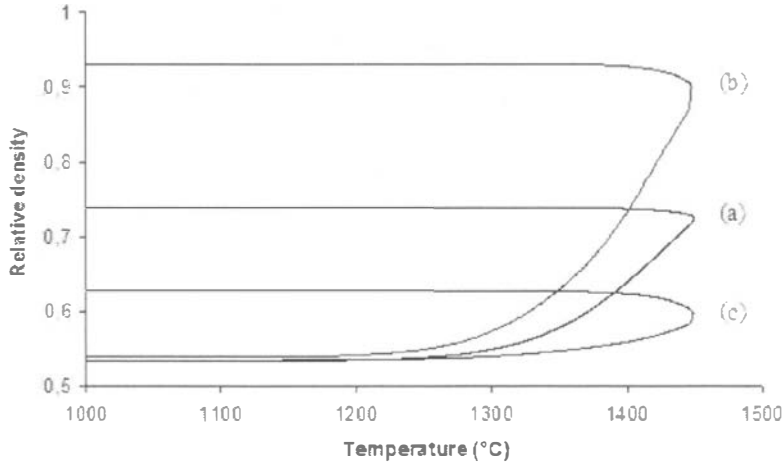
Figure 5. Microstructure fracture of UF* sintered alumina according to conditions presented in table 3.

Effect of intergranular impurities

At any time during sintering, it is possible to create a thermal gradient with dilatometer thanks to particular condition (fast heating rate and high gas flow). Thus we apply different thermal cycles, with high heating rate and high gas flow in the initial stage or all along sintering process.

For UF* samples, the temperature gradient induced by the dilatometer is applied only in the initial stage of sintering (between 20°C and 980°C). Beyond 980°C, the heating rate is 5°C/min (minimization of thermal gradient). The dilatometric curve is reported in figure 6-(a). This sintering cycle leads to a densification of 73.7% TD.

For comparison, the figure 6 also presents the dilatometric behaviour of UF* alumina sintered until 1450°C at two heating rate : 5°C/min (figure 6-(b)) and 20°C/min (figure 6-(c)).



Figure

re 6. densification curves of UF* alumina, from dilatometric experiments.
 (a : 20°C $\xrightarrow{20^\circ\text{C}/\text{min}}$ 980°C $\xrightarrow{5^\circ\text{C}/\text{min}}$ 1450°C / b : 20°C $\xrightarrow{5^\circ\text{C}/\text{min}}$ 1450°C / c : 20°C $\xrightarrow{20^\circ\text{C}/\text{min}}$ 1450°C)

Dilatometric studies reveal that a thermal gradient applied only in the initial stage of sintering (figure 6-(a)) leads to a densification which is far less advanced than when conventional heat treatment is applied over the cycle sintering (figure 6-(b)). The densification of UF* alumina is the less advanced when a thermal cycle is present in all the thermal cycle (figure 6-(c)). On this figure, the gap is more important between curves (a) and (b) than between curves (a) and (c). In consequence, for UF* alumina, the existence of a thermal gradient in the initial stage sintering is the principal source of the densification delay.

In the case of a powder (like UF*) containing impurities coming from attrition contamination (ZrO₂, SiO₂, MgO, CaO), these impurities are initially located in intergranular position. The location of these impurities is therefore different from that of impurities initially present in the powder (dissolved in grains of alumina due to process ex-alun production). The aim of this part is to establish whether or not the impurities location before the gradient application affects the densification.

A long conventional pre-treatment (72 hours at 920°C) is realized. After this pre-treatment, sintering cycle in a dilatometer with a heating rate of 20°C/min up to 1450°C is applied. The density obtained in this case is 91.2%TD. Thus, in the case of UF* alumina (alumina containing initially intergranular impurities), a long thermal schedule (long dwell time) at low temperature drives to a dissolution of impurities before the sintering starts. This can finally increase the densification under thermal gradient.

SUMMARY AND INTERPRETATION OF RESULTS

The experimental study highlights the effects of a thermal gradient applied in the initial stage of sintering. This gradient must be benefit to the further densification in the case of pure alumina. By delaying the necks formation, a temperature gradient applied in the initial stage of sintering can keep a high sintering potential and therefore lead to a better densification.

In other side, this gradient can also block the densification and increase the grain size. This phenomena has been observed in the case of alumina which contains intergranular impurities.

Such grains growth without significant densification has previously been observed in different materials such as Al_2O_3 ¹⁴, ZrO_2 ¹⁵, TiO_2 ¹⁶ or ZnO ¹⁷. The causes advanced by the authors to explain the existence of such porous structure are based on an amplification of evaporation-condensation or surface diffusion mechanisms. In the case of two particles in contact, it produces a rapid enlargement of the neck and then to a grain boundary moving towards the curvature centre, leading finally to a single particle of an important size.

In addition, Petot and al.^{12,13} have demonstrated a modification in the distribution of magnesium impurities (phenomenon of segregation) which is induced by a temperature gradient. By analogy, it is possible to think that in our study, the temperature gradient change the transport mechanisms of matter by a modification of impurities distribution.

Other studies show the influence of the impurities location on the materials sinterability. Gouvea¹⁸ has studied the densification of SnO_2 added MnO_2 . He has shown the effect of foreigners cations distribution before sintering. If the foreigners cations are distributed on the surface of the grains SnO_2 (in the first surface layers of grains) sintering begins at a lower temperature than in cases of foreigners cations initially distributed outside the SnO_2 grains. The authors have proved that in the latter case, the densification begins only when a critical concentration in foreign element is present on the surface grains of the matrix. Below this critical value, they have demonstrated that only the surface of grains is concerned by diffusion. Beyond this limit the material densifies. The authors have concluded a modification of mass transport mechanism depending on the concentration of foreign elements on the grain surface. It results a densification delay if the foreigners elements remained outside the grains.

The results and observations from the present study suggest that the thermal gradient can change the surface diffusion of alumina grains according to impurities distribution within the alumina grains or in the periphery of that grain.

For pure alumina, without intergranular impurities, a strong reactivity of the system is maintain to a higher temperature. So, that leads to a better densification.

For contaminated alumina powder, the present impurities modify the kinetics of matter transport. So, that can lead to grain growth at densification's expense.

CONCLUSION

By this analysis several points can be mentioned and emphasized :

- Comparisons between thermal treatments carried out in the initial stage of sintering (with and without thermal gradient) show that the gradient induces delay of specific surface area drop. In this case, the further densification of the material is improved. The interpretation of these experimental results due to correlate delay of specific surface area drop to a delay in the necks formation. This delay helps to maintain a strong reactivity of the system to a higher temperature and thus a better densification.

- Through complementary experiments, it has been demonstrated that a thermal gradient applied in the initial stage of sintering can affect the impurities dissolution. The mass transport is then modified : the grain growth is promoted at the expense of densification. Optimising the co-doping and a thermal gradient is an interesting way to obtain porous ceramic with stable and controlled microstructures.

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