IMPORTANCE OF THE PROCESSING ROUTE ON THE MORPHOLOGY OF ZIRCONIA CERAMICS

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ABSTRACT

In this paper, the morphology of zirconia ceramics fabricated by tape casting and dry-pressing is evaluated quantitatively and automatically using automatic image analysis and the $P(\ell)$ function. Such investigation gives insight into the densification and grain growth mechanisms.

Key words: mathematical morphology, $P(\ell)$, sintering, densification, grain growth, zirconia.

INTRODUCTION

To produce materials of the highest quality requires careful control of their microstructure. This, in turn, requests the knowledge of their microstructural evolution during the fabrication process (for example, see Brook, 1987). Moreover it has been shown that automatic image analysis is a very suitable tool to investigate the morphology of any material - ceramic, metals, plastics, composites, ...- (Chermant, 1986).

The scope of this paper is to determine the influence of the forming process on the evolution of the microstructure of tetragonal zirconia (TZP ZrO_2 +3 mol % Y_2O_3) during sintering. Densification and grain growth were investigated by automatic image analysis.

EXPERIMENTAL

Tape cast and dry-pressed specimens were prepared from ZrO_2 powder stabilized with 3 mol % yttria (YZ3, Rhône Poulenc, France). An ultrasonic treatment was used with the aid of a dispersant to deagglomerate the powder in a solvent (Chartier & al., 1991). The solvent was an azeotropic mixture of 2-butanone/ethanol (66/34 vol.%) and the dispersant was a phosphate ester (Chartier & al., 1987).

Granules for dry-pressing were achieved by spray-drying this same deagglomerated powder with a binder. The mean agglomerate size was measured to be 56 µm. Tape casting slurries were composed of deagglomerated YZ3 particles dispersed in the solvent, and of polyvinyl butyral as binder and polyethylene glycol and dibutyl phtalate as plasticizers (Boch & Chartier, 1989).

Tape cast green sheets were 250 μm thick, in which 30 mm diameter disks were punched, stacked and thermocompressed (100°C under 60 MPa) to produce 4 mm thick samples. The YZ3 granules were pressed in a floating die under a pressure of 150 MPa to obtain disks of 30 mm diameter and 4 mm thick. The pyrolysis of the organic components was carried out by heating under air at a rate of 0.2°C/mn up to 550°C with a 6 hour plateau.

For sintering in air, the dry-pressed and tape cast specimens were initially heated at a rate of 50°C/mn up to 900°C, then at 20°C/mn up to the sintering temperature (1300,1400 and 1500°C). The sintering time ranged from 5 to 1200 mn. The specimens were then fast cooled out of the furnace. After polishing with various grades of diamond, thermal etching was carried out at 50°C below the sintering temperature during 5 mn to reveal the grain boundaries (Fig. 1).
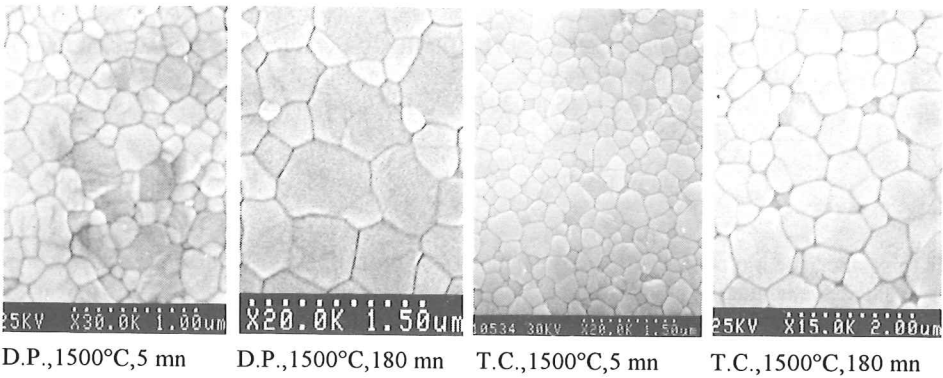

D.P.,1500°C,5 mn   D.P.,1500°C,180 mn   T.C.,1500°C,5 mn   T.C.,1500°C,180 mn

Fig. 1. SEM micrographs of dry-pressed (D.P.) and tape-cast (T.C.) ZrO_2 + 3 mol % Y_2O_3 sintered at 1500°C after 5 mn and 180 mn

The morphological parameters were automatically measured from SEM images on a Nachet NS 1500 (Micro-Contrôle, Evry, France), using the $P(\ell)$ function (Serra, 1982; Coster & Chermant, 1985), which allows the measurement of many morphological parameters including the granulometric density in measure, $g(\ell)$, and the mean chord length, defined in this paper as G. If Z is the frame of measurement, X the set to analyze and ℓ the structuring element, one have for $P(\ell)$ and $g(\ell)$, the density distribution in measure:

$$P(\ell) = \frac{A[E'(X \cap Z)]}{A[E'(Z)]} \qquad (1)$$

$$g(\ell) = \frac{\ell P''(\ell)}{P(O)} \qquad (2)$$

These parameters were statistically measured on at least 1000 grains for each specimen.

RESULTS

The relative density measurements by immersion in distilled water show that for the same sintering conditions, the relative density was always greater and the mean grain size always similar or greater for the tape cast specimens than for pressed ones.

Figure 2 presents the size distribution of ZrO_2 grains and that for the pores, in both tape cast and dry-pressed materials. The ZrO_2 particle size distributions are equivalent, with a mean value of 0.14 μm, and the pore size distribution is ranging from 0.02 μm to 0.20 μm, whatever the processing route is.
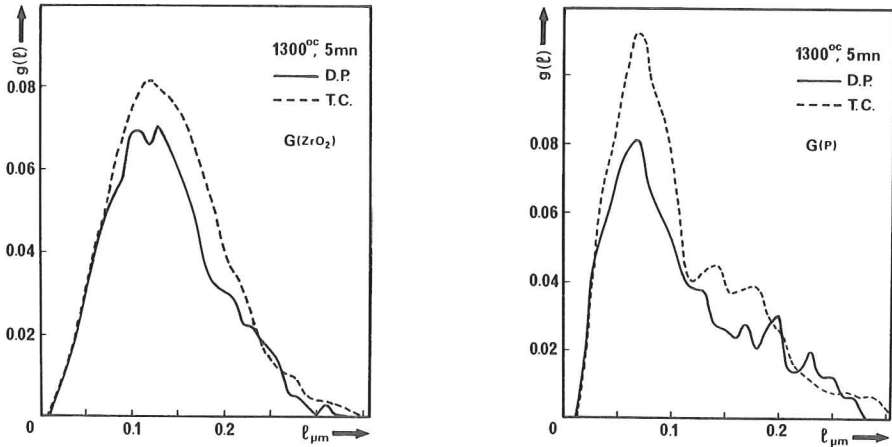

Fig. 2. Density distributions in measure for ZrO_2 grains, $G(ZrO_2)$, and pores, $G(P)$, for dry-pressed (D.P.) and tape cast (T.C.) ZrO_2 +3 mol % Y_2O_3, sintered 5 mn at 1300°C.

During sintering the microstructural evolution can be broadly separated into densification and grain growth (i.e. grain boundary or surface area reduction at constant density (Brook, 1976)). The evolution of the mean grain size of sintered ZrO_2 as a function of the relative density for the two processing routes is shown in figure 3: a relative density of 98.5% is attained before the mobility of grain boundaries leads to exaggerated grain growth. A comparison between these two processing routes indicates that grain growth is faster for the tape cast route.
Following the change in the mean diameter of the grains, G, with sintering time, t, or relative density, ρ/ρ_0, allows one to investigate both grain growth and densification kinetics.
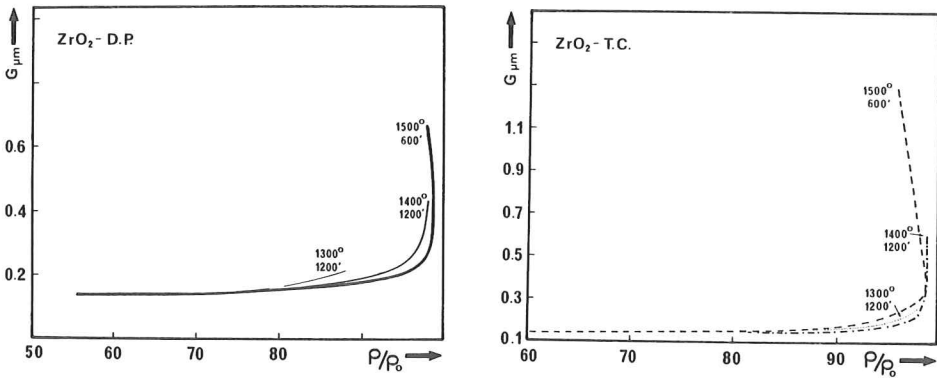

Fig. 3. Mean grain size, G, as a function of the relative density, ρ/ρ_0, in %, for dry-pressed (D.P.) and tape cast (T.C.) ZrO_2 +3 mol % Y_2O_3 sintered at 1300, 1400 and 1500°C for different sintering time (in mn).

Grain growth

Grain growth is a phenomenon which usually reduces the kinetics of densification. The change in the mean grain size, G, with sintering time, t, or temperature, T, is usually given by the form:

$$G^m - G_o^m = kt \exp^{-\frac{Q}{RT}} \qquad (3)$$

with : G_o the initial grain size (0.14 μm), m the kinetic exponent, k a constant, Q the apparent activation energy, R the gas constant and T the absolute temperature.

The slope, m, of the curve $G = f(t)$ gives an indication of the grain growth mechanism. The best correlation for the present results is $m = 3$, (Fig. 4). Among possible mechanisms of normal grain growth with such a kinetic exponent, the most probable is the pore drag process controlled by volume diffusion.The measured activation energy is about 330 kJ/mole, which can correspond to the volume diffusion of zirconium in ZrO_2 or to a diffusion due to complex interactions with present impurities such as silicon or sodium.
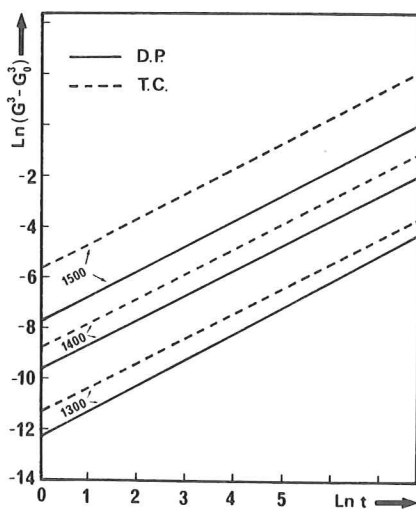

Fig. 4. Mean grain size, $G^3-G_0^3$, as a function of time, t, for dry-pressed (D.P.) and tape cast (T.C.) ZrO_2+3 mol % Y_2O_3 sintered at 1300, 1400 and 1500°C.

Densification

Coble presented in 1961 the principle diffusion controlled mechanisms of densification and showed that appropriate models predict a constant rate of densification when the diffusion coefficient and grain size are constant. To obtain a fine grained microstructure and avoid exaggerated grain growth, the rate of densification must be large in comparison with the rate of grain growth. In the intermediate stage of sintering, when the open porosity is eliminated, Coble's models have been re-examined by Bernache-Assolant (1993). He proposes a rate of

densification, $\dot{\rho}$, given as a first approximation, as a function of the diffusion coefficient responsible for densification ($D_{lattice}$ or $D_{grain\ boundary}$) and of the mean grain size G (c being a constant):

$$\dot{\rho} = c\ DG^{-n} \qquad\qquad (4)$$

with n=3 if volume diffusion (lattice diffusion) controls, or n=4 if grain boundary diffusion controls.

The ultimate densities reached for tape cast and dry-pressed samples were close, i.e. 98.6% of theoretical (6.1 g.cm^{-3}), but were not obtained for the same temperature and time conditions. Densification was faster for the tape cast materials than for those dry-pressed: after 5 mn at 1500°C, 96.6% of theoretical density is obtained for the tape cast samples, while dry-pressed samples only reach 88.4%. Decreasing density was observed for 1500°C after extended sintering times: 15 mn and 180 mn for tape cast and dry-pressed samples respectively. This decrease in density can be attributed to the generation and precipitation of entrapped gas in the material, coming from the decomposition of powder precursors (Smith & Baumard, 1987).

The mechanism of densification, in the intermediate stage (relative density < 92%), was determined for a range of times and temperatures for which a noticeable increase in density and grain size occurred. According to these conditions, the $\dot{\rho}$-G plot for the two processing routes gives a slope with a value close to n=4, (Fig. 5). Thus, the densification is probably controlled by grain boundary diffusion.
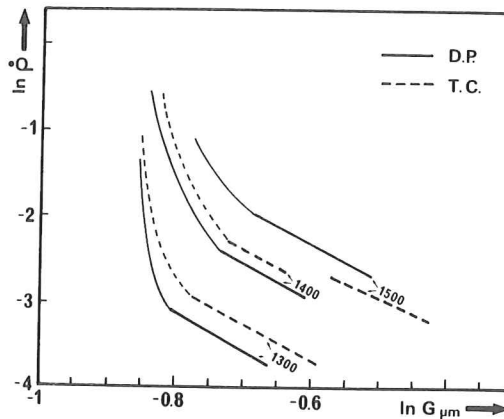

Fig. 5. Rate of densification, $\dot{\rho}$, as a function of grain size, G, for dry-pressed (D.P.) and tape cast (T.C.) ZrO$_2$ +3 mol % Y$_2$O$_3$ sintered at 1300, 1400 and 1500°C.

Whereas the mechanism of densification is the same for tape cast and dry-pressed samples, the densification is faster for tape cast samples.

CONCLUSION

This paper showed that for non-agglomerated starting ZrO_2 powders, the rates of densification and grain growth depend on the processing technique. Tape cast materials exhibit enhanced densification and grain growth compared to dry-pressed ones. The mechanism of densification, i.e. grain boundary diffusion, and of grain growth, i.e. pore drag, are the same whatever the processing route is.

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