Influence of Pore Structure Inhomogeneities in Green Compacts on Strength and Reliability of Y–TZP

A. V. Galakchov & V. Ja. Shevchenko

High-tech Ceramics Scientific-Research Centre, Academy of Science of the USSR, Leninski pr., 31, 117986, Moscow, USSR

Abstract

The pore structure of green compacts produced by slip casting from submicron $ZrO_2(Y_2O_3)$ powders was investigated. It was established that two kinds of agglomerates with different densities exist in the green compacts. Increasing the relative content of large interagglomerate porosity in the compact from 0·32 to 0·47 leads to a decrease in the relative density of the sintered bodies from 0·97 to 0·94 and in the mean strength from 617 to 300 MPa. The Weibull modulus is also decreased from 22·5 to 5·5.

Das Gefüge von Grünlingen aus $ZrO_2(Y_2O_3)$ Pulvern mit einer Korngröße kleiner 1 μm, die durch schlickerguß hergestellt wurden, wurde untersuch. Dabei zeigte sich, daß zwei Arten von Agglomeraten unterschiedlicher Dichte in den Grünlingen auftreten. Die relative Zunahme ausgedehnter Porosität zwischen den Agglomeraten von 0·32 auf 0·47 im Grünling führt in gesinterten Körpern zu einer Dichteabnahme von 0·97 auf 0·94 und zu einer Festigkeitsabnahme von 617 auf 300 MPa. Der Weibullmodul erniedrigt sich ebenso von 22·5 auf 5·5.

On a étudié la structure de la porosité de compacts obtenus par coulage en moule poreux de poudre submicronique de $ZrO_2(Y_2O_3)$. On a établi que ces compacts possèdent deux types d'agglomérats, présentant des densités différentes. Lorsque l'on augmente la teneur relative du compact en porosité située entre les agglomérats de 0·32 à 0·47, la densité des échantillons frittés passe de 0·97 à 0·94, la résistance mécanique moyenne de 617 à 300 MPa et le module de Weibull chute de 22·5 à 5·5.

1 Introduction

In view of the growing usage of ultrafine powders in the technology of advanced ceramics, the effects connected with inhomogeneities in the pore structure in green compacts are becoming the subject of active research.[1–4] Such inhomogeneity is expressed as fluctuations of density in microvolumes due to the local differences in particle packing. One of the reasons for the density fluctuations is the presence of dense clusters of individual particles, i.e. agglomerates. The pore structure inhomogeneities in green compacts lead to the development of structural defects in material during sintering process. For example, the presence of dense agglomerates in a relatively weak matrix leads to the appearance of internal crack-like voids.[2,3] In compacts made from agglomerated powders, large pores can be formed in the earlier stage of sintering.[4]

In this article the results of an investigation of the influence of pore structure parameters in green compacts on the sintering and mechanical characteristics of Y–TZP (tetragonal zirconia polycrystal doped with yttria) are presented.

2 The Preparation and Characteristics of Powders

Powders of $ZrO_2 + 3 \, mol\% \, Y_2O_3$ were prepared by coprecipitation using a 2M solution of both $ZrOCl_2$ and YCl_3 and with the addition of ammonia. After precipitation, the gel was cleaned with distilled water. The intermicellar water was changed with ethanol. The washed gels were calcined at 650°C for 3 h in air.
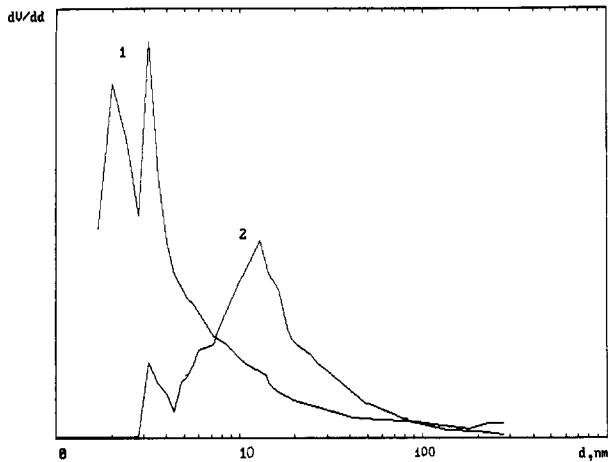
According to the results of DTA, the temperature

Fig. 1. The distribution of pore volume for 1, initial amorphous and 2, synthesized powder after calcination.

Fig. 3. Volume distribution for agglomerates in sythesized powders.

of crystallization of the amorphous gel was 450°C. The X-ray analysis shows that the product of crystallization was tetragonal ZrO_2. The specific surface of the gels and synthesized powders were determined by the BET adsorption method (three-point BET using Autosorb-1; Quantachrom Corp.). The adsorbate was liquid nitrogen. The specific surface of the gel was $142 \, m^2/g$. The specific surface value of the powders was decreased to $36 \, m^2/g$. The

Fig. 2. ZrO_2 powders (3 mol% Y_2O_3). Bar = 100 μm.

pore volume distribution in the gel and powders, measured from the adsorption isotherm, is presented in Fig. 1. The gels were found to have a fine pore structure with two kinds of pores which were predominantly of sizes 2 and 3·2 nm respectively. After calcination the character of the pore distribution in the powder is also bimodal. Small pores disappeared and the volume concentration of pores with size 3·2 nm decreased strongly. New structural formations appear in the powder. This fact is confirmed by the appearance of a wide peak in the range of pore diameters 10–200 nm. During the calcination of the amorphous gel the dissolution of the smallest pores by the sintering process takes place and first-order agglomerates with inter-agglomerate pore sizes from 10 to 200 nm are formed. The integral volume of pores (with diameters less than 250 nm) does not decrease strongly: from $0·27 \, cm^3/g$ in the gel up to $0·25 \, cm^3/g$ in the powders. Figure 2 shows the morphology of the powders. It is clear that the powders are agglomerated. The volume distribution of the agglomerates measured by conductometry (Culter Counter, model TA-2) is presented in Fig. 3. The diameter of the large agglomerates ranges from 1·6 to 20 μm, with mean value 4·4 μm.

3 Characteristics of Pore Structure in Green Compacts

The samples were prepared by water slip casting into plaster moulds. Three kinds of moulding were prepared. At the same water content (50 wt%) the slips have different values of pH: 2·66, 3·71 and 4·30. After air drying the compacts were aged at 400°C and the apparent density of the compacts was
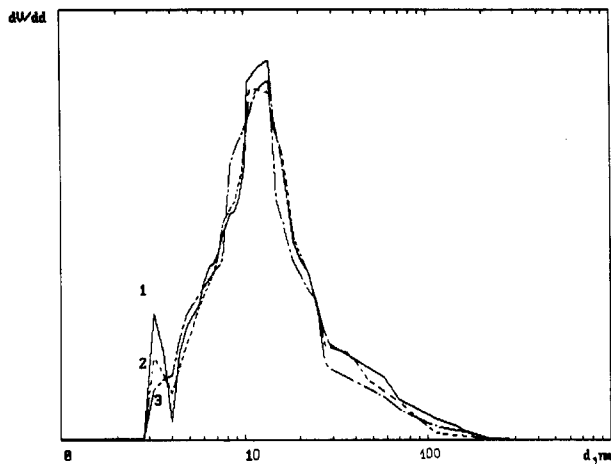
Fig. 4. Distribution of pore volume in compacts, prepared from slips with different pH. 1, ——, pH 4·30; 2, ———, pH 3·71; 3, —·—, pH 2·66.

measured by the mercury displacement method. The distribution of pore volume was measured by the adsorption method, as shown in Fig. 4. The character of this distribution is the same as obtained before for the powder (see Fig. 1) with two peaks located at $d \approx 3$ nm and $d \approx 12$ nm. For the purpose of the quantitive analysis of pore structure it is convenient to separate the distributions into sub-regions connected with typical elements of structure. The volume of pores with sizes up to 4 nm is connected with intraagglomerate porosity in agglomerates which are named as the agglomerates of the first order. Pores with sizes from 4 to 200 nm are interagglomerate pores with respect to the agglomerates of the first order. It is possible to determine the volume of the intraagglomerate pores in the agglomerates of the first order and the volume of the interagglomerate pores between these agglomerates from adsorption measurements. The volume of

pores with sizes from 200 to 70 000 nm is due to the existence of larger agglomerates (presented in Fig. 2). Such pores are interagglomerate pores between these agglomerates. These were designated as agglomerates of the second order. The highest limit of dimension for pores of the second order (70 000 nm) corresponds to the maximum pore sizes, which are taken into account for determination of density by the mercury displacement method. Intraagglomerate pores in agglomerates of the second order are interagglomerate pores between agglomerates of the first order ($d = 4$–200 nm). The volume of the interagglomerate pores between agglomerates of the second order is possible to determine as the difference between the volume of the pores with sizes up to 200 nm and the integral pore volume in the compact, which could be determined from the values of the apparent density of the compact and the material's true density.

So the pore structure of compacts has a special hierarchial character. The creation of such pore structure in powder compacts is common for agglomerated powders and is often encountered in practice.[5,6] The obvious realization of such structures is presented in Fig. 5.

The relation of pore volumes connected with pores of different types in the compacts prepared from slips with different pH are presented in Table 1. In Fig. 6 these data are presented graphically. With increasing slip acidity (with pH decreasing) and with no visible changes in the integral pore volume of the compacts, the regular increase in volume concentration of the large pores (interagglomerate pores between agglomerates of the second order) occurs. The growth of the large size pore volume occurs by a decrease in the content of the smallest pores

Interagglomerate pore in agglomerate of the 1-st order

Interagglomerate pore between agglomerates of the 2-nd order

Interagglomerate pore between agglomerates of the 1-st order (intraagglomerate pore in the agglomerate of the 2-nd order)

Individual particle

Agglomerate of the 1-st order
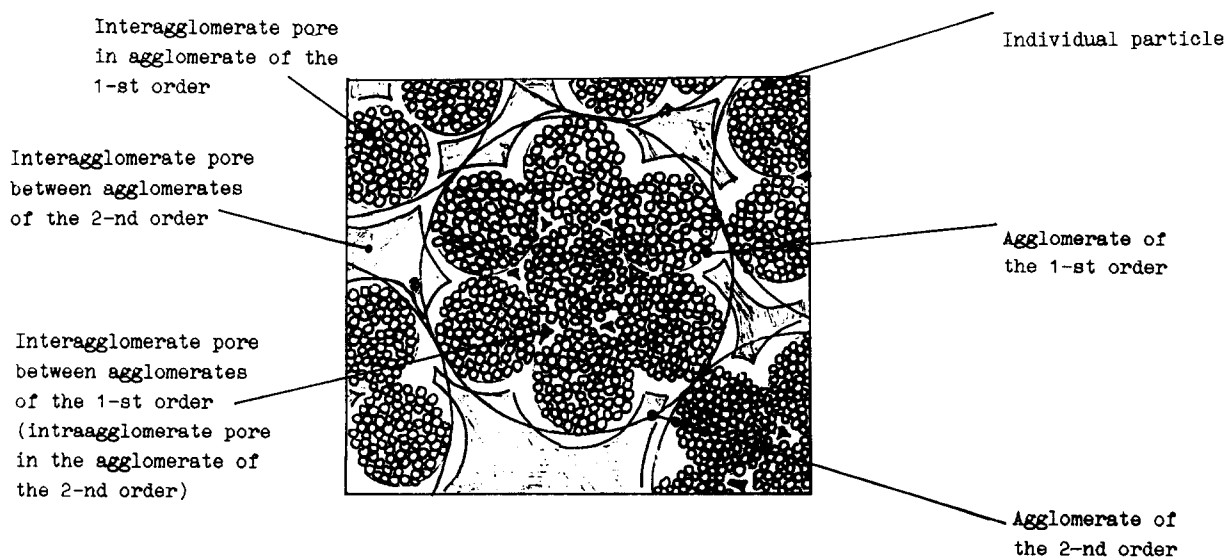
Agglomerate of the 2-nd order

Fig. 5. Scheme of particle packing in compacts prepared from agglomerated powders.

Table 1. The specific pore volumes in subregions for samples prepared from slips with different pH

Range of sizes of pores in subregion of pore size distribution	Type of pores	Volume of pores (cm^3/g)		
		pH 4·30	pH 3·71	pH 2·66
$0 < d < 4$ nm	Intraagglomerate pores in agglomerates of the first order	0·002 1	0·001 5	0·001 1
$4 < d < 200$ nm	Interagglomerate pores between agglomerates of the first range (intraagglomerate pores in agglomerates of the second order)	0·244 0	0·231 5	0·196 5
$200 < d < 70\,000$ nm	Interagglomerate pores in agglomerates of the second order	0·139 4	0·168 1	0·200 3
Integral volume of pores in compacts	—	0·385 5	0·401 1	0·397 9

(intraagglomerate pores in agglomerates of the first and second orders). It is possible to estimate some characteristics of the agglomerates from the data given in Table 1. For example, the apparent density of the agglomerates can be calculated using the expression:

$$\rho_{i+1} = \frac{\rho_i}{1 + \rho_i V_{i+1}}$$

where ρ_i is the apparent density of ith order agglomerates. V_i is the specific, volume of intraagglomerate pores in the agglomerates of ith order, in cm^3/g. (For the calculation of the apparent density of the first-order agglomerate ρ_1, was used the value of the density of individual particles ρ_0. For tetrogonal modification of ZrO_2, ρ_0 is equal to 6·10 g/cm^3). The results of apparent density calculations are presented in Table 2. The density of the first-order agglomerates is nearly equal to the theoretical density, i.e. these agglomerates are

formed from the primary particles by sintering during the calcination of the gels.

The agglomerates of the second order represented large 'friable' forms. The creation of second-order agglomerates are managed by van der Waals forces and also by the forces of electrostatic interaction between particles and agglomerates in slip. The dimensions of the powder particles (agglomerates of the first order) are possible to regulate in the powders synthesis stage, but the sizes and distribution of agglomerates of the second order are regulated by different technological operations on the compaction stage, for example, by mechanical breakage of agglomerates by grinding or by regulation of the intensity of repulsive interactions between individual particles in dispersion. The method of destroying 'weak' agglomerates in the compacts by isostatic pressure is also very effective.[7]

4 Density and Strength of the Sintered Samples

The moulded samples were air sintered at 1450°C for 1 h. The density of the samples were determined by the Archimedes method, and the strength by three-point bending tests. The surfaces of sintered samples, with dimensions 4 × 4 × 60 mm, were ground before
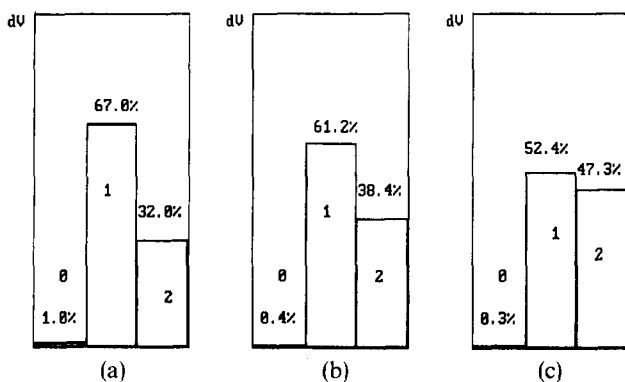
Fig. 6. Relative volume content of pores of different types in compacts, prepared from slips with different pH. 0, Intraagglomerate pores in agglomerates of the first order; 1, interagglomerate pores between agglomerates of the first order (intraagglomerate pores in agglomerates of the second order); 2, interagglomerate pores between agglomerates of the second order. (a) pH 4·30; (b) pH 3·71; (c) pH 2·66.

Table 2. Apparent density of agglomerates in compacts prepared from slips with different pH

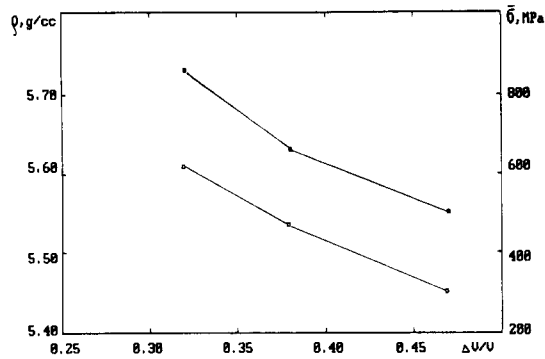| Order of agglomerates	Apparent density (g/cm^3)		
	pH 4·30	pH 3·71	pH 2·66
1	6·02	6·04	6·06
2	2·44	2·52	2·77
Integral apparent density of compacts	1·82	1·77	1·78

Fig. 7. ■, Density and □, mean strength of sintered samples as a function of the relative volume content of large interagglomerate pores in the green compact.

testing (without polishing). The loading rate was 0·1 mm/min.

The density and mean strength of the material as a function of the relative content of large inter-agglomerate porosity (relative volume of inter-agglomerates pores of the second order) are presented in Fig. 7. The increase in the fraction of large interagglomerate pores in compacts, initially having nearly the same integral porosity, decreases essentially the density and strength of sintered material. According to the theoretical results of Lange and Kellett,[8] large pores with high coordination numbers have limited potential for sintering. After a certain level of shrinkage the further removal of pores requires a significant grain growth. Large interagglomerate pores with high coordination numbers are detectable on the surface of ground samples (see Fig. 8; $\Delta V/V = 0\cdot47$, pH 2·66). These pores are defects which decrease not only the mean strength of the material, but also its reliability. The probabilities of failure are presented in Fig. 9. For
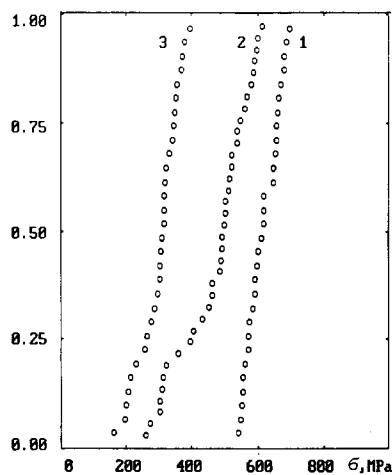

Fig. 8. Failure probability for sintered samples. 1, pH = 4·30, $\bar{\sigma}_0 = 616\cdot0$ MPa, $m = 22\cdot6$; 2, pH = 3·71, $\bar{\sigma}_0 = 469\cdot6$ MPa, $m = 6\cdot9$; 3, pH = 2·66, $\bar{\sigma}_0 = 299\cdot3$ MPa, $m = 5\cdot5$.
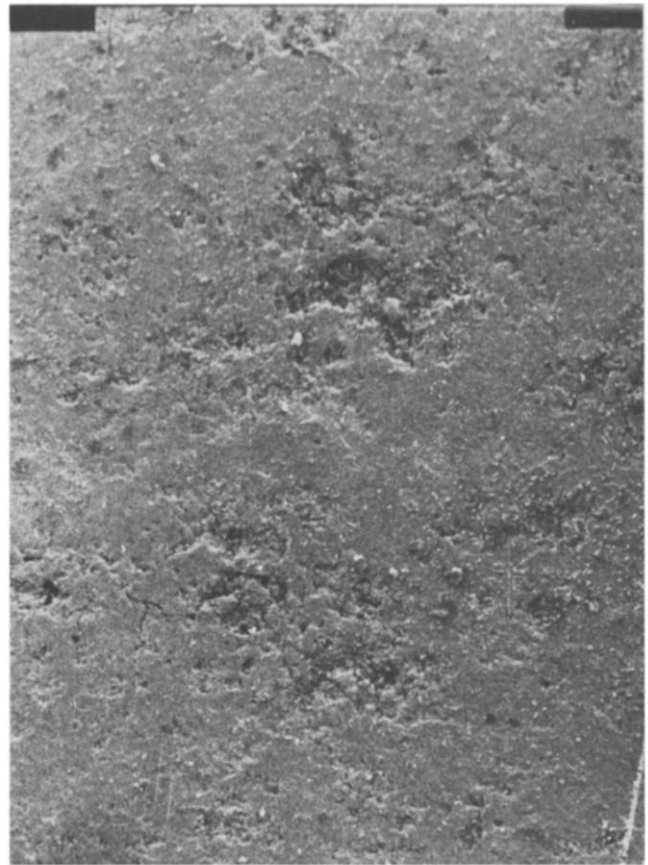

Fig. 9. Grinding surface of sintered samples with a high content of large interagglomerate pores (pH 2·66, $\Delta V/V = 0\cdot47$). Bar = 10 μm.

samples prepared by sintering of compacts with low levels of porosity inhomogeneity, the Weibull modulus was essentially higher than that for materials with a higher inhomogeneity of pore structure. For the samples sintered from compacts with $\Delta V/V = 0\cdot32$ (pH 4·30), the Weibull modulus was $m = 22\cdot6$, while for compounds sintered from compacts with $\Delta V/V = 0\cdot47$ (pH 2·66), it was only $m = 5\cdot5$.

The results presented here indicate the importance of control on the pore structure inhomogeneities in green compacts in the technology of ceramics.

References

1. Lange, F. F., Powder processing science and technology for increased reliability. *J. Amer. Ceram. Soc.*, **72**(1) (1989) 3–15.
2. Lange, F. F. & Davis, B. I., Processing-related fracture origins. III. Differential sintering of ZrO_2 agglomerates in Al_2O_3/ZrO_2 composites. *J. Amer. Ceram. Soc.*, **66**(6) (1983) 407–8.
3. Evans, A. G., Considerations of inhomogeneities effects in sintering. *J. Amer. Ceram. Soc.*, **65**(10) (1982) 495–501.
4. Dubok, V. A., Kabanova, M. I. & Pavlenko, N. P., Variations of the pore sizes during sintering of different PSZ powders. *Powder metallurgy*, (12) (1988) 18–20, in Russian.

5. Toner, J. & Onoda, J. Y., Fractal dimensions of model particle packings having multiple generations of agglomerates. *J. Amer. Ceram. Soc.*, **69**(11) (1986) 278-9.

6. Aksay, I. A. & Kikuchi, R., Structure of colloidal solids. In *Sci. Ceram. Chem. Process, Proc. 2nd Int. Conf. Ultrastruct. Process., Ceram., Glasses, and Compos., Palm Coast, FL, 1985*, NY, 1986, pp. 513-24.

7. Galakchov, A. V., Viazov, I. V. & Shevchenko, V. Ja., Compacting and sintering of agglomerated ultrafine ZrO_2 (3% mol Y_2O_3) powders. Refractories, (9) (1989) 18-23, in Russian.

8. Lange, F. F. & Kellett, B., Influence of particle arrangement on sintering. In *Sci. Ceram. Chem. Process*, ed. L. L. Hench & D. R. Ulrich, Wiley, NY, 1986, pp. 561-74.