Effect of bead-milling treatment on the dispersion of tetragonal zirconia nanopowder and improvements of two-step sintering

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The advantages of a good colloidal processing of tetragonal zirconia for achieving a full densification and a small grain size were determined in this study. The optimization of slurry preparation was studied to obtain well-dispersed suspensions. A deagglomeration technique was applied by bead-milling using grinding media of 50 μm diameter and initial particle size and green density were improved. Colloidal processing was considered responsible for the improvements of particle packing that increase the green density. A conventional sintering at low temperatures and two-step sintering were observed to be more effective with the final bead-milling treatment.

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1. Introduction

The colloidal processing of nanopowders is the most important and the initial step in ceramics conformation and has been proved to be an effective method of controlling and improving certain properties.^{1,2)} The dispersion of nanoparticles in a suspension can be stabilized by electrostatic or electrosteric repulsion, which is controlled by changing the pH of the suspension and/or adding a polyelectrolyte, which adsorbs onto the particle surface.^{1)–3)} Final properties are strongly affected by the rheology of the slurry; several studies have shown that inhomogeneities can be inhibited by controlling and manipulating the interparticle forces in the suspension during processing and forming.^{4)–7)} To obtain well-dispersed aqueous suspensions, several critical factors related to the rheology, such as the effect of dispersant content on viscosity, particle size distribution and green density of slip-cast compacts, must be studied. After this study the optimal conditions of dispersion can be estimated. Ultrasonication treatment is a very useful deagglomeration process, but heavily agglomerated particles cannot be redispersed. Thus, in order to redisperse these blocks of particles, we apply bead-milling using beads of 50 μm diameter or smaller and a high rotation speed. The use of small attrition media has been proved very effective for breaking the agglomeration up to primary particles.^{8)–11)}

Many attempts of improving the sinterability of ceramics were studied previously. For example, adding a liquid phase during sintering can enhance the sinter activity;^{12)–14)} however, the addition of additives can lead to the formation of amorphous grain boundary phases and sometimes an abnormal grain growth. A

conventional sintering with a constant heating rate was used to obtain dense compacts; however, this technique is always accompanied by the grain growth in the final stage.¹⁵⁾ Some years ago, a new method called two-step sintering was developed by Chen and Wang.¹⁶⁾ With this method, it is possible to obtain fully dense ceramics without the grain growth, and the authors explained that this suppression is due to the difference in kinetics between grain boundary diffusion and grain boundary migration. The two-step sintering started to be a useful technique for obtaining very good final properties and is now widely used in the ceramic field with excellent results.^{17)–21)}

In this study, first we compared the effects of the bead-milling treatment in colloidal processing in order to demonstrate that the sinterability of the samples is strongly related to the initial conditions of dispersion showing an enhanced sinter activity with an optimum colloidal processing with no sintering aids. Then, we also studied the advantages of the two-step sintering compared with the normal sintering. As a result of this study, we propose an improvement of colloidal processing, from powder dispersing to fully dense 3 mol% yttria-stabilized tetragonal zirconia with a small grain size sintered at low temperatures.

2. Experimental procedure

2.1 Materials

A commercial powder of 3 mol% Y_2O_3 doped tetragonal ZrO_2 (3YTZ, Tosoh Co, Tokyo, Japan) with a mean particle size of 65 nm and a BET surface area of 15.3 m^2/g was used. Aqueous suspensions were prepared; they contained 30 vol% (72.2 mass %) of solid loading for the optimization of the rheological conditions in colloidal processing and 10 vol% (39.3 mass %) for bead-milling dispersion. The powder was dispersed in distilled water with a polyelectrolyte (poly (ammonium carboxylate), ALON A-6114, Toagosei Co., Ltd., Tokyo, Japan).

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2.2 Sample preparation

2.2.1 Colloidal processing

Aqueous ceramic suspensions with 30 vol% of solid loading were prepared by dispersing the ZrO_2 powder in distilled water with different amounts of polyelectrolyte. The aqueous ceramic suspensions were dispersed in an ultrasonic stirrer (Nissei model USS-1) with 35 W (Nihonseki Kaisha Ltd., Japan) for 15 min. Then, the slurry was exposed to an ultrasonic homogenizer (Nissei 1200T) at a frequency of 19.6 kHz (Nihonseki Kaisha Ltd., Japan) for 10 minutes in order to redisperse the agglomerated particles.²²⁾

The suspension was outgassed in a desiccator to eliminate air bubbles and slip cast over plaster molds with a Teflon film of $0.2\ \mu\text{m}$ pore size separating the slurry from the mold to avoid contamination. The slip-cast samples were dried slowly to avoid cracking and cold isostatically pressed at 392 MPa. Green density was determined by the Archimedes method in kerosene.

2.2.2 Bead-milling processing

The heavily agglomerated particles cannot be redispersed by ultrasonication. For this reason, we use a bead-milling equipment (**Fig. 1**) (Ultra Apex Mill Type UAM-015, Kotobuki Industries Co., Ltd., Kure Japan) with ZrO_2 beads with a diameter of $50\ \mu\text{m}$ at a rotation speed of 4000 rpm, and the volume of the vessel where the wall and stirring discs are made of zirconia is $320\ \text{cm}^3$. This treatment proves that is possible to obtain well-mixed and dispersed suspensions.⁸⁾⁻¹¹⁾

The particle size distribution was measured using a particle size analyzer to evaluate the dispersion of the suspension (UPA-UT151, 0.8–6500 nm *NANOTRAC*[®] equipment Nikkiso, Co., Ltd., Japan).

The suspension obtained after 60 minutes of treatment was evacuated, slip-cast and cold isostatically pressed at 392 MPa for comparison with the samples cast without bead-milling.

2.3 Slurry characterization

The particle size distribution was used to observe the evolution of dispersion and the degree of agglomeration. The zeta potential of the powder was measured with a laser electrophoresis analyzer (LEZA-600, Otsuka Electronics Co., Ltd.). The viscosity was measured with a Brookfield cone and plate viscosimeter CAP 2000 (USA). After outgassing in a desiccator, the suspension was slip-cast in a porous alumina mold and the green density of cast samples was measured by the Archimedes method in kerosene.

Fig. 1. Bead-milling equipment using beads with diameter ranging from 15 to $50\ \mu\text{m}$.

2.4 Sintering and characterization of sintered samples

Green samples were sintered in air at different temperatures in the range of 1373 to 1773 K for 3 h at a heating rate of 5 K/min. The sintering conditions for the two-step program were determined using reference studies.¹⁷⁾⁻²¹⁾ Different sintering programs were performed experimentally and results were compared. The sintered density was measured by the Archimedes method in water. The relative density of the zirconia was based on $6.06\ \text{g/cm}^3$. The microstructure of the sintered bodies was observed by high-resolution scanning electron microscopy (SEM; JSM-840, JEOL Ltd., Tokyo Japan) using polished and thermally etched surfaces. The grain size was measured by a linear intersection method using Scion Image Beta 4.03 for Windows XP.²³⁾

3. Results and discussion

3.1 Effects of dispersant addition (on rheological properties, particle size and green density)

The zeta potential as a function of pH is presented in **Fig. 2** showing an isoelectric point of 4.85. Other authors reported different values from 4.7 to 8.1 for TZ-3Y.²⁴⁾⁻²⁷⁾ These large differences are due to the different methods used to prepare powders, different types of dispersant used, different amounts and ionic strengths.

One important parameter we can observe in the zeta potential measurement is the range of working pH. All the references show a zeta potential of around $-50\ \text{mV}$ in the pH range of 8.5–10. This information gives us the range where it is possible to have good powder dispersion. The polyelectrolyte used as a dispersant at the working pH is completely dissociated^{3),23)} in accordance with the reaction $\text{RCOONH}_4 \leftrightarrow \text{RCOO}^- + \text{NH}_4^+$. The RCOO^- groups of the deflocculant adsorb onto the minority of positive surface sites of YSZ, even though the net surface charge is negative at an alkaline pH.²⁸⁾

Figure 3 shows the behavior of the viscosity. It can be observed that the rheology of the system is affected by the amount of dispersant added. The adsorbed polyelectrolyte on the surface of the powder enhanced the surface charge and the viscosity decreased. For polymer addition that is more than the optimum, we have two effects that contribute to the increase in viscosity; one is the increment in ionic strength resulting in a decrease in the negative surface charge due to the large compression in the double layer³⁾ leading to the increment in viscosity, and the other is the possibility of adsorption forming

Fig. 2. Zeta potential versus pH value for dispersion of zirconia with 0.3 wt% of dispersant added.

Fig. 3. Rheological study of a zirconia suspension as a function of dispersant content.

Fig. 4. Particle size distribution versus milling time.

Fig. 5. Relative density of tetragonal zirconia as a function of sintered temperature (°C) for two colloidal processes and effect of the two step sintering.

Table 1. Experimental Conditions for the Two-step Sintering Performed and Final Density

Two Step Sintering Programs						
Program	TEMP 1(°C)	time 1(min)	TEMP 2 (°C)	time 2 (h.)	Density(g/cm ³)	% of TD
1	1300	1	1100	15	5.84	96.4
2	1300	1	1200	15	6.05	99.9
3	1200	1	1100	15	4.94	81.6
4	1400	1	1150	15	5.69	93.9
5	1400	1	1200	15	5.88	97.1

an extended link called bridging flocculation.²⁸⁾

In Fig. 3, it can also be observed that with an excess polymer, the particles tend to agglomerate forming clusters that are very difficult to break even with an ultrasonication treatment. This phenomenon has been widely studied and reported.^{26),29)} When the dispersant amount is less than the optimum, the electrostatic repulsive forces generated by the adsorbed polymers are insufficient for overcoming the van der Waals attractive forces. The total potential between particles remains attractive and flocculation occurs. As the dispersant amount increases, the electrostatic repulsive forces attains a value that is sufficient strong for overcoming the van der Waals forces and the dispersion becomes

optimum presenting a minimum in the particle size measurement.

Slip casting was performed with each suspension with a different amount of dispersant forming the green compacts. The more highly dispersed suspensions present a better packing showing the highest green density. Figure 3 also shows the optimum conditions of high green densities for the suspensions with minimum amounts of dispersant. The optimum condition for dispersion is clearly presented for the three different parameters measured, namely, viscosity, particle size distribution and green density. We can assume that the best dispersant content we can use to disperse our system is 0.3 wt%.

3.2 Bead-milling process

As we can observe in Fig. 3, the best conditions for disperse zirconia with the normal colloidal processing show the minimum particle size of 150 nm. Considering that the primary particle size is 65 nm, we can assume that there are still some agglomerations in the final slurry. **Figure 4** shows the evolution of the particle size with the time of bead-milling. Two important conclusions can be drawn from this plot. The first conclusion is that the initial distribution of particle size is large with a d_{90} of 270 nm and a d_{10} of 90 nm. After bead-milling for 60 min, the distribution becomes narrow with a d_{90} of 150 nm and a d_{10} of 55 nm. The second conclusion is that the mean particle size decreases from 150 to 90 nm, which is close to the primary particle size.

The bead-milled slurry was slip-cast and dried. The results for green density show a density of 3.74 g/cm^3 (61.6% of theoretical density (TD)); this value is higher than the green density obtained by colloidal processing without bead-milling (56.1% of TD) proving that a higher dispersion generates a better packing enhancing the density.

3.3 Normal and two-step sintering processes

Figure 5 shows the densification curves for the two different processes. It is easy to observe that bead-milling exhibits a higher sinterability. The reason for this improvement is the better packing; this idea is in accordance with the basic studies on sintering performed by Kingery and François³⁰⁾ and Vasylykiv et al.^{31),32)} revealing that the densification of zirconia at lower temperature is possible only when a highly uniform packing is achieved. Kingery and François studied the behavior of pores and indicated that the pores with coordination numbers lower than a critical number disappear during the pressureless sintering. In our case, the samples with higher green densities present better initial conditions including a lower porosity and also a small pore size and are expected to present an optimum sinterability.

Preliminary results show that the samples are completely dense at 1400°C. The sintering shrinkage starts at around

1100°C, and after this point, the densification increases. The samples were held at the final temperature for 3 h in order to observe the densification.

The two-step sintering study was based on previous studies.^{17)-20),33)} The obtained facts guide us in performing different two-step sintering programs in order to determine the best sintering conditions for our system. The programs we tried are shown in **Table 1**. The program used as the two-step sintering program for our samples enabled us to obtain a higher rate of densification with a first step (T1) of 1300°C and no holding time and a second step (T2) of 1200°C for 15 h.

3.4 Microstructure

Figure 6 shows the results for the grain size vs theoretical density in the sintered samples; we can observe that the average grain size does not change significantly with or without milling treatment. In the figure, note that the bead-milling affects directly the sinterability, making possible to eliminate the porosity at a

Fig. 6. Grain size versus relative density (%) for the two different colloidal processes and effect of the two step sintering.

Fig. 7. SEM micrographs of samples sintered at 1250°C and two-step sintering for bead-milling (a) and (c) and same sintering conditions without bead-milling (b) and (d).

lower temperature, and the grain sizes for both colloidal treatments are the same. The results for two-step sintering are also plotted in Fig. 6 showing the optimum densification and grain growth characteristics. Differences in densification and grain growth characteristics between samples subjected to two-step sintering (Fig. 6) are considerable. In the sample without bead-milling, the agglomerated parts start to sinter in the first step, generating porosity that cannot be eliminated at low temperatures in the second step. However, the bead-milled sample can start sintering homogeneously in the first step and completely sinter in the second step of the program. It is clearly observed that two-step sintering is the best sintering technique that enables a high rate of densification and a low rate of grain growth, particularly for fully deagglomerated samples.

Figures 7(a) and (b) show the final microstructures of the samples sintered at 1250°C and subjected to two-step sintering, respectively. The samples are densified with an average grain size of 155 nm in Fig. 7(a) and 125 nm in Fig. 7(b). Figures 7(c) and (d) show the microstructures of the samples without milling processing, indicating that a certain degree of porosity remains. The grain size of these samples is 160 nm for 1250°C and 150 nm for the two-step sintering.

The porosity observed in the samples without bead-milling is directly related to the inefficient colloidal processing. Agglomerates start sintering earlier than the bulk ceramic exhibiting a local densification in the first stage, creating a high porosity that is difficult to eliminate. This observation explains the existence of pores in Figs. 7(c) and (d).

4. Conclusion

Bead-milling processing proves to be a very effective method for breaking heavily agglomerated particles with sizes remaining from 150 to 90 nm, leading to a high particle packing and in consequence to a high green density, which is 61.6 % of the theoretical density (TD). For slip casting without bead-milling treatment, the green density is 56.1% of TD.

Sintering experiments were performed to determine the best normal sintering and two-step sintering conditions. Results show a complete densification at 1250°C for normal sintering and a final structure with an average grain size of 155 nm. The sintering is improved with the two-step sintering with the selected sintering program showing a complete densification with a final average grain size of 125 nm.

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