Effect of the Granule Properties and Compaction Pressure on the Green and Sintered Densities of Al$_2$O$_3$/15 vol%ZrO$_2$

Dong-Woo SHIN, Dae-Hyun YOON, Cheol-Jin KIM, Young-Sun CHUNG* and Keun Ho AUH*

Division of Materials Science and Engineering, Kyongsang National University, AMEI, Kyungnam, Chinhae, 660–701, Korea

*Ceramic Processing Research Center (CPRC), Hanyang University, Seoul 133–791, Korea

Al$_2$O$_3$/15 vol%ZrO$_2$ の成形体及び焼結体密度に及ぼす顆粒特性及び成形圧力の効果

申 東佑・尹 大賢・金 哲珍・鄭 龍善*・吳 根錫*

慶尚大学材料工学部, 尖端素材研究所, 慶南, 菁州 660–701 韓国

*漢陽大学セラミックス工程研究センター, ソウル 133–791 韓国

The dependence of green and sintered densities of zirconia-toughened alumina (ZTA: Al$_2$O$_3$/15 vol% ZrO$_2$) on the properties of spray-dried granules and compaction pressures was studied to differentiate the dominant processing parameter controlling sintered properties. Two sets of spray-dried granules, which differed largely in terms of the morphology and yield stress of granules, were compacted at various uniaxial pressures in the range of 80 MPa to 120 MPa. The green and sintered densities varied depending on the granule properties and compaction pressure. However, both sets of granules formed by cold isostatic pressing at 500 MPa exhibited the same green and sintered densities of about 63% and 99%, respectively, relative to the theoretical density, regardless of the variation of granule properties. This work confirmed that high cold isostatic pressure could overcome the effect of granule properties on the green and sintered densities. The strength of sintered specimens was determined from the size of large hollows in the spray-dried granules remaining after compaction. Details of the compaction behavior in terms of the granule properties were discussed.

Key-words: Spray-dried granule, Apparent yield point of granule, Compaction behavior, Green density, Sintered density, Mechanical properties

1. Introduction

Common ceramic processing includes spray-drying of milled slurry prior to compaction and subsequent sintering to utilize the higher flowability of large and spherical granules for improved reproducibility of green density. The parameters controlling granule properties and the effect of the properties of a spray-dried granule on the compaction behavior were investigated thoroughly in numerous works. However, little study has been done on the relationship between the compaction behavior and the properties of a sintered body.

A spray-dried individual granule normally containing less than 3 mass% of organic binder and plasticizer shows about 50% intragranular porosity. The higher the plasticity of the binder, the higher the green density, to some extent. The glass transition temperature ($T_g$) of binder, below which the binder is brittle and above which it shows plasticity, is one of the important factors that control compaction behavior. The dry pressing should be performed at temperatures below $T_g$ to obtain high green density. $T_g$ of the binder decreases with increasing amounts of moisture and organic plasticizer which disrupt the bonding strength of binder and reduce its hardness.

The mode of compaction shifts from the rearrangement of granules to deformation and fracture at low pressure to fill intergranular pores. The particular stress causing the onset of plastic deformation and fracture of granules is called the apparent yield point (AYP). The AYP of a granule could be an indicator of the degree of plasticity. In fact, the lower the AYP, the higher the degree of plasticity. Besides AYP, the morphology and size distribution of granules are also important in determining their flowability. In practice, granules showing low AYP (high plasticity) and highly spherical shape without any large internal pores can lead to a denser packing configuration. As a result, the shape and properties of granules could affect not only green density but also sintered density, since we expect the higher green density to result in a higher sintered density under the same heat-treatment conditions.

However, little work has been done to show any systematic relationship between the granule characteristics and the sintered properties. The density and strength of the sintered body could be more affected by the large hollows existing in the undeformed granules, during compaction process. The aim of this work is to show how the granule properties can influence the compaction behavior at different compaction pressures and with different methods, i.e., uniaxial dry pressing and cold isostatic pressing, and also show how the different compaction responses can affect the strength and density of a sintered specimen. Two sets of spray-dried granules which differed largely in terms of AYP and amount of hollows were prepared by varying the amount of binder. Then the variations of green and sintered densities, and mechanical properties depending on the granule properties were examined. Moreover, the dominant processing parameter between the granule properties and compaction conditions in determining the density and strength of sintered ZTA were shown.

2. Experimental procedure

Al$_2$O$_3$ (A-16SG, Alcoa, USA) and ZrO$_2$ (SC20, MEL, U.K.) were carefully weighed for ZTA (Al$_2$O$_3$/15 vol% ZrO$_2$). The composition was milled in a ball mill for 24h using a 91 mass% Al$_2$O$_3$–9 mass% SiO$_2$ jar and milling media. The powder was weighed to be 30 vol% when loaded in a water slurry. Two different slurries were prepared depending on the amount of binder added. Polyvinyl alcohol (PVA) binder (Gelvatol 20–60, Monsanto Co., St. Louis, Mo) of 0.5 mass% relative to powder was added into one batch, and the other contained no binder. The particle size of milled slurries was measured using the particle size analyzer (Microplus, Malvern, U.K.). The characteristics
of the two slurries after milling for 24h are given in Table 1. Both slurries were spray-dried under the same conditions, i.e., inlet and outlet temperatures of 130°C and 80°C, respectively, and r.p.m. of 15500. Both granules A containing no binder and granules B containing 0.5 mass% PVA were stored in a chamber with a constant relative humidity (rh) of 75% and temperature of 25°C for 72h to provide some moisture to retain the plasticity of granules. The moisture contents of spray-dried granules A and B after storing in the chamber were 0.4 and 0.2 mass%, respectively, relative to the weight of powders dried completely in a dry oven at 120°C for 24h. Thus the granules without binder (A) were revealed to absorb more water than the binder-containing granules (B) when held at 75% rh at 25°C. The size distributions and shapes of the spray-dried granules were determined from the analysis of SEM micrographs. At least 1000 granules for each set of granules were analyzed using Image-Pro software (Media Cybernetics, USA).

The compaction diagram, i.e., density vs. logarithm of pressure curve in the low-pressure region up to 10 MPa, was plotted as shown in Fig. 2 to determine the apparent yield point of the granules. The preweighed spray-dried granules taken from the constant-temperature (25°C) and -humidity (75% rh) chamber were loaded immediately into a 1.5-cm-diameter hardened steel die lubricated with stearic acid, and then the die was tapped to induce uniform filling. The tapped density was determined from the mass of the loaded powder and the height of the powder after tapping. The powder was then compressed at the rate of 0.5 mm/min on a universal testing machine to obtain the load-displacement curve. The data of load-displacement were converted to the green density vs. pressure curve. The AYP of the granules was then taken as the intersection of the horizontal line intersecting the tapped density of the loaded powder and the line extrapolated from the straight line segment up to 10 MPa.7)

The effect of granule properties on the compaction behavior in the high-pressure region was studied by measuring the change of green densities with respect to the compaction pressure from 80 MPa to 120 MPa in 10 MPa increments for the two sets of granulated powders. The spray-dried granules stored in the controlled atmosphere of 75% rh and 25°C for 72h were compacted uniaxially in the lubricated steel die with rectangular dimensions of 50 mm × 40 mm. The density was determined from the dimensions and mass of the ejected compact. The dimensions were measured 24h after ejection to consider the springback effect of the pressed compact. Densities obtained from about 50 compacts at each pressure were averaged. Half the compacts were further isostatically pressed at 500 MPa after uniaxial pressing.

All of the ZTA compacts were heat-treated at a heating rate of 5°C/min to 1600°C and held at 1600°C for 2h. The bulk density of sintered samples was measured by the Archimedes method in water. The sintered specimens were cut into bars (3 mm × 4 mm × 40 mm) and diamond-ground along their length for 30 min. Four-point flexural strengths were determined from as-ground specimens with an outer span of 20 mm and an inner span of 7 mm. The ratios of tetragonal ZrO2 particles to monoclinic ZrO2 particles for the spray-dried granules and as-sintered surfaces were determined from X-ray diffraction data by measuring the relative intensities of the monoclinic and tetragonal reflections.8) The theoretical densities of green and sintered specimens were calculated using the t-ZrO2/m-ZrO2 ratio. The hardness of sintered specimens polished to a 0.5 μm finish using diamond paste was measured using a Vickers hardness indenter with a 100 N load. Fracture surfaces were observed by SEM to examine the strength-controlling flaws.

3. Results and discussion

3.1 Granule characteristics

The morphologies of two sets of spray-dried granules are shown in Fig. 1. Granules A containing no binder were nearly spherical and showed little hollows in granules, whereas a large degree of asperity and a number of hollows and donut-shaped granules were observed in granules B to which 0.5 mass% PVA was added. The distributions of aspect ratio and size, and the ratio of hollow area to the total cross-sectional area of granules were determined from analysis of at least 1000 granules for each set of granulated powder in SEM pictures. These values are given in
Table 2. Granules B showed a wider distribution of aspect ratio and about 10 times larger hollow area in comparison with granules A, indicating a higher deviation from sphericity. The relative tapped densities of granules A and B were 31% and 28%, respectively. The higher tapped density of granule A could be a result of the higher sphericity and fewer hollows.

Considering the binder content of granules B together with the lower moisture content, they were expected to be harder and more brittle. The relative green density as a function of compaction pressure was measured and is shown in Fig. 2. The AYP of granules B was at 0.4 MPa whereas no change of slope was observed in granules A. This indicates that the plastic deformation or fracture of granules A began upon applying the compaction pressure, whereas for granules B, the rearrangement of granules occurred up to 0.4 MPa prior to deformation or fracturing of granules. For granule A, a weak bonding force between constituent fine particles and a high moisture content could cause the high plasticity without sliding of granules at the beginning of compaction.

3.2 Green and sintered densities

The change of green densities with respect to the uniaxial pressures from 80 to 120 MPa and the isostatic pressure of 500 MPa after compaction at various uniaxial pressures is shown in Fig. 3. The values of density at each compaction pressure are the average of 50 samples; their standard deviations are also presented. In the case of granules A, the green density increases with increasing pressure up to 100 MPa and then decreases due to lamination. Such lamination did not occur up to 120 MPa for granules B, and thus the green density increased with increasing pressure up to 120 MPa. However, the green density of granules B was consistently lower compared to that of granules A at the given uniaxial pressure.

Taken together with the characteristics of granules A and B, the compaction responses of the two sets of granules are schematically presented in Fig. 4. Granules A showed...
higher sphericity with fewer hollows and smaller average granule size compared to granules B. This yielded a higher tapped density (~31%) of granules A than that (~28%) of granules B, as demonstrated in A-1 and B-1 of Fig. 4, respectively. Granule A containing 0.4 mass% of moisture showed high plasticity and thus began to deform upon applying pressure, which reduced the number of intergranular pores existing between the granules as well as the intragranular pores within each granule adjacent to the top punch (A-2). The dots and small circles shown in Fig. 4 represent small intragranular pores and hollows, respectively. In the case of granules B, the rearrangement of granules, a typical initial stage of compaction, occurred up to 0.4 MPa before shifting to the next stage of fracturing into finer granules (B-2). By increasing the pressure for granule A, the granules nearer to the top punch could be deformed to a greater extent, thus the transmission of applied stress from the surface to the interior of the compact became less effective when the granules in the vicinity of the surface were deformed to a platelike shape (A-3). The degree of the pressure gradient between the surface and the interior of the compact, caused by the larger deformation of granules nearer to the top surface, could increase with increasing compaction pressure. The variation of elastic strain throughout the compact due to the pressure gradient can cause the laminations, when ejection occurs perpendicular to the direction of punch travel, if the difference in elastic recovery stresses is higher than the fracture strength of the compact (A-4). On the other hand, the reduction of intergranular pores occurred in granules B beyond the AYP of 0.4 MPa, mainly by fracturing of hard granules (B-3). Since the binder and lower moisture content of granules B caused strong bonding between particles and low deformability, respectively, the granules could be fractured into finer agglomerates rather than being deformed plastically as granules A. The surface of compacts pressed uniaxially at 100 MPa indicates that the granules A deformed to a platelike shape and granules B fractured into a number of finer and more spherical agglomerates, as shown in Fig. 5. The applied pressure can be transmitted more effectively through hard and spherical agglomerates. Thus, the lower degree of variation of elastic strain throughout the compact made of granule B, combined with high green strength due to the binder, could result in no laminations, when ejection occurs perpendicular to the direction of punch travel, if the difference in elastic recovery stresses is higher than the fracture strength of the compact (B-4). However, the persistent hollows existing in nonfractured granules B and intragranular pores in the fine agglomerates led to lower green density in comparison with granules A at a given pressure.

Isostatic pressing at 500 MPa for the compacts formed uniaxially at various pressures increased the compaction density to nearly the theoretical value of 63%, despite the granule properties and the fact that the relatively large variation in the green density of the compacts uniaxially compressed depends on the applied pressures. This indicates that the shapes and properties of granules could be second-order effects in comparison to the effect of isostatic pressure for high compaction density. Thus, the disadvantages of granule characteristics for a dense compact can be overcome by increasing the forming pressure in isostatic pressing. Isostatic pressing at high pressures is also beneficial in reducing the deviation of compaction densities, as shown in Fig. 3.

The influence of compaction pressures on the sintered densities for the two sets of granules is shown in Fig. 6. The fraction of t-ZrO₂ in the surfaces of sintered specimens was in the range of 47 to 56 vol% depending on the sintered density. The theoretical densities of sintered ZTA's were determined using various ratios of t-ZrO₂ to m-ZrO₂. The
relative green density of the uniaxially compacted granules A was 56% to 62%, and the density was improved to about 64% after pressing isostatically, as shown in Fig 3 (A). The sintered density of the compacts made of granules A was nearly constant with the value of about 99% of theoretical density, irrespective of the variation of green densities. However, in the case of granules B, the higher the green density, the higher the sintered density. It is also worth noting that the deviation of sintered densities of the compacts pressed isostatically was reduced significantly compared with that of uniaxially pressed specimens for both sets of granules.

The different trends of granules A and B in the relationship between green and sintered densities might originate from the persistent hollows present in granules B. A number of as-spray-dried granules B contained hollows, as shown in Fig. 1 (B). While increasing the compaction pressure, fracturing of hard granules B into finer agglomerates increased. Some granules containing hollows remained unbroken, even at high compaction pressure, due to the pressure gradient. These persistent hollows were likely to deteriorate the sintered density. The number of hollows remaining after compaction were reduced linearly with increasing applied pressure, and accordingly, the green and sintered densities increased with increasing compaction pressure, as demonstrated in Figs. 3 (B) and 6 (B). On the other hand, the green density was likely governed by the persistent inter- and intragranular pores rather than the remaining hollows, since a few granules A contained hollows. These pores could be removed easily during sintering because the size of pores was markedly smaller than that of the hollows. Therefore, the sintered density of the compacts consisting of granules A did not vary with the green density, and showed a nearly constant value of about 99% of the theoretical. Note that although the compacts pressed isostatically exhibited consistently higher green density compared with the uniaxially pressed ones for both sets of granules, the sintered density of uniaxially compacted samples was the same as the density of isostatically pressed ones for granules A, whereas for the granules B, the isostatic pressing resulted in higher sintered density.

3.3 Mechanical properties
The 4-point bending strength of sintered ZTAs as a function of the compaction conditions was measured and is shown in Fig. 7. The average strengths of sintered ZTAs after uniaxial and isostatic pressings were about 400 MPa and 420 MPa, respectively, for both sets of granules. The strength reduction of the specimens compacted uniaxially beyond 100 MPa might be caused by compaction defects.
such as laminations, as expected from Fig. 3(A). With respect to the relationship between the sintered density and bending strength, the variation of sintered densities within 1% did not significantly affect the strength. In fact, the strength was determined by the size of the largest flaw existing near the tensile surface in the bending configuration rather than the number of pores represented by the density.

Hollows exist in both granules A and B, although the number of hollows in granules B is considerably larger compared with granules A, as indicated in Table 2. Most of the hollows could be eliminated by fracturing and deforming the granules at high compaction pressure, yet a few remained in the undeformed granules due to the pressure gradient within the compact. These persistent hollows retarded the densification of their surrounding region during sintering. Presumably, the gas contained in the hollows expanded at high temperature and compensated the driving force of sintering. The fracture surface of sintered specimens of granules A is an example of the low-density region surrounding a large flaw (Fig. 8). Such regions were also often observed in the ZTAs fabricated using granules B. Large flaws such as hollows which are not completely removed during compaction could become an origin of fracture in the sintered samples, as demonstrated in Fig. 8. Isostatic pressing at high pressure could have been effective in reducing the number of large hollows throughout the compact and may have contributed to the higher strength, particularly in ZTAs fabricated using granules B.

The level of porosity near the surface region of sintered specimens could be represented by the hardness values. Vickers hardness of sintered ZTAs as a function of compaction condition is given in Fig. 9. The tendency of hardness changes generally agrees with the trends of sintered density and strength with respect to the compaction conditions, i.e., higher values for isostatically formed samples compared to the uniaxially compacted ones for granules B, and a small difference in the values between the compacts pressed isostatically and uniaxially for granules A. In addition, the hardness of ZTAs made of granules A is higher than that of ZTAs prepared using granules B under the same compaction conditions. The high plasticity of granules A caused an effective reduction of intragranular pores in the granules near the surface of the compact, whereas brittle granules B were fractured into finer agglomerates with a certain amount of intragranular pores, as indicated in A-4 and B-4 of Fig. 4.

4. Conclusions

The sintered density and mechanical properties of ZTA were analyzed in terms of the characteristics of spray-dried granules and their compaction responses under various compaction conditions. The green density of the samples pressed uniaxially from 80 to 120 MPa varied depending on the sphericity and plasticity of granules. However, the green and sintered densities of the compacts pressed isostatically at 500 MPa were nearly constant values of 63% and 99% relative to the theoretical density, respectively, irrespective of granule properties. This indicated that the shape and properties of spray-dried granules were the dominant factors controlling the green and sintered densities of the specimens compacted in a uniaxial press, but the granule properties could be a second-order effect in comparison to the effect of isostatic pressure in determining the green and sintered properties for the specimens compacted isostatically at high pressure. The strength of sintered ZTAs was not significantly affected by the compaction pressures from 80 to 500 MPa. The fracture surfaces of sintered ZTAs showed that the fracture origin in a less densified region surrounding a large void was likely the hollows remaining after compaction.

Acknowledgment. This work was supported by the Grant No. KOSEF 95-0300-01-01-3 from the Korea Science and Engineering Foundation.

References