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Granule performance of zirconia/alumina composite powders spray-dried using polyvinyl pyrrolidone binder

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Abstract

Polyvinyl pyrrolidone (PVP) was used as a binder in spray-drying a slurry containing zirconia/alumina composite powder and its influence on granulation and granule deformability was compared with those of polyvinyl alcohol (PVA) and polyethylene glycol–hydroxyethyl cellulose cobinder (PEG–HEC). Although the most spherical solid granules were obtained from the slurry containing PEG–HEC, the granules containing PVP were the most deformable during compaction. It was apparent that a high-viscosity organic additive mixture added to the slurry resulted in highly spherical solid granules, and a low T_g of the mixture led to a high deformability. The flexural strengths of composites prepared from granules containing PVP, PEG–HEC, and PVA were 634, 578, and 468 MPa, respectively, which corresponds to the ascending order of T_g of the binders mixed with plasticizers.

Keywords: Spray-drying; Composites; ZrO_2; Strength

1. Introduction

Spray-drying is a primary processing step in producing ceramic products by dry pressing. This process consists of the transformation of an aqueous slurry into dry spherical powders, often called granules, by spraying the slurry, which contains ceramic powders, a dispersant, binder, plasticizer, antifoaming agents, and if necessary a lubricant, into a hot drying medium. There are three main advantages of granulation: the resulting powders have flowability, a high packing density, and strong compactability.[1,2] Despite these advantages, the granules often lead to internal defects, which can cause a premature fracture and low reliability of the sintered parts.[3–5] These problems arise from the fact that the granules with large internal pores do not collapse during compaction and remain after sintering. The formation of large donut-shaped open pores or deep craters is associated with the migration of ceramic particles from the interior of the granule onto its surface during the hot drying process.[3,6]

The binder is the most important ingredient for spray-drying, since the binder determines the flowability, bulk density, and compaction behavior of the granules.[7] An adequate binder for spray-drying should confer high green strength to the compact article at the lowest possible addition. The parameters controlling binder performance are the glass transition temperature (T_g), polymer backbone structure, molecular weight, viscosity, and hygroscopicity. The binders commonly used in spray-drying are water-soluble polymers such as polyvinyl alcohol (PVA),[8] cellulose,[9] polyethylene glycol (PEG),[10] and polyacrylate.[7] The selection criteria for the binder are based on its ability to form granules that readily deform during compaction, to burn-out cleanly before sintering, and to give a high compact density and strength. In addition, to prevent a hard granule surface from forming, the binder should undergo minimal migration onto the granule surface while spray-drying the powder.[6]

Polyvinyl pyrrolidone (PVP) is a water-soluble polymer with amide groups, which is thermally crosslinked into a three-dimensional molecular network that becomes thermally stable after crosslinking.[11] PVP evaporates without leaving a residue during binder burn-out[12] and low-molecular weight PVP acts as a plasticizer when the humidity is high, since its T_g decreases as the relative humidity increases.[13] PVP has been

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successfully used as an additive for the formation of crack-free thin films, such as $BaTiO_3$,[14] TiO_2[15] and CeO_2[16] as a dispersant for the production of Al_2O_3 hollow fiber membrane[17] and hydroxyapatite tapes[18] and as a binder for aqueous-based alumina tape casting.[19] In this study, PVP was used as a binder for spray-drying zirconia/alumina composite powders, and the granule properties were compared with those spray-dried using the PEG–hydroxyethyl cellulose (HEC) cobinder and PVA.

2. Experimental procedure

ZrO_2/Al_2O_3 composite powder was prepared by adding 20 vol% Al_2O_3 to (Y,Nb) – TZP with a composition of 90.24 mol% ZrO_2, 5.31 mol% Y_2O_3, and 4.45 mol% Nb_2O_5, as reported elsewhere.[20] Slurries containing PVP consisted of 30.0–35.0 vol% composite powders, 0.175–0.4 wt% ammonium polyacrylate as a dispersant (Duramax D-3005; Rohm & Haas, Philadelphia, PA), 0.25–0.75 wt% triethylene glycol (TEG) (MW: 150; Yakuri, Osaka, Japan) as a plasticizer, and 0.5–1.5 wt% PVP (MW: 1,300,000; Aldrich, Milwaukee, WI) in the composite powder. To compare binder performance, two slurries containing 1.0 wt% cobinder of 0.7 PEG (MW: 200; Yakuri)-0.3 HEC (200–300 cps; Tokyo Kasei, Tokyo, Japan) and 1.0 wt% PVA (MW: 35,000; Aldrich), with 0.5 wt% PEG as the plasticizer, were prepared. Before adding the binders, all the binders were dissolved in distilled water at 80 °C to prepare 10 wt% binder solutions.

The floc sizes of the composite powder were determined using a particle size analyzer (LS230; Beckman Coulter, Miami, FL). For the measurements, the amount of solid loading in the slurry was fixed at 30 vol%. The viscosities of the organic additives were measured as a function of the shear rate between 1 and 225 s^{-1} using a viscometer (DV-III + rheometer; Brookfield Engineering Laboratories, Stoughton, MA) at 25 °C. The organics were 0.7 wt% PEG–0.3 wt% HEC, 1 wt% PVP–0.5 wt% TEG, and 1 wt% PVA–0.5 wt% PEG solutions. The glass transition temperature (T_g) of the organic additives was measured using differential scanning calorimetry (DSC2010, TA Instruments, New Castle, DE). The samples were heated at a heating rate of 10 °C min^{-1} under nitrogen atmosphere, quenched at a maximum cooling rate, and then reheated at the same heating rate used in the first scan. T_g was determined at the midpoint of the transition region in the second run.

Before spray-drying, the slurry formulations were ball-milled for 24 h, and then spray-dried using a disk-type spray dryer (DCR-2; Sakamoto, Nagasaki, Japan), when the inlet and outlet temperatures were set at 200 and 150 °C, respectively. After completing the spray-drying, only granules sieved smaller than 100 mesh (149 μm) and larger than 325 mesh (44 μm) were collected. To prepare sintered specimens, the granules were pressed isostatically into plates at 175 MPa and sintered for 5 h at 1550 °C. The sintered density of the specimens was measured using the Archimedes method and the flexural strength was determined as the average of 4-point flexure testing of five specimens whose dimensions were 3 mm × 4 mm × 40 mm.

3. Results and discussion

In general, the powder content in the slurries used for spray-drying ranges from 20 to 40 vol%.[6] The degree of dispersion of the slurry changes the yield stress of the slurry and subsequently governs the shape of the sprayed granules.[3] For solid spherical granules the yield stress needs to be high, which can be attained from a high-solids-content slurry, a low-deflocculent slurry, or a high-viscosity-grade binder.[3,6] In Fig. 1, the influence of the amount of ammonium polyacrylate dispersant on the dispersion of the composite powders was delineated by measuring the floc size as a function of the dispersant concentration. When the amount of dispersant exceeded 0.3 wt%, the slurries were completely dispersed and the mean floc size was about 0.6 μm, which corresponds to the average particle size of the composite powder. On the addition of dispersants below 0.3 wt%, the powders started to flocculate and the mean floc size increased as the amount of dispersant decreased. At 0.25 wt% dispersant, the mean floc size was about 2 μm, which corresponds to the size before complete dispersion. Slurries containing below 0.2 wt% dispersant could not be sprayed because the viscosity was too high.

The influence of the amount of dispersant on granule shape is shown in Fig. 2(a) and (b) where the amounts were 0.25 and 0.3 wt% of the composite powder, respectively. The slurry compositions were fixed to 32.7 vol% solid loading, 1 wt% PVP binder, and 0.5 wt% TEG plasticizer. The slightly flocculated slurry prevented the particles from being dragged to the surface to form a shell during the evaporation of water, leading to the solid spherical granules in Fig. 2(a). In contrast, the granules prepared from well dispersed slurries have donut-shaped features (Fig. 2(b)). These hollow granules resulted from the formation of a solid shell by drawing the finely dispersed powders from the droplet interior to the droplet surface along with capillary-

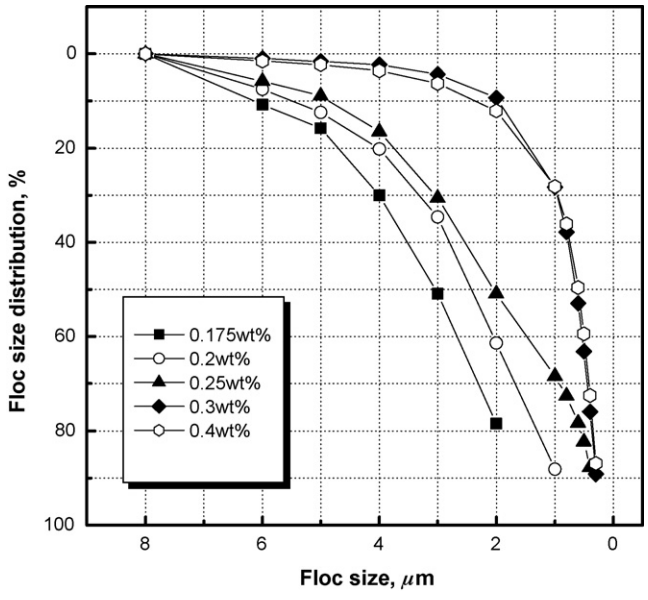

Fig. 1. Variation of the floc size distribution of the zirconia/alumina composite powder with the addition of ammonium polyacrylate.

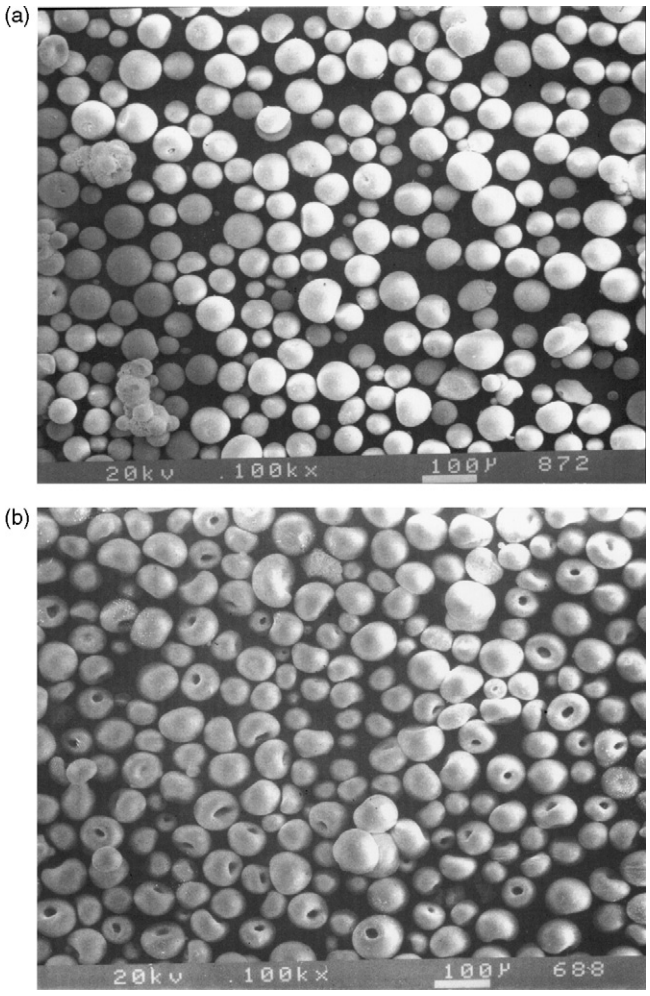

Fig. 2. Granules prepared by spray-drying slurries containing (a) 0.25 wt% and (b) 0.3 wt% ammonium polyacrylate dispersant.

induced moisture flow during drying.[3] The hollow granules have a lower average density and a lower packing density.[5]

Hollow granules tend to form when the binder content is relatively high, the solid loading in the slurry is relatively low, and the inlet temperature is relatively high.[21] In this study, the optimum PVP content for the solid granule shape was determined to be 1.0 wt% of the composite powder in a slurry consisting of 32.7 vol% solid loading and 0.25 wt% dispersant. When the amount of binder was increased to 1.5 wt%, hollow granules were produced probably due to segregation of the excess binder to form a tough droplet surface with low permeability.[6] Internal evaporation caused the formation of a vapor bubble, and the donut-shaped granules formed when the bubbles broke.[6,21] Hollow granules were also formed as the amount of the binder was lower to 0.5 wt%, probably because the yield stress of the slurry containing 0.5 wt% PVP does not exceed the critical value for the formation of solid granules.[3] When the solid loading was lower than 32.7 vol%, a considerable fraction of the granules had craters on the granule surface. Conversely, the slurry containing more than 32.7 vol% composite powder could not be sprayed because the viscosity was too high. Typical granule shapes obtained from the slurry with the optimal composition

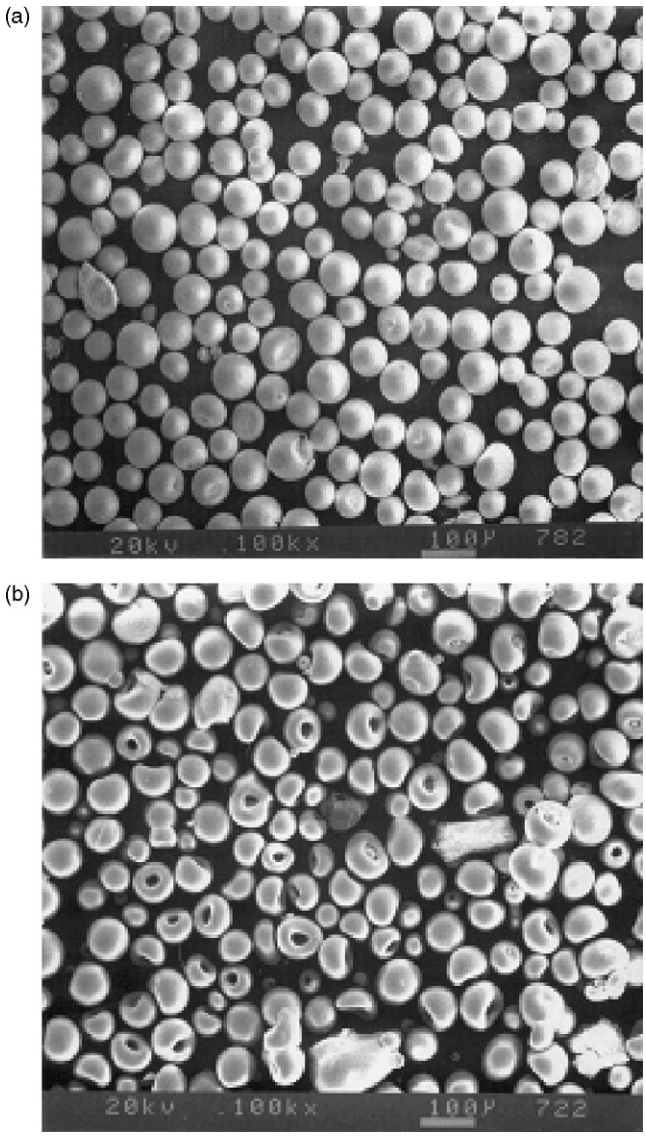

Fig. 3. Granules prepared by spray-drying slurries containing (a) 0.7 wt% PEG–0.3 wt% HEC cobinder and (b) 1.0 wt% PVA and 0.5 wt% PEG.

are shown in Fig. 2(a). To compare the influence of binders on granule properties, the slurry composition was fixed at 32.7 vol% powder, 0.25 wt% dispersant, 1 wt% binder, and 0.5 wt% plasticizer throughout this study.

It has been reported that the cobinder of 0.7 PEG–0.3 HEC results in solid spherical alumina granules, which result in high compaction and high sintered density.[9] Indeed, the zirconia/alumina composite granules spray-dried using the slurry containing the 0.7 wt% PEG–0.3 wt% HEC cobinder in the composite powder had a solid spherical shape, as shown in Fig. 3(a). Conversely, the slurry containing 1.0 wt% PVA and 0.5 wt% PEG produced hollow granules, as shown in Fig. 3(b). The granule shape depends on the binder migration as the moisture within the droplet interior is evaporated.[6] Since the migration is affected by the viscosity of the binder solution mixed with the plasticizer, the viscosities of 10 wt% binder solutions of PEG–HEC, PVA–PEG, and PVP–TEG were measured; the results are shown in Fig. 4. The high-viscosity of the PEG–HEC solution resulted

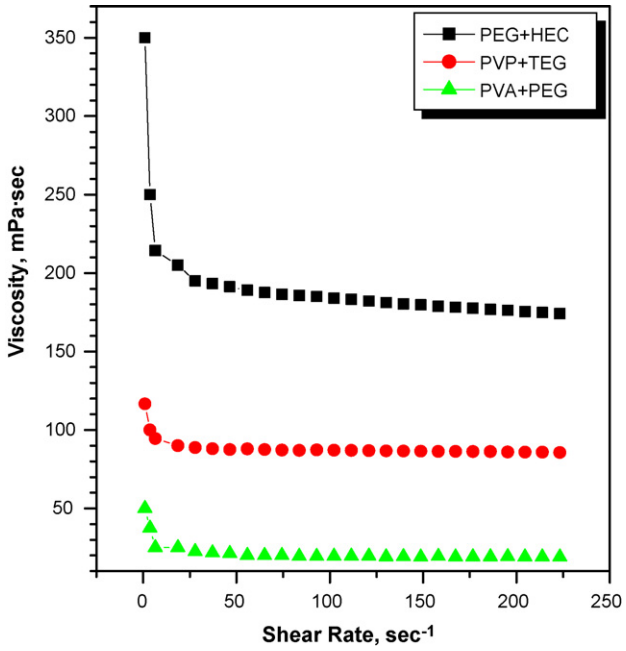

Fig. 4. Viscosities of binder solutions consisting of 0.7 wt% PEG–0.3 wt% HEC, 1.0 wt% PVP mixed with 0.5 wt% TEG, and 1.0 wt% PVA mixed with 0.5 wt% PEG as a function of shear rate.

from the stiff hydrocarbon backbone structure of the cellulose and might lead to a uniform distribution of the binder in the droplet during drying.[6] In contrast, the low-viscosity PVA having the flexible vinyl backbone and the low-molecular weight (MW: 35,000) readily migrated to the droplet surface to form a low permeability surface and hollow granules formed as the vapor bubble confined within the surface collapsed. The viscosity of the solution containing PVP was intermediate even though PVP has the same vinyl backbone as PVA. This is because the molecular weight of PVP (MW: 1,300,000), used in the present study, was much higher than the PVA. Thus it is obvious that in the fixed amounts of solid loading and dispersant, a high-viscosity of migrating liquid tends to form solid granules.

Fig. 5(a)–(c) show the influence of the amount of PVP on granule fracture after compaction at 175 MPa, where the amount of TEG was varied to maintain a PVP/TEG weight ratio of 2. When the binder content was below 1.0 wt%, the compacts were fractured completely, so that no granule boundaries were observed regardless of the granule shape, as shown in Fig. 5(a) and (b). Conversely, the majority of the boundaries of granules containing 1.5 wt% PVP were not fractured, as shown in Fig. 5(c). The increased binder concentration on the granule surface resulted in a granule with a rigid surface that resists fracture and deformation during compaction since the deformability of the granules depends on the stiffness of the granule surface.[6] Nevertheless, the granules containing 1 wt% cobinder and PVA were not fractured completely after compaction, as shown in Fig. 6(a) and (b), respectively. The degree of granule fracture increased in the order PVA, 0.7 PEG–0.3 HEC, and PVP. It has been reported that the granule deformability depends on the T_g of water-soluble binders[22,23] and the granule size distribution.[23,24]

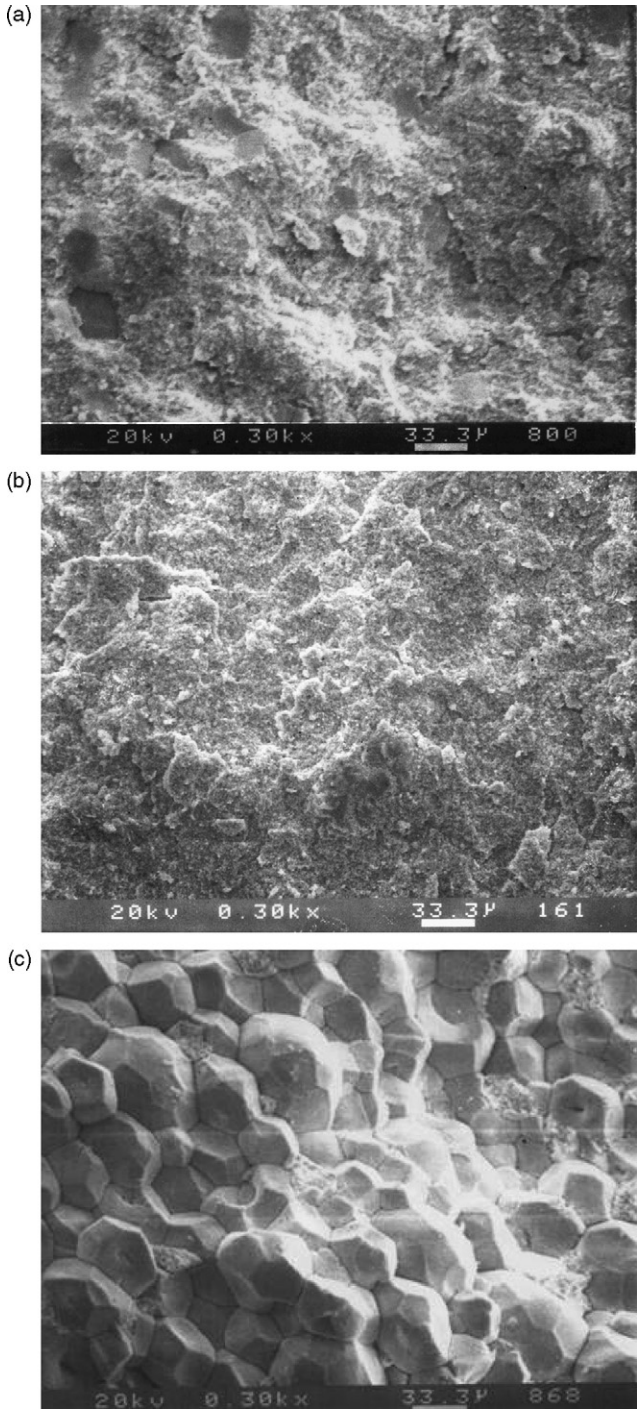

Fig. 5. Fracture surfaces of granule compacts prepared by spray-drying slurries containing (a) 0.5 wt%, (b) 1.0 wt%, and (c) 1.5 wt% PVP binder. The weight ratio of binder to TEG plasticizer was fixed at 2.

The T_g of 10 wt% PVA and PVP solutions mixed with the plasticizers and 10 wt% 0.7 PEG–0.3 HEC solution were measured; the results are listed in Table 1 along with the T_g of 10 wt% PVA and PVP solutions only. It is apparent that the fracture of granules is not related to the T_g of the binders directly, but to the T_g of the organic mixtures. This is because the brittleness of the granule surface is not determined by the T_g of the binder, but by that modified with the addition of plasticizers.

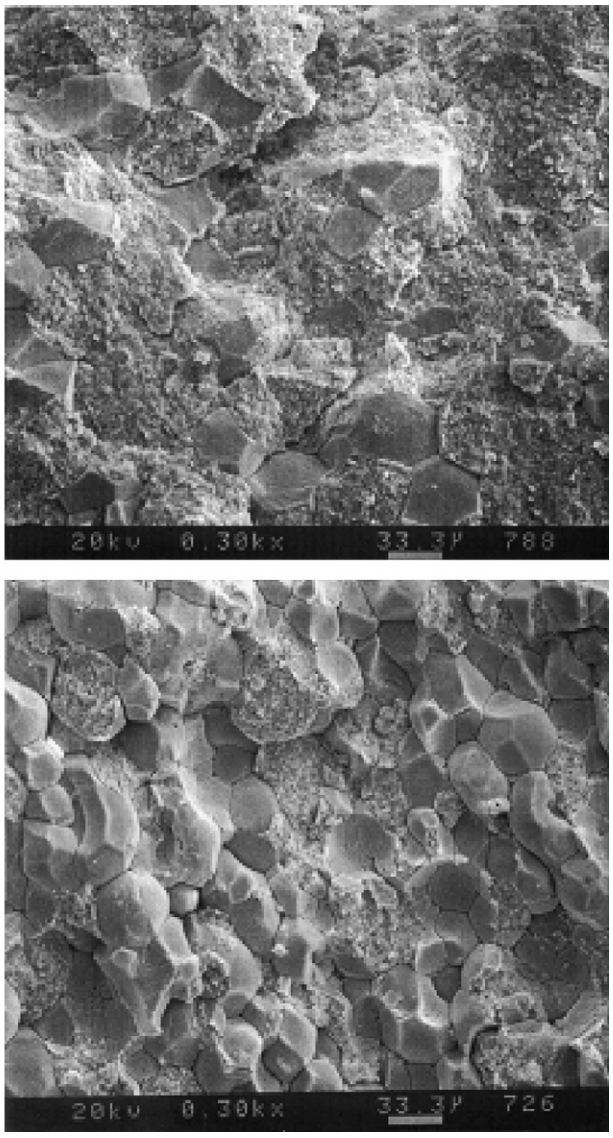

Fig. 6. Fracture surfaces of granule compacts prepared by spray-drying slurries containing (a) 0.7 wt% PEG–0.3 wt% HEC and (b) 1.0 wt% PVA mixed with 0.5 wt% PEG.

The unbroken granule boundaries form intergranular pores after sintering of compacts pressed from spray-dried granules, which become the major strength-limiting defects in sintered ceramics.[23–25] To investigate the influence of the binders on the flexural strength, zirconia/alumina granule compacts containing PVP, PEG–HEC, and PVA were sintered; the density and flexural strength are compared in Table 2. The densities

Table 1
Glass transition temperatures, T_g, of 10 wt% solutions of various binders and binders mixed with plasticizers

Organics	T_g (°C)
PVP	30.2
0.7PEG–0.3HEC	10.0
PVA	23.8
1.0 PVP–0.5 TEG	−17.6
1.0 PVA–0.5 PEG	18.2

Table 2
Bulk density and 4-point flexural strength of zirconia/alumina composites spray-dried using slurries containing various binders

	PVP	0.7 PEG–0.3 HEC	PVA
Density (g cm^{-3})	5.595	5.539	5.517
Strength (MPa)	634	578	468

correspond to 99.7, 98.7, and 98.3% of the theoretical density (5.612 /cm^3) of the 80 vol% zirconia/20 vol% alumina composite and are closely related to the deformability of the granules containing the binders shown in Figs. 5(b), 6(a), and (b). This is because the persistent granule boundaries, which did not adjoin during compaction, remain as intergranular pores even after sintering, resulting in a low density. The intergranular pores become crack-like defects from shrinkage lower than the surrounding material during sintering.[24,25] The size of strength-limiting flaws

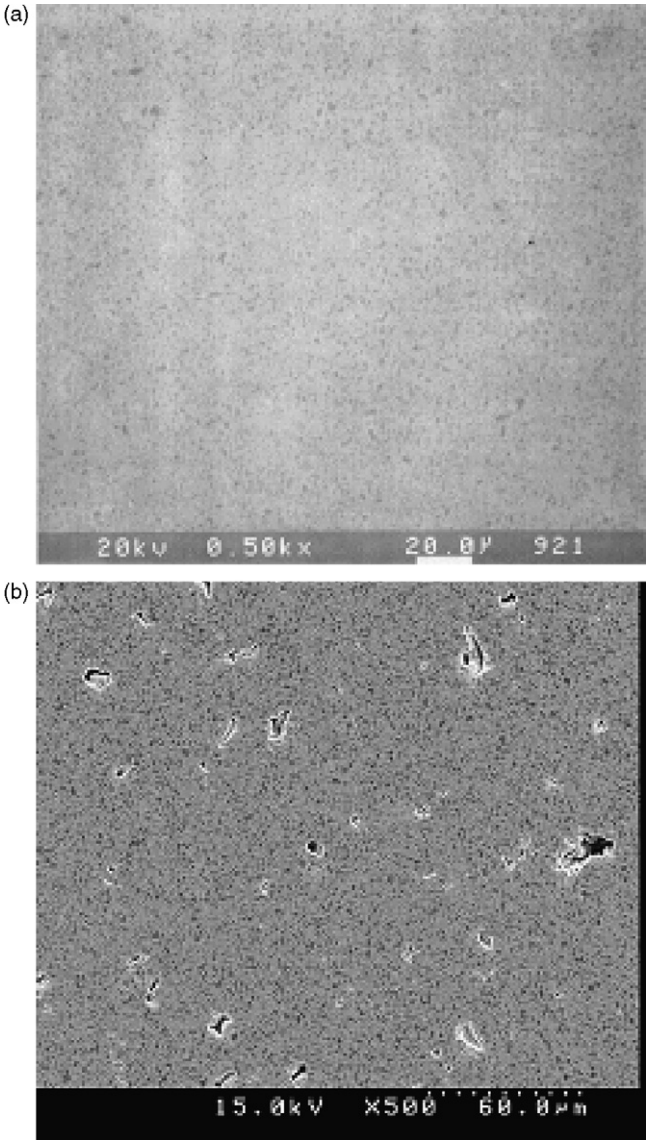

Fig. 7. Polished surfaces of sintered granule compacts prepared by spray-drying slurries containing (a) 1.0 wt% PVP mixed with 0.5 wt% TEG and (b) 1.0 wt% PVA mixed with 0.5 wt% PEG.

is inversely related to the deformability as indicated in Fig. 7(a) and (b), so that the strength is highest for the composite prepared from the granule compact containing PVP and lowest for the composite in which PVA is involved. Therefore, the strength of the composites is proportional to the deformability of compacts formed by using granules with a controlled size distribution. This supports the postulate that the strength of the ceramics is governed not by the granule morphology, but by the deformability of the granule surface zone.[11,25]

4. Conclusions

Highly deformable solid spherical granules of zirconia/alumina composite powder were obtained from a slightly flocculated slurry containing 32.7 vol% solid loading, 0.25 wt% ammonium polyacrylate dispersant, 1.0 wt% PVP binder, and 0.5 wt% TEG plasticizer. The sphericity of granules was improved as the viscosity of binder solution mixed with plasticizer increased, and the deformability of the granules was enhanced as T_g of the solution decreased. The flexural strength and sintered density of zirconia/alumina composites were proportional to the deformability, and the composite prepared using the slurry containing the PVP binder had the highest strength and density of 634 MPa and 99.7% TD, respectively.

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