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Mechanical properties of flo-deflocculated and milled powders in the $Al_2O_3/ZrO_2(CeO_2)$ system

M. BURELLI, S. MASCHIO
University of Udine, Department of Science and Chemical Technology-via Cotonificio 108, 33100 Udine, Italy

S. MERIANI
University of Trieste, Department of Materials Engineering and Applied Chemistry-via A. Valerio 2, 34127 Trieste, Italy

Samples of alumina, zirconia and their mixtures were prepared using powders produced by two different processes. The first process only involved the flo-deflocculation of diluted suspensions whereas the second required two steps, first flo-deflocculation and then ball milling of the slurries. Materials comprising a matrix containing a relatively small quantity of the dispersed phase (20 vol% and 80 vol% ZrO_2) show better properties when they are produced from flo-deflocculated powders. When samples contain a large quantity of the dispersed phase, milling after flo-deflocculation is beneficial because it provides better homogeneity, which provides greater density and strength although toughness is not significantly improved.

1. Introduction

Among structural ceramics, alumina and zirconia have been the subject of many successful research programmes aimed at identifying their properties both at room temperature and at higher temperatures. Zirconia has also been a very popular focus of research in materials science and engineering because of its electrical properties and transformation toughening features.

Alumina has a very high hardness and a good strength but a low toughness whereas zirconia has a high strength, good toughness but a relatively poor hardness. The addition of a dispersed phase based on tetragonal ZrO_2 solid solutions may enhance the toughness and strength of alumina, due to its stress-induced, tetragonal–monoclinic transformation [1–4]. It has also been observed that a relatively small quantity of alumina can be added to powders of partially stabilized zirconia to make monoliths with strength, toughness and hardness characteristics higher than those exhibited by the pure zirconia matrix because the grain size remains much smaller [5–7] throughout the sintering process.

In both cases, the dispersed phase accounts for less than 20 vol% of the mixture. In contrast, studies of alumina and zirconia blends containing a large quantity, i.e. 40 to 60 vol% of the dispersed phase are less frequently reported in the literature [8–9].

The aim of this investigation was to gain a deeper insight into a specific kind of ceramic composite: alumina and zirconia blends which require the mixing of two powders. Mixing can be performed by the colloidal method, involving the mixing of two compatible dispersed states. The colloidal approach presents several problems because many dispersions are not compatible and mixing can cause spontaneous flocculation. Furthermore both during and after mixing, sedimentation may result in phase separation. If compatibility of the dispersed states is maintained then mixing will be successful and the homogeneity of the mixture can be preserved by subsequent flocculation.

Spontaneous agglomeration can be avoided in a colloidal system by introducing electrostatically repulsive forces between particles that can be consolidated by natural or forced sedimentation. It was assumed that if agglomeration could be avoided, the uniformity of the consolidated state would reflect the uniformity of the colloidal state.

Mixing can be performed using diluted or concentrated suspensions. Diluted suspensions are preferred when a small quantity of dispersed phase must be introduced into the matrix [10, 11] and concentrated suspensions are used if a homogeneous mixture of components in nearly similar weight proportions is to be produced [12]. In the former case, the minority phase is dragged by the matrix during flocculation and in the latter the high solid content of the suspension prevents the segregation of either component [13–18].

Conventional techniques for preventing segregation fall into the following categories: agglomeration, high solid fractions, high viscosity and high consolidation rates. In agglomeration, interparticle surface forces are manipulated so that flocculation overcomes differences in the sedimentation rates of individual particles and allows them to drop together. However within a suspension containing a large fraction of solids, high viscosity may inhibit segregation by opposing resistance to particle motion in the liquid medium.

In the present investigation, samples of alumina, zirconia and their mixtures were prepared using powders produced by two different processes. The first process involved only the flo-deflocculation of diluted suspensions whereas the second required two steps, first flo-deflocculation and then ball milling of the slurries containing a large fraction of solids added with an organic binder.

The effects of the different processing routes were evaluated by measuring strength, toughness and hardness for the two series of samples.

2. Experimental procedures

Commercial-grade alumina (Sumitomo AKP15) and zirconia powders (Tosoh 12Ce-PSZ) were used as the starting materials which were weighted in appropriate proportions to produce mixtures containing 20, 40, 60 and 80 vol% of zirconia in alumina. All powders were dispersed in de-ionized water to which sufficient HCl had been added to obtain a pH of 2.5 and to stabilize suspensions containing 5 vol% of solid phase. These suspensions were stirred for 30 min, aged 3 h, stirred for a further 30 min and flocced at pH 8 by adding NH_4OH.

The clear supernatant was removed and the flocced powder was washed several times with water to remove the ammonium chloride ions. All wet mixtures were divided into two batches. One batch was then dried. Sufficient water was added to the other batch to make a slurry with 50 vol% of solid and the batch was then milled 2 h with zirconia (Y-TPZ) balls in plastic jar with 3 wt% of an organic binder (Resicel V2, F.lli Lamberti).

The dry powders were sieved through a 100 μm screen, uniaxially pressed at 50 MPa then isostatically pressed at 200 MPa and formed into bars. Green samples were fired in a muffle furnace for 1 h at 1550 °C using a heating rate of 10 °C min^{-1}. Density was measured by the water displacement method.

The breaking load was measured in a four-point bending jig (20 mm inner, 40 mm outer spans) and the mean value of 10 tests was reported as the sample strength. The hardness was evaluated by the Vickers indentation method applying a load of 100 N. Crystal phases were identified by standard X-ray diffraction methods using Co radiation. The toughness was measured by the ISB (indentation strength in bending) method [19]. The microstructure was examined by means of a Leica stereoscan scanning electron microscope (SEM).

3. Results and discussion

The relative densities of samples prepared from the flo-deflocculated powders and from the milled powders are reported in Fig. 1. It may be observed that specimens obtained from milled powders reached higher densities than those achieved by samples prepared with flo-deflocculated mixtures, except for pure zirconia.

Both curves show that the greater the quantity of zirconia, the higher the density. At the selected sintering temperature zirconia reaches a density close to the theoretical value. Alumina would require higher temperatures or a longer soaking time to do so. For this reason zirconia-rich samples exhibit relative densities higher than those evidenced by alumina-rich samples. It may also be noted that samples containing 80 vol% alumina and 20 vol% zirconia are less dense than pure alumina because when a small quantity of zirconia is added to alumina, it may act as an anti-sintering aid, as has been reported by Lange and Hirlinger [10].

The greatest difference between powders obtained using either process is observed when the percentages of the two components are comparable, i.e., in the 40–60 vol% of zirconia range. At such concentrations, the flo-deflocculation method is less efficient, as is reported in Fig. 2 where the microstructure of a sample containing 60 vol% ZrO_2 shows large regions of segregated Al_2O_3 and ZrO_2.

This evidence proves that segregation may occur during the flocculation step and that further milling substantially improves phase dispersion, as shown by the higher density of milled samples of the same com-

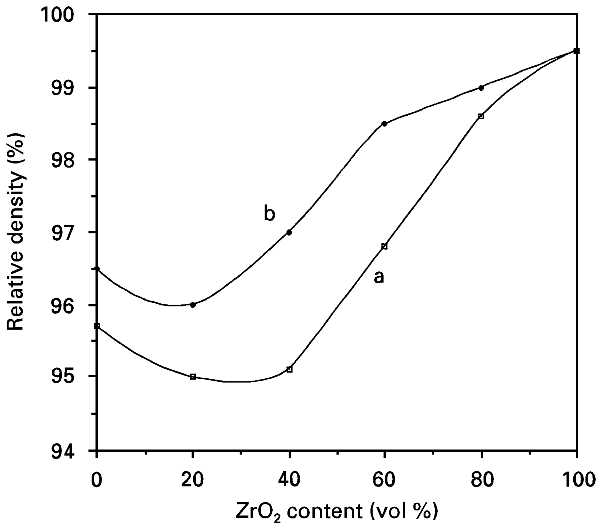

Figure 1 Relative density as a function of composition of the samples obtained from flo-deflocculated (curve a) and flo-deflocculated and milled powders (curve b).

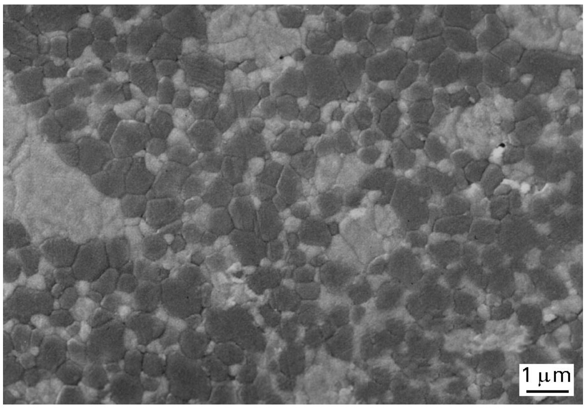

Figure 2 SEM micrograph of a sample containing 40 vol% Al_2O_3 and 60 vol% ZrO_2 produced with flo-deflocculated powders.

position. The microstructure of a sample containing 60 vol% of ZrO_2 prepared with powders milled after deflocculation is reported in Fig. 3.

This result can be explained if we bear in mind that milling is carried out on slurries containing an elevated quantity of solid and in the presence of an organic binder since both contribute to increased viscosity. In a highly viscous suspension the milling effect of the grinding balls may be somewhat reduced but particle reaggregation is also lessened, as has been reported by Roeder *et al.* [12].

The strengths of samples prepared by both methods are reported in Fig. 4. Samples containing a relatively small amount of the second phase (20 and 80 vol% ZrO_2) exhibit a higher strength when made of flo-deflocculated powders. Those containing 40–60 vol% ZrO_2 show higher strength when produced with powders milled after flo-deflocculation. This feature is due to the better dispersion of the components, which prevents agglomeration and the subsequent formation of pores and flaws within the sintered body. It is worth pointing out that single-phase samples exhibit the same strength values regardless of whether they have been flo-deflocculated or milled.

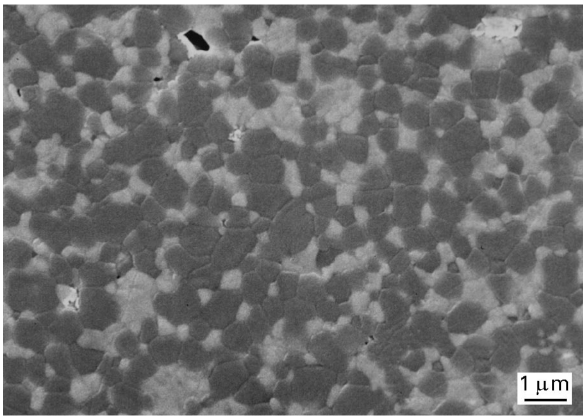

Figure 3 Microstructure (SEM) of a sample containing 40 vol% Al_2O_3 and 60 vol% ZrO_2 produced with flo-deflocculated and milled powders.

The strength data of 20 and 80 vol% ZrO_2 appear to be in conflict if they are correlated with the density data reported in Fig. 1. Less dense samples made from flo-deflocculated powders show higher strength whereas milled-powder samples exhibit lower strength despite their higher density.

The explanation for this apparent paradox lies in the fact that milling causes a marked reduction in zirconia grain size. This size reduction improves the density but not the transformability of the tetragonal zirconia grains. It is well known that tetragonal zirconia grains do not undergo the stress-induced transition to the monoclinic form when smaller than a critical size and, when this is the case, they cannot contribute to sample strength during the fracture test.

In contrast flo-deflocculated powders contain larger tetragonal zirconia grains which can contribute to the overall sample strength, despite a lower sample density, because they are readily transformable.

This interpretation was supported by X-ray diffraction analysis applied to the fracture surfaces. After the sintering process, all samples contained zirconia in the tetragonal form whereas after the rupture test, part of the zirconia had been transformed into the monoclinic form. The fracture surfaces of samples made from milled powders exhibited a monoclinic versus tetragonal ratio of about 50% while the fracture surfaces of samples made from flo-deflocculated powders showed a higher ratio of up to 80%, which is a consequence of the better transformability of the larger zirconia grains.

It is worth pointing out that alumina grains tend to become trapped in the matrix of samples containing 80 vol% zirconia when they are prepared by flo-deflocculation and milling. As a result, alumina particles are not able to exercise their pinning effect on the zirconia matrix grains, which consequently may grow larger as in a pure zirconia body. Neither strength (Fig. 4) nor toughness (Fig. 5) are improved by the

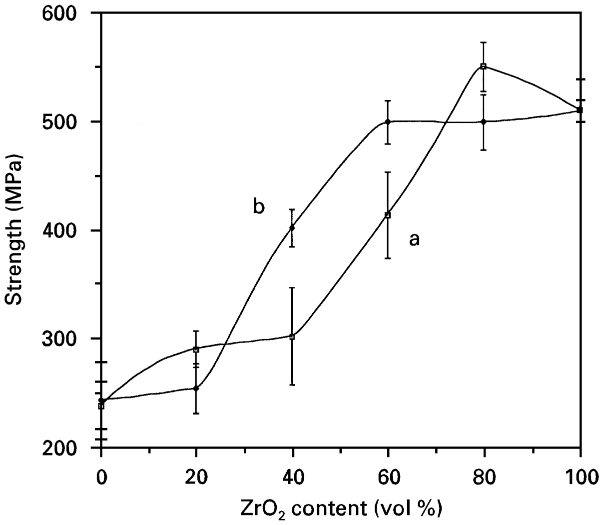

Figure 4 Strength as a function of composition for samples obtained from flo-deflocculated (curve a) and flo-deflocculated and milled powders (curve b).

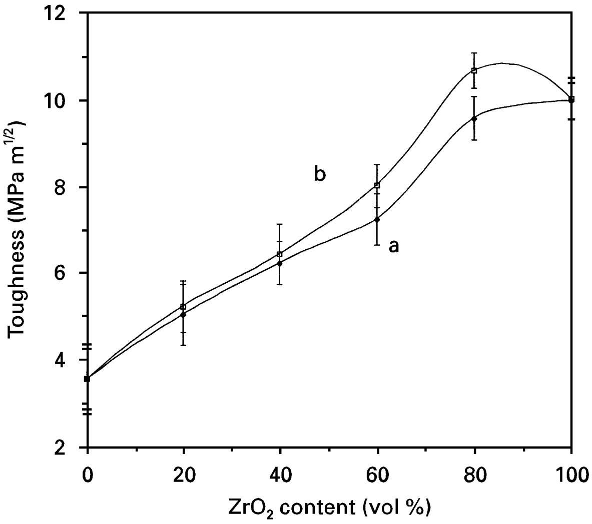

Figure 5 Toughness as a function of composition for samples obtained from flo-deflocculated (curve a) and flo-deflocculated and milled powders (curve b).

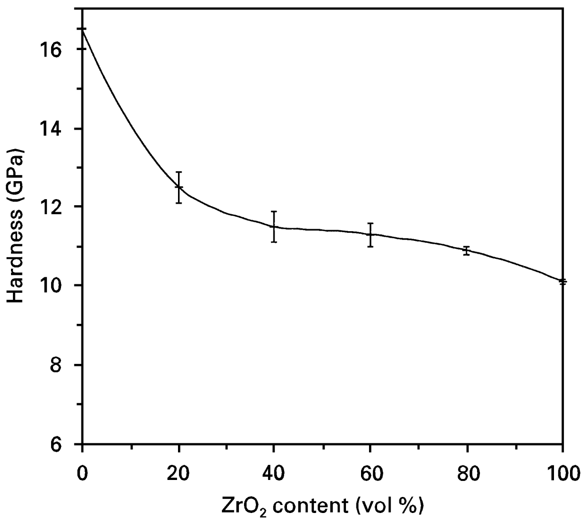

Figure 6 Hardness as a function of composition for either type of sample.

addition of 20 vol% alumina in a deflocculated and milled mixture with zirconia.

The two curves reported in Fig. 5 show that the effect of milling on toughness is less significant than for strength. The difference between the two kinds of powders is less than 10% which falls within the error bar of the measured values.

Hardness as a function of composition is reported in Fig. 6 where data could not be differentiated by powder processing type because the optical microscope is not able to perceive any reliable differences between the two kinds of samples.

4. Conclusions

Ceramic composites made of zirconia and alumina can be obtained by mixing powders by flo-deflocculation which may be followed by further ball milling. Materials comprising a matrix containing a relatively small quantity of the dispersed phase (20 and 80 vol% ZrO_2) show better properties when they are produced with flo-deflocculated powders. Further milling may cause excessive size reduction of the zirconia grains, which may not exhibit phase transformation benefits to mechanical properties.

However where samples contain a large quantity of the dispersed phase, milling after flo-deflocculation becomes a beneficial treatment because it provides a better homogeneity. This results in a higher density and in greater strength, although toughness is not significantly improved.

Acknowledgements

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