Ultrasonic Deagglomeration, and Low-Temperature Sintering of Zirconia-Alumina Nano-Composites

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Abstract

Yttria-stabilized zirconia nano-powder, which only contains extremely small uniform aggregates, was prepared using ultrasonic powder deagglomeration technique. The control of agglomeration in the nano-size powder is of utmost importance in order to obtain highly sinter-reactive ceramic. The nano-aggregates are the smallest microstructural units, which determine the resulting green microstructure and sintering behavior. The densification of the zirconia ceramic at low temperatures was possible only when a very homogeneous microstructure, i.e. a highly uniform packing of nano-aggregates was achieved in the green compacts. Using the colloidal technique and low-temperature sintering we prepared the zirconia-alumina (1-5 wt.% of γ-alumina) nano-composites. We showed that full-dense nano-grained ceramic, with average grain size of 95 nm, have been sintered at 1150 °C from hydrolytic-derived 3mol% yttria-stabilized zirconia doped with γ-alumina powder. Nanostructured yttria-stabilized zirconia ceramic was shown to reach hardness of 12.5 GPa. Addition of alumina allowed the intensification of sintering process, obtaining of finer grain microstructure, and hardness increasing to 16.2 GPa.

Keywords: Nano-technology, zirconia-alumina composites, ultrasonic deagglomeration, sintering

1. INTRODUCTION

The processing of nanostructured materials is a part of an emerging and rapidly growing field referred to as Nanotechnology. Studying in this field emphasizes the generation of materials with controlled structural characteristics, research on their processing into bulk materials with engineering properties and technological functions.[1]

Tetragonal zirconia polycrystal (TZP) ceramic attracts the major attention because of the possibility of obtaining the nano-grained bulk ceramic with controllable microstructure and improved mechanical properties.[3-11] Small quantities of alumina are known to aid densification, and have recently been shown to enhance tensile deformation in superplastic flow of zirconia ceramic. However, the exact location of the Al_2O_3 in the sintered microstructure and hence the role it plays in densification, and mechanical properties is unclear at present.[33,34]

It has been shown earlier that agglomeration with a very open arrangement of crystallites develop the large pores or pore clusters during sintering. On the other hand, closely packed agglomerates may undergo preferential intra-agglomerate sintering over inter-agglomerate sintering and pull away from neighboring particles, leaving large voids which are difficult to eliminate.[1, 5-19, 30-33, 35-40] The densification of zirconia (3Y-TZP) ceramic at low temperature is only possible when a highly uniform packing of nano-aggregates can be achieved in the green compact.[1-30] To achieve this, the minimization of the agglomeration became the first aim of this study.

Particle agglomeration is a natural result of the dominant effect of interparticle forces when the particle size is less than 1 μm. Agglomeration refers to adhesion of particles to each other because of van der Waals forces of attraction, which is significantly larger in case of nanoparticles. If weak forces hold the nano-size particles together, the agglomerates are referred to as soft agglomerates. Those agglomerates can be easily redispersed in a suitable liquid medium or breaking up in the dry state. In contrast, strong forces due to dissolution-reprecipitation during synthesis and post-synthesis treatment at the contact regions, which form necks, and (or) subsequent solid necking due to pre-sintering (high-temperature calcination) result in hard agglomerates.[4-21] For these reasons, nano-sized powders readily agglomerate during processing. Once the nano-powder is hardly agglomerated, the strength of the dried agglomerate is too high to realize the benefits of the nano-size primary crystallites.

The ultrasonic treatment is very effective in dispersing powder slurries.[7, 16] In liquids, ultrasonic waves induce pressure waves, which generate cavities. The size of cavities oscillates around a constant value, and bubbles develop and burst at the surface of the liquid. Transient cavitation takes place at high pressure. The size of cavities oscillates around an increasing value before collapsing violently with release of much energy. High-pressure ultrasonic waves had been successfully applied to the dispersion of ceramic slurries, for colloidal processing.[20, 21] The influence of microtip ultrasonication on degree of nano-powder aggregation-agglomeration will be described in this paper. Here the agglomerates indicate the assembly of particles held together by forces weak enough to be overcome by reasonable means such as ultrasonic irradiation, media-milling, etc.; whereas aggregates indicate the assembly of particles held together by forces which cannot be overcome by reasonable means.[7-15]

Controlling powder dispersion in suspensions effectively improves the sintered microstructure of ceramic because powder dispersion greatly influences the

consolidated compact density and green microstructure.[2] Although the preparation of a fine microstructure is only possible by using nano-powders, redispersion is needed to properly disperse such powder, because nano-particles spontaneously agglomerate in suspensions.[25-29] The dispersion of zirconia and alumina particles in suspension is stabilized by electrosteric repulsion, which is controlled by adsorbing polyelectrolyte ionized onto the particle surface.[25-28] That's why colloidal technique coupled with ultrasonic redispersion were developed to prepare the uniform green bodies virtually free of agglomerates, which resulted in a markedly low in sintering temperature.

In this study the influences of the γ-alumina content in 1 – 5 wt% alumina-doped zirconia as far as sintering conditions of zirconia and alumina-zirconia composites on the microstructure were finally considered.

2. EXPERIMENTAL PROCEDURE

The starting reagents were zirconium oxychloride hydrous ($ZrOCl_2 \cdot 10H_2O$ (98% pure)), urea (NH_2CONH_2 (99% pure)), yttrium oxide (Y_2O_3 (>99.5% pure)) (High Purity Chemicals Co., Saitama, Japan), HCl (Kanto Chemical Co, Tokyo, Japan). All water used in the study was doubly distilled and deionized. Yttrium chloride preparation technique was described earlier.[6-8] Stock aqueous solutions of concentration 0.1 M of Zr^{4+} + 3 mol% of $2Y^{3+}$ were produced.[6-11] The mixed urea-contained sol with an initial pH =1.2 was filled in a Teflon vessel and hydrothermaly treated at 155 °C for 10h. The urea decomposed into NH_3 and CO_2 through reaction with H_2O and the sol's pH changed to ~ 8.5. The homogeneous precipitate formed was hydrous yttria-doped ZrO_2, which crystallized under hydrothermal conditions to tetragonal form.[7, 8]

The resulting products were washed with distilled water to remove NH_4Cl, and subsequently separated from supernatant by centrifuge (10,000 rpm for 5 – 60 min) until the supernatants were clear. Washing with water had been followed by ethanol washing (C_2H_5OH, 99.5% Kanto Chemical Co., Japan) with subsequent centrifuging and final slow evaporation of the residual ethanol (T= 60 °C). Each wash cycle, was followed with re-dispersion of the washed powders using an ultrasonic horn (Model USP-600, Shimadzu, Kyoto, Japan). Microtip ultrasonication was used to break up powder agglomerates in suspension.[7] The efficiency of dispersion was estimated from the evolution of the degree of aggregation-agglomeration. The efficiency was analyzed using a laser particle-size analyzer (LPSA) (Model LSPZ-100, Otsuka Electronics, Osaka, Japan). A very small amount of each powder sample was mixed with distilled water for the analysis. 6 to 8 measurements were usually made for each prepared powder sample for the sufficient reproducibility of the experimental data.

The temperature range of 450 – 800 °C, and holding time of 1 – 2 h were used for powder's calcination. Phase identification was determined from X-ray diffractometry data (XRD) (Model JDX-3500, JEOL, Tokyo, Japan). Observation via transmission electron microscopy TEM (Model JEM-2000-EX, JEOL, Tokyo, Japan) operated at 200 kV was used to determine the primary crystallite size and aggregate size distribution.

Aqueous suspensions were prepared containing 18 to 25 vol% powder of 3 mol% yttria-stabilized zirconia (3Y-TZP) and 1 to 5 wt% alumina-doped 3Y-TZP by

adding the dispersant (ammonium polycarboxylate (ALON A-6114), Toaghosei Co., Tokyo, Japan). The γ-alumina powder (Al_2O_3 NanoTek, CI chemical Co., Tokyo, Japan) was added into suspensions. All suspensions were prepared at room temperature under same conditions of mixing the powder with a magnetic stirrer and with ultrasonic redispersion. The homogeneous aqueous suspensions were obtained by mixing with a magnetic stirrer for 24 h. Before the consolidation, the suspensions were evacuated in a vacuum desiccator to eliminate air bubbles. Consolidations of the suspensions by slip casting and subsequent cold isostatic pressing (CIP) at 400 MPa were applied. The densities of the sintered bodies were measured by the Archimedes method. Relative density of zirconia ceramic was based on a 6.06 g/cm^{3}, relative densities of zirconia-alumina composites were calculated according to the wt% of Al_2O_3 in each composite.

The samples were sintered pressurelessly in air at the temperature of 1150 °C and times ranging from 2 to 50 h, in order to produce ceramic with a range of densities and grain sizes. The samples were heated at 5 °C/min to the desired temperatures, held for the prescribed times, and furnace-cooled.

3. RESULTS AND DISCUSSION

The particle size analysis (LPSA) data for the aqueous suspension of hydrolytically precipitated 3mol% yttria-stabilized zirconia (3Y-TZP) powder are shown in Fig. 1. The measured initial particle size is quite large, which implies that the secondary particles (aggregates of primary crystallites) agglomerate. The agglomerates remained in zirconia powder, which was only water-washed, dried and calcined could not be completely broken up during subsequent processing.
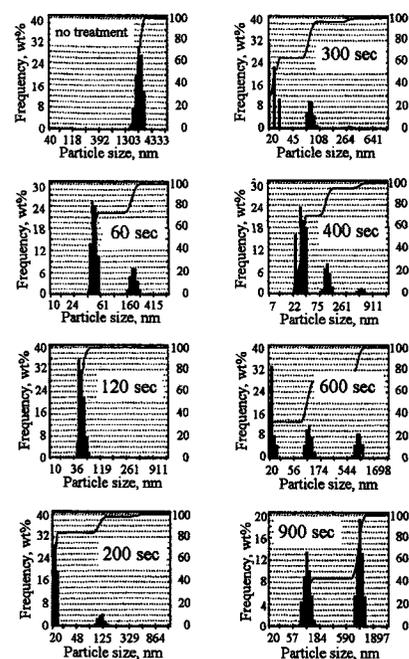
Fig. 1. Particle size distribution of 3Y-TZP powder ultrasonicated for the prescribed times.

Agglomerates of 1.5 – 3.7 μm, were present in the produced powder washed with water and ethanol without intermediate ultrasonic treatments (i.e. without debonding). It was shown that 3Y-TZP powders could be

sufficiently deagglomerated (Fig. 1) in aqueous suspension by micro-tip ultrasonic treatment applied for a specified time (~120 sec.). Extended ultrasonication, however, leads not only to the following minimization of the aggregate size, but also to reagglomeration of the powder (Fig. 1, ultrasonication time 200 – 600 sec). Long-term ultrasonication (>600 sec) reagglomerated powder.

The possible reasons why agglomerates form during preparation, and once more during ultrasonication are as follows. From capillary pressure arguments the surface tension of the water is a critical component in the bonding (agglomeration) of the neighboring particles. The capillary pressure of water for the extremely fine nano-size zirconia primary particles, which are on the order of 8 ± 4 nm in size, is extremely high. This can explain the aggregation of bounded primary crystallites and agglomeration of the aggregates during synthesis.

Long-time ultrasonication re-agglomerate the powder in suspension (Fig. 1) because of ultrasonic cavitation (produced by stress induced in the liquid media by the sound waves) provoke the high temperature and pressure (of several atmospheres). As a result, solid necking of the neighboring particles took place during cavitation bubbles implosions.
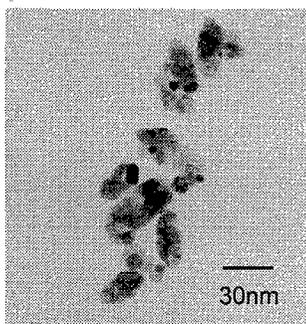
Fig. 2. TEM micrograph 3Y-TZP nanoaggregates.

To minimize necking of neighboring aggregates the calcination temperature of 560 °C was chosen.[7-10] TEM micrograph of the resulting 3mol% yttria-stabilized zirconia powder is shown in Fig. 2. Primary crystallites with average size of ~ 8 nm, are aggregated into the secondary nanoaggregates with mean aggregate size of 20–40 nm.

Aqueous suspensions with the minimum viscosity were prepared by changing the solid content and the amount of additional dispersant. Suspension's stability as far as good dispersion is the main trend of the uniform green microstructure. The high viscosity of suspensions implies the rapid flocculation of the particles in as-slipcasted suspension. Non-uniform packing leads to localized, inhomogeneous densification during subsequent sintering.

The optimum solid content of the suspension of 3Y-TZP nano-powder was found to be 20 vol%. Figure 3 shows the changes of the zirconia and alumina-doped zirconia aqueous suspensions viscosities (at the share rate of 100 s⁻¹) over the amount of dispersant. The amount of dispersant 4.5 – 5 wt% was appropriate for obtaining well-dispersed suspension from zirconia powder and from alumina-doped (1.25, 2, 2.5 and 5 wt% of γ-Al$_2$O$_3$) zirconia. At the lower or higher amount of dispersant the

suspension became too stiff for slip casting immediately or during the first 2 hours. The green densities of zirconia and alumina-zirconia composites after slip casting and slip casting with subsequent CIP are shown in Table 1.
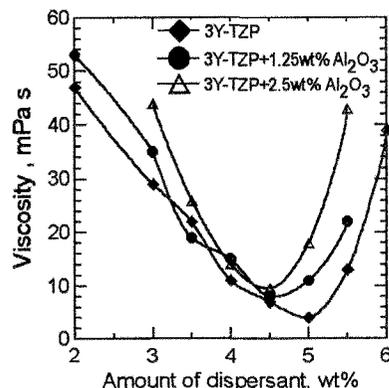
Fig. 3. Viscosity of zirconia and zirconia-alumina suspensions versus the amount of dispersant (at a share rate of 100 s⁻¹).

Table 1. Relative densities of slipcasted, and slipcasted and CIPed powder samples.

Chemical composition	Relative density of slipcasted samples, %	Relative density of slipcasted and CIPed samples, %
3Y-TZP	46	52
3Y-TZP + 1.25 wt% Al₂O₃	48	53
3Y-TZP + 2.0 wt% Al₂O₃	48	53
3Y-TZP + 2.5 wt% Al₂O₃	51	56
3Y-TZP + 5.0 wt% Al₂O₃	46	53
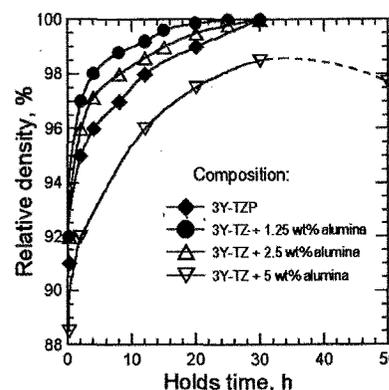
Fig. 4. Presureless sintering at constant temperature of 1150 °C.

Isothermal sintering behavior was studied at 1150 °C. The isothermal sintering results for the 3Y-TZP and alumina-doped 3Y-TZP samples are shown in Fig. 4, where relative densities are plotted as a function of the sintering time. At this temperature the grain size remained in the nano-scale range.[7, 8] The relative density of ceramic samples prepared from 3Y-TZP powder reached 91% during heating (5 °C/min) to the prescribed temperature, and 95% after 2 h holding. Densification, D = 97% was demonstrated by sintering at 1150 °C for 12 h. Sintering at 1150 °C with a longer hold of 30 h allowed to receive ceramic 99.5% dense. Addition of small amount of γ-alumina allowed the ceramic densification to be intensified in comparison with alumina-free samples. 1.25wt% Al₂O₃-doped zirconia ceramic demonstrated

99% densification after only 12 hours holds. Full-dense ceramic was obtained after 20 h hold.

The microstructure of the zirconia ceramic (3Y-TZP) sintered at 1150 °C for 30 h is shown in Fig. 5. The average grain size is about 110 nm. Figure 6 shows the SEM microstructure of the 2.5 wt% Al_2O_3 – 3Y-TZP composite sintered at a temperature of 1150 °C for 20 h. These figures coupled with Fig. 4 indicate, that the addition of nano-size γ-alumina powder increased reactivity and reduced hold time necessary for the complete densification. Addition of the alumina intensified the sintering process, shortened the sintering time and allowed the ceramic microstructure to remained in a nano-scale region. The average grain size of 1.25 and 2.5 wt% alumina-doped zirconia ceramic was 94 nm and 87 nm respectively. 3Y-TZP ceramic was shown to reach hardness of 12.5 GPa, and alumina doping increased hardness to 16.2 GPa.
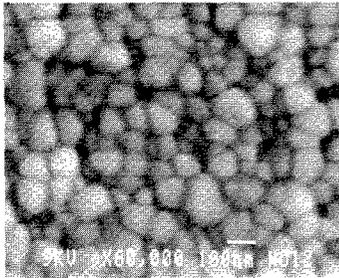
Fig. 5. SEM micrograph of 3Y-TZP ceramic sintered at 1150 °C for 30 h.
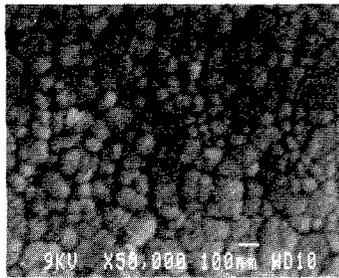
Fig. 6. SEM micrograph of 3Y-TZP + 2.5 wt% γ-alumina ceramic sintered at 1150 °C for 20 h.

4. CONCLUSION

We can conclude from this research that microtip ultrasonication is very effective in deagglomeration of zirconia nanopowder. Addition of γ-alumina intensified the sintering process. We showed that dense alumina-doped zirconia nano-ceramic was obtained by low-temperature sintering at 1150 °C.

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