

Deagglomeration of Zirconia Nano-Powder

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Abstract

Nano-particles agglomeration occurs during wet chemical synthesis of nano-size ceramic powders and during post-synthesis treatment. Agglomeration of nano-powder is the most common origin for strength limiting flaws in ceramic materials. The dispersion of powders in suspensions is important for the preparation of compacts with uniform green microstructure. Nano-size tetragonal 3mol % yttria doped zirconia powder was produced by hydrothermal precipitation from sol, which consists of metal chlorides and urea followed by washing-drying treatment and calcination. The effects of powder washing by water and ethanol with subsequent centrifuging on powder properties, as far as the possibility of tertiary agglomerates to be broken up using micro-tip ultrasonication are shown experimentally. Ultrasonication was found to be very effective in minimizing of secondary particle size, deagglomeration of the powder, re-dispersing of zirconia after all washing-centrifuging cycles and minimizing the mean aggregate size after final calcination. Uniformly aggregated tetragonal zirconia nano-powder with mean secondary particle size of ~ 40 nm and without hard agglomerates was received.

Keywords: Nano-powder, zirconia, ultrasonic deagglomeration, nano-ceramic

1. INTRODUCTION

Synthesis of advanced ceramics especially nanoparticles is one of the major fields in materials-processing technology. Monodispersed nano-particles are important material in the fabrication of ceramic having improved properties: thermal, ionic conducting, electrical, mechanical, catalytic and optical.¹⁻³ Powders production methods are still needed for synthesizing high-quality fine powders with required size, size uniformity, morphology, and composition purity.² The above characteristics of the powder determine the later-stage processing and sintering properties and the microstructure of the final ceramic materials. For example, uniform powder shape and narrow size distribution allow reducing of serious microstructural defects in sintered ceramics by enhancing the powder flow and packing efficiency during slip casting and CIP.¹⁻⁷

The densification of zirconia ceramic at relatively low temperatures is only possible when a homogeneous microstructure, i.e. a highly uniform packing of nano-size secondary aggregates of primary crystallites is present in the green compact. Although many advantages can be achieved by using relatively monodisperse powders, an additional problem, the formation of agglomerates, is present in the preparation process of nanometer powders by chemical method.¹²⁻²⁴ Minimization of the agglomeration is the subject of many research projects, in order to attain low-temperature sintered bodies with uniform nano-grained microstructure.²⁻²⁵

Formation of hydrous-zirconia particles from metal chlorides (oxychlorides) has been studied

extensively.^{8, 9, 18} However, characterization of nano-size product due to synthesis parameters and post-synthesis treatment, particularly possibility of the ultrasonic deagglomeration of as-prepared powder particles, as far as washed, dried and calcinated powder, has not been reported earlier. 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 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 sintering (high-temperature calcination) result in hard agglomerates or aggregates.^{11-15, 18-25} For these reasons, nano-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 critical parameter, which was chosen for optimization in this study, was the mean secondary aggregate size of the powder after synthesis, post-synthesis treatment and after calcination.

The ultrasonication is very effective in dispersing colloidal suspensions for slip casting.^{19, 20} In liquids, ultrasonic waves induce pressure waves which generate cavities. Stable cavitation takes place at low pressure. 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. In this case, 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.^{19, 20} The description of the influence of microtip ultrasonication on degree of nano-powder aggregation-agglomeration at different processing steep will be given in this paper.

2. EXPERIMENTAL PROCEDURE

The starting reagents were zirconium (VI) oxychloride (hydrous $ZrOCl_2 \cdot 10H_2O$ (98% pure)), urea, yttrium oxide (>99.5%) (all produced by High Purity Chemicals, Saitama, Japan) and hydrochloric acid (Kosochemical, Japan). A homogeneous aqueous solution of yttrium chloride was obtained by mixing with a magnet stirrer for 48 hours. A stock aqueous solution of concentration 0.1 M of Zr^{4+} + 3 mol% of $2Y^{3+}$ was produced and kept with a magnet stirring at 20 °C for homogenization. The 500 ml of mixed sol in which the initial pH was ~1.2 were hydrothermally treated. Each sample was filled to 80 vol% in a 250 ml Teflon vessel held in an outer pressure vessel. After the vessel had been sealed, it was placed in a drying oven in order to heat the sample to 150 °C for different times. 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. The resulting products were washed with distilled water for several times to remove Cl ions, residual ammonia and other anionic impurities 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% reagent grade, Kanto Chemicals, Japan) with subsequent centrifuging and final slow evaporation of residual ethanol ($T=60$ °C), using drying oven. After each wash cycle, the washed powders were re-dispersed in water or ethanol (depending on the processing step) using an ultrasonic horn (Model USP-600, Shimadzu, Kyoto, Japan). Microtip ultrasonication was used to break up powder agglomerates in suspension. The slurry was stirred for 10 min prior to ultrasonication. The ultrasonic apparatus consisted of a 20 kHz generator and a probe with a titanium tip. The probe was immersed 30-50 mm below the slurry surface. A range of ultrasonication times of 30 – 800 sec, at a frequency of 20 kHz and power of

160 W, was used to determine the effect on the aggregate (agglomerate) size. The efficiency of dispersion was estimated by changing of the degree of aggregation (agglomeration). The efficiency was related to the mean size of the aggregates (agglomerates). The particle size distribution was analyzed using a laser particle-size analyzer (Model LSPZ-100, Otsuka Electronics, Osaka, Japan). A very small amount of powder was mixed with distilled water for the analysis. As-dried powders were calcined in an oven. The temperature range of 450 – 900 °C, and holding time of 1 – 6 h were used for calcination. The best temperature-time regime has been chosen for the calcination. Phase identification of the oxide powders after drying and calcinations was determined from X-ray diffractometry data (XRD) (Model JDX-3500, JEOL, Tokyo, Japan). The primary crystallite size of yttria-stabilized zirconia powders was determined through an X-ray diffraction line-broadening method. The surface area was studied using the Brunauer-Emmett-Teller (BET) method (Model SA 3100, Coulter, Hialeah, FL). Observation via transmission electron microscopy TEM (Model JEM-2000-EX, JEOL, Japan) operated at 200 kV was used to determine the primary crystallite size and aggregate size distribution.

3. RESULTS AND DISCUSSION

Fig. 1 (a, b) shows, that using of urea hydrolysis method in the preparation of zirconia nano-powder, allowed obtaining of hydrous zirconia, which crystallized into a ~ 100 % purely tetragonal phase.

The degree of aggregation-agglomeration is also strongly dependent on hydrolysis time, and post-synthesis treatment: washing of the precipitate, treatment during washing, centrifuging, drying and finally the temperature-time conditions of calcination. The amount of residual chloride in the as-calcined zirconia powder is important because there is an indication that sintering starts at higher temperature when the ceramic powder contains more chloride.¹⁶

The mean particle size measurements for the aqueous suspension as a function of the number (times) of washes followed by centrifuging for yttria-zirconia precipitates hydrolyzed during 32, 20 and 10 hours are shown in Fig. 2. The measured initial particle size is quite large, which implies that the precipitate agglomerate. The mean secondary aggregate sizes decrease steadily with washing for all powder suspensions. These results suggest an increase in suspension stability due to the removing of some surface contaminations in the aqueous system. The best

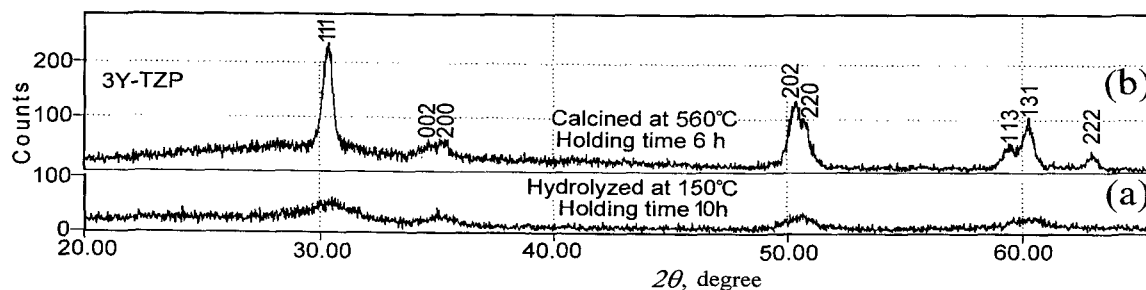


Fig. 1. XRD patterns of 3 mol% yttria-doped zirconia powders (3Y-TZP).

de-agglomeration was achieved for the powder prepared by the shortest hydrolysis. However, the washing-centrifuging treatment was useful only up to 4 times. The continuing of centrifuging, that is necessary for removing of supernatant, re-agglomerate the powder.

The agglomerates remained in zirconia powder prepared from 0.1 M urea-contained sol and only water-washed, dried and calcined could not be complete uniformly broken up during subsequent treatment. Agglomerates of 0.2 – 2.7 μm , are present in all powders obtained from solution reactions with subsequent washing with water and ethanol without intermediate ultrasonic treatments (i.e. without debonding).

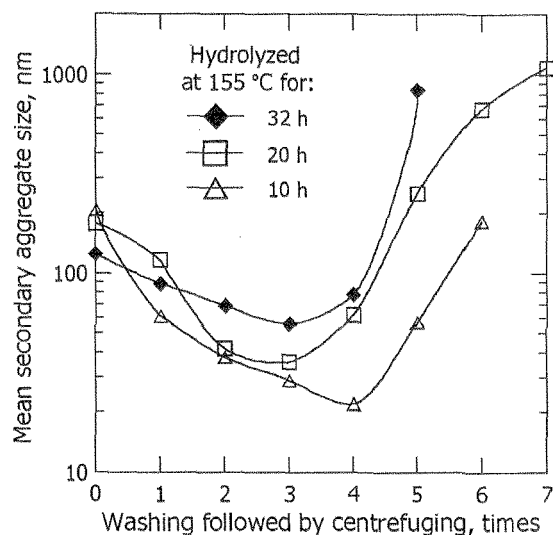


Fig. 2. Influence of hydrolyzes time and numbers of washes with subsequent centrifuging on the mean secondary aggregate size of 3Y-TZP precipitant (for optimum ultrasonication time).

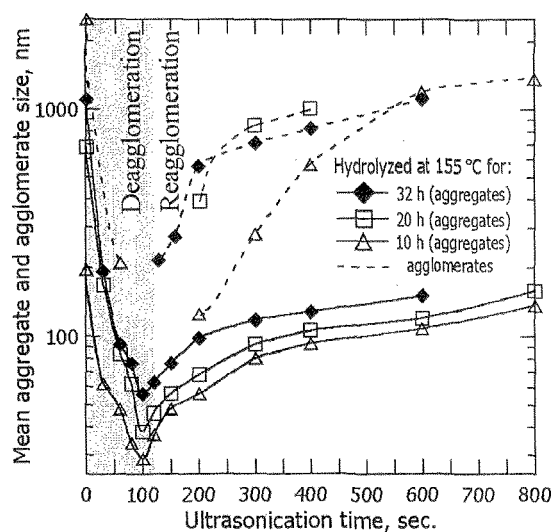


Fig. 3. Mean secondary aggregate and agglomerate size dependence on time of ultrasonic treatment.

The mean size of hydrous-zirconia aggregates and agglomerates (Fig. 3) in aqueous suspension could be

reduced by microtip ultrasonication applied during specified time of 100 ± 20 sec. The following ultrasonication, however, leads to the coarsening of the secondary aggregates and subsequent re-agglomeration of the powder. Possible reasons why tertiary agglomerates forms again are as follows. From capillary pressure arguments the surface tension of the washing liquid is a critical component in the development of agglomerates. The surface tension of water is nearly 3 times higher than that of ethanol, and the capillary pressure for water system would thus be 3 times large than that for ethanol system. The capillary pressure for the extremely fine nano-size hydrous-zirconia primary particles, which are on the order of 8 ± 4 nm in size, is extremely high. This can also explain the formation and existence of the secondary dense aggregates of such fine particles and agglomerates of such aggregates during hydrolytic precipitation and re-agglomeration due to cavitation during long-time ultrasonication, and also re-agglomeration of the superfine particles (Fig. 3) closely packed during long-time centrifuging (after removing the most of chlorides).

Finally, surface chemistry arguments suggest that the agglomeration of water-washed powders involves hydrogen bonding of surface hydroxyl groups on the precipitate. Once hydrogen-bonded, the molecule of water may bridge the surface hydroxyl groups of neighboring just synthesized particles, thus bonding the aggregates of primary particles into agglomerates.

Some difference in the situation should be described for the powder subsequently washed with ethanol. No tendency appears for bridging between neighboring aggregates of primary particles (i.e. no tertiary agglomerates are formed). Surface ethoxide groups, which formed during ethanol washing decomposed during subsequent drying at 80 °C without neck formation. However, after drying of washed powders the surface of as prepared fine powder can absorb up to ~ 3 wt.% of water (if cooling to room temperature applied). Such water amount is enough for the "water bridges" formation, the particles can be densely packed during initial stage of heating for calcination, and some solid necks usually form during subsequent calcination.

To avoid such a water bridging we did not cooled the dried powder to room temperature and started the calcination directly after drying. All the above is true if the powders were dried in an oven at a relatively low temperature (< 100 °C) and with holds at least 24 h. In such a case, drying is slow and the particle size after drying is dependent on the dispersion conditions of ethanol suspension prior to drying. Figure 4 contains the particle size distribution of ethanol-washed hydrous zirconia powder before drying: (a) 100 sec, (b) 200 sec of ultrasonic treatment, and finally, (c) 600 sec of ultrasonic treatment. We can assume, that no re-agglomeration occurs during sonication after ethanol washing. It means, that ethanol removed water from the particle's surfaces and excluded re-bonding due to water bridging. We have obtained evidence, which shows that ethanol selectively removed surface hydroxo-groups and water, and those

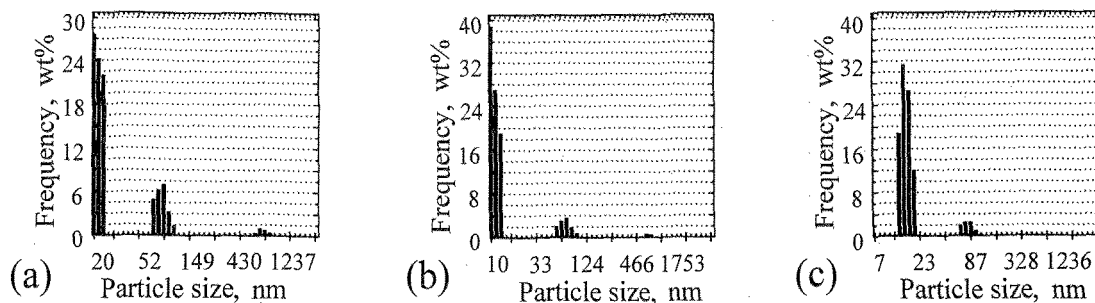


Fig. 4. Particle size distribution of hydrous zirconia powder washed and debonded with ethanol, and ultrasonicated for: (a) 100 sec, (b) 200 sec, (c) 600 sec.

removal leads to the elimination, or significant reduction of hard agglomerates.

The calcination of super-active primary particles at the temperatures higher than 600 °C usually results in formation of the solid necks between neighboring primary crystallites and due to the existence the circuits of such a necks the hard incompressible agglomerates are usually form. To avoid (or at least to minimize) the solid necking the calcination temperature of 560 °C had been chosen. Transmission electron micrograph of the resulting yttria-stabilized zirconia is shown in Fig. 5. Primary crystallites with average size of ~ 10 nm, are mainly aggregated into the secondary nano-aggregates with mean aggregate size of ~ 40 nm.

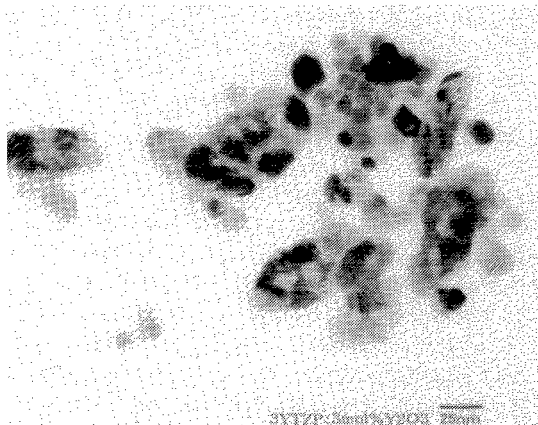


Fig. 5. Transmission electron micrograph of aggregated 3Y-TZP nano-particles. (Urea hydrolysis at 150 °C for 10 h, calcination at 560 °C for 6 h.)

4. CONCLUSION

We can conclude from this research that zirconia nano-powder obtained via described manner is well dispersed and almost non-agglomerated. The degree of zirconia nano-powder aggregation-agglomeration was successfully changed with accompanying of washing-centrifuging treatment by microtip ultrasonication. It is confirmed that microtip ultrasonication is very effective in deagglomeration of oxide nano-powders. As a result of this study, it was found to be possible to avoid the tertiary agglomeration of calcined yttria-stabilized zirconia nano-powder and to minimize the resulting secondary aggregate size close to the value of ~ 40 nm.

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