# Colloidal processing of low-concentrated zirconia nanosuspension using osmotic consolidation

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## ARTICLE INFO

## ABSTRACT

Colloidal processing was applied to a water-based suspension with 5 vol% zirconia nanoparticles of 10–15 nm in size. The nanosuspension was concentrated by evaporation or by a newly developed method of osmotic dehydration. The viscosity and stability of concentrated nanosuspensions were investigated. Osmotic consolidation of both nanosuspensions, concentrated by evaporation and osmotically dehydrated, was performed in a solution of polyethylene oxide separated from the nanosuspensions using a permeable membrane. Osmotic pressure generated a water flow from the nanosuspension to the polymer solution, concentrating the nanosuspension and eventually consolidating the nanoparticle network. The pore size distribution in dried nanoparticle compacts and pore size evolution during sintering were evaluated and discussed. The nanozirconia compacts were densified by pressure-less sintering to a relative density of up to 99.7% while maintaining the nanocrystalline structure.

## 1. Introduction

Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) are zirconia-based ceramics where most of the fine submicrometer-sized grains are stabilized to a tetragonal phase at room temperature. High strength and fracture toughness, which make these ceramics attractive candidates for many demanding applications, are the result of transformation toughening based on stress-induced tetragonal-to-monoclinic phase transformation [1,2]. Recently, extensive effort has gone into the synthesis and densification of zirconia nanoparticles and the investigation of properties of nanocrystalline yttria-stabilized zirconia ceramics [3]. The reason for such interest in nanocrystalline zirconia ceramics lies in their unique properties such as low-temperature densification [3–6], superplastic deformation [7–9], biological activity [10,11], low thermal conductivity [12], higher diffusivity [13], modified ionic and electron conductivity [12,14], and highly promising mechanical properties. Many authors have reported very high fracture toughness of yttria-stabilized tetragonal zirconia nanoceramics [15–17]. A comparative study has shown that nanocrystalline zirconia optimized from the viewpoint of grain size and yttria content can provide up to three times higher fracture toughness than submicrometer-grained 3Y-TZP [18]. The outstanding mechanical properties also make tetragonal zirconia an interesting candidate for transparent ceramics. In contrast to the less powerful cubic modification, however, high optical birefringence is the main factor which restricts the transparency of pore-free tetragonal zirconia. Klimke et al. [19] demonstrated that a mean grain size of < 40 nm and 100% tetragonal phase are necessary to obtain an in-line transmission of about 50% (at 640 nm wavelength and a thickness of 1 mm). It is believed that it will be possible to utilize the unique properties of tetragonal nanozirconia in particular applications once the processing methods allow fabricating nanocrystalline zirconia bodies with the optimal microstructure free of processing defects [15].

However, the use of nanoparticles represents one of the most challenging tasks in the field of bulk ceramics processing. Due to an inherent tendency of nanoparticles to strong agglomeration, the compacted green bodies exhibit an irregular and loosely packed structure. Such nanoparticle compacts cannot be densified to full density via pressure-less sintering while maintaining the nanocrystalline structure free of defects [4,20]. Colloidal processing of nanoparticles is a useful approach to dispersing and/or removing the agglomerates and obtaining stable and well-dispersed nanoparticle suspensions [21]. To fully exploit the advantages of colloidal processing, ceramic bodies must be formed and consolidated directly from the slurry state [22]. However, the consolidation of low-concentrated ceramic nanosuspensions brings extraordinary difficulties and the common wet-shaping techniques must be adapted to the processing of nanosuspensions. High-speed centrifugation [23,24], slip casting [25,26] or pressure

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filtration [27] were used to consolidate zirconia nanosuspensions, nevertheless, all these methods suffer from serious drawbacks. Slip casting is limited by the low suction power of the gypsum mould. The compacting pressure in slip casting usually does not exceed 0.1 MPa [28]. High-speed centrifugation and pressure filtration can exert much higher compacting pressures but, unfortunately, local differences in the compacting pressure result in inhomogeneously packed particle compacts [23,27]. Moreover, in most cases the nanosuspension had to be prepared with a reasonable concentration (in the range of 15–30 vol%), which is much higher than the usual concentration used for optimal colloidal treatment of nanoparticles.

This paper investigates an alternative method for consolidating nanoparticle suspensions into bulk ceramic bodies, using osmotic forces [29]. With the osmotic consolidation method, a nanosuspension is placed within a semipermeable membrane, which is immersed in an appropriate polymer solution. Unlike the solvent molecules, the polymer chains cannot penetrate the semipermeable membrane. The solvent from the nanosuspension passes through the membrane to dilute the polymer solution in order to equilibrate the chemical potential of the solvent on both sides of the membrane. With advancing solvent removal from the nanosuspension the nanoparticles consolidate. Osmotic consolidation has a potential for very homogeneous particle packing because osmotic pressure is generated in the solvent and the nanoparticle network responds homogeneously to this tension [30]. Polyethylene oxide is one of the most suitable polymers for osmotic consolidation because of its availability in different molecular weights, high solubility in water, and one of the highest osmotic potentials available. Using a polyethylene oxide solution, the osmotic driving pressure can reach up to 12 MPa [29,31], which is a pressure about two orders of magnitude higher than the pressure reached in slip casting, and is similar to maximum pressures used in pressure filtration. In this paper, we demonstrate that the osmotic consolidation method can successfully be used to concentrate and, in the end, consolidate the low-concentrated zirconia nanosuspension, and that the homogeneously packed green bodies can be densified via pressure-less sintering into almost fully dense bodies with nanocrystalline structure.

## 2. Experimental procedure

Zirconia nanopowder stabilized by 3 mol% yttria (MELox Nanosize 3Y, Mel, UK), supplied as a stable 5 vol% water nanosuspension, was used for the colloidal processing experiments. Prior to consolidation by the osmotic method, the zirconia suspension had to be concentrated in order to obtain a reasonably large and homogeneous nanoparticle compact. Two approaches to dehydrating the nanosuspension were applied. In the first case, the nanosuspension was concentrated by evaporation of water at a temperature of 45 °C, in the other case the suspension was osmotically concentrated in a 20% water solution of polyethylene oxide (L-8, Alroko, Japan, $M_w = 80,000$) using a cellulose tube membrane with a molecular cut-off of 3500 Da (SpectraPor 3, Spectrum Laboratories, USA). Two kinds of suspension were concentrated: as supplied untreated nanosuspension and nanosuspension treated with an addition of a dispersant, triammonium citrate (TAC) (Aldrich-Sigma, Germany). The ceramic suspensions were repeatedly dispersed for 5 min with ultrasonic homogenizer (U 400-S, IKA Labortechnik, Germany) during the dehydration (always before the rheological measurements and the final consolidation). To osmotically consolidate the concentrated suspensions, a cellulose tube membrane with a diameter of 11.5 mm and a length of 60 mm was filled with the concentrated suspension, sealed with closures, and immersed in a 20 wt% water solution of

polyethylene oxide for 72 h. The same membrane grade and polyethylene oxide as for osmotic dehydration were used. The osmotically consolidated bodies were ground to plates (10 mm × 30 mm × 2 mm), dried at a temperature of 20 °C and relative humidity of 80% until weight losses ceased, and then left to dry completely in laboratory conditions. The plates were optionally heated to 120, 600, 800, 1000 and 1050 °C, and finally sintered at 1100 °C for 2 h.

Particle size distribution in the zirconia nanosuspension was measured using a laser diffraction particle size analyzer (LA-960, Horiba, Japan). An electro-acoustic technique (Zeta-APS, Matec Applied Sciences, USA) was used to measure both the particle size distribution and the zeta potential of the suspensions. Tetramethylammonium hydroxide and nitric acid were used to control the pH of the suspensions. The rheological behaviour of the nanosuspensions was measured in the steady shear mode, using a rotational rheometer (HAKE MARS II, Thermo Scientific, Germany) equipped with a double gap cylinder sensor system. The pore size distribution in green and partially sintered bodies was investigated via mercury intrusion porosimetry (PoreMaster 60, Quantachrome, USA) and nitrogen adsorption (Autosorb iQ, Quantachrome, USA). The densification curves were determined using a high-temperature dilatometer (L75/50, Linseis, Germany). The density of sintered bodies was determined by the Archimedes method. The solid loading of the suspensions and the relative density of the deposit were calculated using the value 5.94 g cm$^{-3}$ (crystallographic density of the powder), whereas the relative density of presintered and sintered ceramic bodies was calculated using the value 6.08 g cm$^{-3}$ (theoretical density of sintered tetragonal zirconia). The average grain size of sintered bodies was determined using the linear intercept method on at least three SEM micrographs of polished and thermally etched samples. The linear intercept grain size was corrected by a factor of 1.56 to yield the true grain size [32]. Where multiple measurements were available, a mean value with the confidence interval at a significance level of 0.05 was given.

## 3. Results and discussion

### 3.1. Colloidal treatment and dehydration of zirconia nanosuspension

The supplied 5 vol% zirconia nanosuspension (Melox 3Y) had primary particles of 10–15 nm in size (see Fig. 1) and a specific surface area of more than 90 m$^2$ g$^{-1}$. The particles were stabilized in the suspension without any additives at pH=3.8. Fig. 2 shows particle size distribution as measured in the suspension. Two analysing methods provided slightly different results. The acoustic attenuation method (Zeta-APS) determined the median particle size at 65 nm whereas the laser diffraction method (LA-960, Horiba) determined the median particle size at 77 nm. Both particle size distributions are relatively narrow and the difference can be attributed to the different measuring principles. However, it is clear that the particles measured in the suspension were bigger than the individual primary particles shown in Fig. 1. The particles in the suspension were most probably constituted by week agglomerates of a few primary particles.

The effect of the ionic dispersant, triammonium citrate (TAC), on the diluted 1.5 vol% nanosuspension was investigated. Table 1 shows the natural pH and zeta potential of the zirconia nanosuspension after the addition of different amounts of the dispersant (the amount of TAC was calculated with respect to zirconia). Fig. 3 shows the zeta potential as a function of pH for nanosuspensions with different amounts of the dispersant. The pH value of an isoelectric point determined from Fig. 3 is also shown in Table 1. It follows from these results that the addition of more than 1.7 wt%