Effect of ammonia on the agglomeration of zirconia nanoparticles during synthesis and sintering by Spark Plasma Sintering

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Abstract

Synthesis conditions have important impacts on the properties of ultrafine nanoparticles; understanding the interdependences of such properties on specific synthetic parameters can lead to controlled and optimized products. Here we discuss the effect of coprecipitation conditions during the synthesis of ultrafine yttria stabilized zirconia (YSZ) nanoparticles and gadolinium doped YSZ. We focused on the effect of ammonia concentration as precipitating agent. Although based on the nucleation theory one expects smaller particle sizes for higher concentrations of NH_4OH , the usage of 1M or 5M of NH_4OH lead to similar grain sizes (<6 nm). However, the more concentrated condition led to highly agglomerated powders. This was attributed to an increase in the ionic force in the precipitating environment that caused particle coagulation. The resultant powders thus showed significantly different densification behaviors during sintering using Spark Plasma Sintering, with the agglomerated powders achieving lower relative densities.

Keywords: Nanoparticles, Sintering, Ceramics, synthesis, agglomeration, SPS

1. Introduction

In a typical coprecipitation process for the synthesis of oxide nanoparticles, an induced super-saturation allows the decrease in critical radius for nucleation in solution [1]. The basic principle of this super-saturated condition is the reaction between cations and anions from two different solutions to form precipitates of hydroxides which undergo thermal decomposition into oxide nanoparticles. The process can be performed by either a “normal” strike, where the precipitating agent (e.g. OH^-) is added drop wise into the cationic solution; or by a “reverse” strike, where the cationic solution is dropped into the precipitating agent. The reverse strike method is expected to deliver more homogeneous particles [2, 3, 4], while ensuring highly super-saturated condition that helps to nucleate very small sized precipitates – exploiting concepts of homogeneous nucleation theory [1]. In this context, it is expected that a high concentration of precipitating agent could lead to smaller nanoparticles.

Here we study the effect of concentration of ammonia as a precipitating agent on the synthesis of yttria stabilized zirconia (YSZ). YSZ nanoparticles are of interest for the lowering of sintering temperature of solid state electrolytes for fuel cells [5, 6]. While nanoparticles increases the driving force for densification, sintering is also strongly dependent on the powder's characteristics [7, 8], such as size distribution and surface contaminations [9]. The goal of this work is to understand the dependences of YSZ nanoparticles on the synthesis conditions and impacts on densification. Because of the expected decrease in activation energy for oxygen vacancy mobility in cubic zirconia caused by the addition of gadolinium [10], we also studied the effect of Gd doping on the microstructure of the synthesized powders and sintering. Sintering of Gd-doped (1-4 mol%) and Gd-free YSZ nanoparticles was studied using spark plasma

sintering. This technique enables high heating rates under applied pressures, reducing sintering times and allowing dense samples with reduced grain growth [11-13].

2. Experimental Procedures

YSZ (12 mol% Y_2O_3) was synthesized with zirconium oxi-nitrate hydrate $[\text{ZrO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}]$ (Aldrich, 99%) and yttrium nitrate hexahydrate $[\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ (Aldrich, 99.999%) as metal precursors. The nitrates were dissolved in deionized water to form 0.3 M solutions and added drop wise in a solution containing 1.0 M or 5.0 M ammonia (NH_4OH), representing excess of 2.5 and 5.0 times the stoichiometric ratio, respectively. Gadolinium nitrate hexahydrate $[\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ (Aldrich, 99.999%) was added to achieve 1, 2, 3, and 4 mol% Gd, in 11, 10, 9, 8 mol% Y doped zirconia, maintaining the quantity of trivalent ions in all samples. The precipitates were collected by centrifugation and washed with ethanol. These hydroxide nanoparticles were dried overnight at 100°C and grinded before calcination. The calcination temperature was determined by heating the hydroxides in a Differential Scanning Calorimeter (DSC/TG) (Setsys, Setaram Instrumentation) at 1200°C at a rate of $10^\circ\text{C}/\text{min}$. Obtained oxide nanoparticles were characterized in terms of chemical compositions, crystalline phase (X-ray diffraction, XRD) and surface area, and transmission electron microscopy, as detailed in Supplemental Materials. The obtained nanopowders were sintered into pellets (5 mm diameter) using spark plasma sintering (SPS) (model 825S, Syntex, Tokyo, Japan) at 950°C for 5 min with 600 MPa pressure under vacuum. A graphite die with a silicon carbide insert was used to allow high pressures, as detailed elsewhere [14] and then polished and finally re-oxidized in oxidizing atmosphere at 750°C for 5 h to remove any carbon contaminants. The relative densities for all the pellets were measured using Archimedes method.

3. Results and Discussion

Coprecipitation from nitrates is expected to produce hydroxides which in turn need to be calcined to crystallize the oxide phase. The calcination temperature was studied by DSC/TG to determine the lowest temperature to allow oxide formation while avoiding coarsening (Supplemental Materials, Figure 1S). The data show 450°C is enough to induce crystallization. The crystallite sizes of the oxide nanoparticles obtained by calcining the hydroxides precipitated using 1M or 5M NH₄OH are listed in Table 1. The XRD patterns from which those data were extracted from are shown in Figure 1. No impurities or second phases could be detected. All XRD patterns show fluorite structure peaks. There were no significant changes in the patterns in terms of peak position or shape regardless of synthetic condition or Gd content (differences within experimental error, Table 1S shows the lattice parameters). Differences in crystallite sizes were also within experimental deviations, revealing no significant effects of doping or ammonia concentration. Chemical composition analyses showed nominal concentrations as accurate descriptions of the actual composition. Representative data from microprobe for 4 mol% Gd doped YSZ synthesized with 1M NH₄OH is shown in Table 2S.

The surface areas of all nanoparticles are also listed in Table 1. Noticeable differences are found when comparing those calcined from the precipitates from 1M and 5M ammonia. For 12YSZ, the surface area for the sample prepared from 1M was 128 m²/g, more than twice the value of 5M (52 m²/g). Similar trend is observed for the Gd-doped YSZ nanoparticles regardless of Gd content, suggesting it is an intrinsic synthetic procedural issue.

The fact that the surface area is smaller for the higher ammonia concentration suggests the formation of solid-solid interfaces (hard agglomerates). Note that if the powder is agglomerated, nitrogen cannot penetrate through the agglomeration and thus results in lower

surface areas when using BET analysis. This phenomenon is likely related to an increase in ionic force of the precipitating medium, causing the aggregation of the precipitated hydroxides right after their nucleation. DLVO theory (Derjaguin, Landau, Venvey and Overbeek) establishes that the interaction between approaching particles in solution is the combination of van der Waals attraction and the electric repulsion potentials. If the repulsion energy is higher than the attractive forces, a potential barrier for the agglomeration appears, which if larger than thermal energy shall impede agglomeration. The strength of this repulsive effect can be related to the Debye-Huckel screening length ($1/\kappa$), which is a function of concentration (C_i) and valence (Z_i) of ions in solution [1]:

$$\kappa = \sqrt{\frac{F^2 \sum_i C_i Z_i^2}{\varepsilon_r \varepsilon_0 R_g T}} \quad (1)$$

Here, F is the Faraday's constant, ε_0 is the permittivity of vacuum and ε_r is the dielectric constant of the solvent, T is temperature, and R_g the gas constant. The electric potential at the solid surface decreases with increased concentration and valence state of counter ions. Physically, a large number of ions in solution compensate the charges more adjacently to its surface, decreasing the screening length. Higher concentration ammonia would thus result in more agglomerated hydroxides, and consequently agglomerated oxide nanoparticles.

The extent of agglomeration is revealed from the surface area analyses (Table 1) but also seen from TEM micrographs (Figure 2). Although the particles are fairly agglomerated in both cases, particles are more individualized for 1M NH_4OH , where particle edges are clearly identified, and suggest weak agglomeration (in contrast to the dense agglomerates seen for the 5M ammonia precipitation condition).

In order to study the effects of the agglomeration degree on sintering, the nanoparticles were sintered using SPS using fixed parameters. Relative densities (with respect to theoretical)

are plotted as a function of dopant concentration in Figure 3 and show a clear effect of the ammonia concentration on the sinterability of both pure and Gd doped YSZ samples. The agglomerated samples (prepared by 5M ammonia) show at least a 2.5% lower density as compared to the same composition with less agglomeration (prepared by 1M). The results are consistent with earlier reports on the effects of particle agglomeration on YSZ nanoparticles under conventional sintering [7], where agglomerates are observed to affect initial stage of sintering such that dense agglomerates may pull away from the surrounding matrix and leave small lenticular cracks. This type of crack-induced pore is difficult to be closed and limits full densification. The results suggest that the applied pressure during SPS (600MPa) is not high enough to break the agglomerates in the samples prepared by 5M ammonia, causing a similar effect.

While the precipitation condition remarkably affects densification, Gd effects are comparatively less. For the samples prepared with 1M ammonia, the density decreases for 1mol% Gd, and incrementally increases with Gd content. This can be attributed to the segregation of the rare earth to the surfaces and grain boundaries [14], which is known to decrease densification kinetics [15], as well as affecting the dihedral angle which is responsible for pore stability in the final stage of sintering [14]. A combination of these two effects is likely in place, but more systematic works are needed. The results for the samples prepared with 5M ammonia resemble the behavior found in the less agglomerated samples, but since the agglomeration is affecting densification, the trends are less clear.

4. Conclusion

Gd doped and Gd free YSZ nanoparticles were synthesized using two precipitating agent (ammonia) concentrations. The results showed that although one would expect a decrease in

particle size with increasing concentration of ammonia due to the increased super-saturation condition, the ionic force of the precipitation bath leads to severe agglomeration of the hydroxides due to depletion in the electrical double layer that is translated to the oxide phase after crystallization. This leads to lower surface area (agglomeration) and a consequent decrease in sinterability.

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Figure Captions

Figure 1. X-ray diffraction patterns for Gd-free and Gd-doped YSZ nanoparticles synthesized with (a) 1M NH_4OH or (b) 5M NH_4OH

Figure 2. Transmission electron microscopy images of YSZ nanoparticles synthesized with 1M or 5M NH_4OH . Significant agglomeration is observed in the samples precipitated using 5M ammonia as compared to 1M, where individual particles can be easily identified. Scale bar is 10 nm.

Figure 3. Relative densities of YSZ with different Gd content (dopant concentration) and synthesized with either 1M or 5M NH_4OH . Synthesis influences densification due to agglomeration.

Table 1. Crystallite sizes and surface areas for Gd-free and Gd-doped YSZ nanoparticles prepared by using 1M or 5M ammonia.

Concentration	5 M ammonia		1 M ammonia	
Sample	Crystallite size (nm)	Surface area (m ² /g)	Crystallite size (nm)	Surface area (m ² /g)
12 YSZ	5.7 ± 0.3	52±0.17	6.4 ± 0.4	128±1.05
1Gd-11YSZ	6.0 ± 0.3	94±0.58	6.1 ± 0.3	128±1.08
2Gd-10YSZ	5.7 ± 0.2	88±0.55	6.0 ± 0.3	124±0.99
3Gd-9YSZ	6.1 ± 0.3	90±0.83	5.8 ± 0.4	125±1.11
4Gd-8YSZ	6.2 ± 0.2	83±0.46	5.6 ± 0.5	126±1.07

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