

PHASE STABILIZATION IN NANOCRYSTALLINE ZIRCONIA

S. Shukla and S. Seal

Advanced Materials Processing and Analysis Center (AMPAC) and Mechanical, Materials, and Aerospace Engineering Department (MMAE), 4000 Central Florida Blvd., University of Central Florida, Orlando, FL 32816, USA

Received: June 29, 2003

Abstract. Nanocrystalline as well as submicron-sized tetragonal-zirconia (ZrO_2) particles have been successfully synthesized using the sol-gel technique utilizing hydroxypropyl cellulose (HPC) as a polymeric steric stabilizer. The synthesized ZrO_2 particles are characterized using transmission electron microscopy (TEM) and x-ray diffraction (XRD) to determine the nanocrystallite size and crystal structure respectively. The ZrO_2 particles of size 200-300 nm and 15-20 nm, having tetragonal crystal structure, are obtained under the processing conditions $R=5$, $[HPC]=0.0$ g/L and $R=30$, $[HPC]=2.0$ g/L respectively. Large R -value and high HPC concentration are observed to be conducive for synthesizing nanocrystalline tetragonal ZrO_2 particles. The stabilization of metastable tetragonal phase in nanocrystalline ZrO_2 is the result of minimizing the surface energy.

1. INTRODUCTION

Zirconia (ZrO_2) is a well-known ceramic oxide material used for variety of applications. It has three stable forms: monoclinic, tetragonal and cubic. The physical and chemical properties of zirconium oxide are closely related to its different crystal phases and determine its applications in industry. For example, the martensitic transformation of tetragonal zirconia into monoclinic zirconia improves the mechanical properties of composite materials [1]. The high ionic conductivity of ZrO_2 in cubic form at high temperatures permits its use for sensing oxygen [2]. Tetragonal- ZrO_2 is used as a catalyst and catalyst support [3,4] for various gas phase reactions. It has also been used as a ceramic membrane instead of silica, titania or alumina due to its better alkaline resistance and biocompatibility [5]. It is now well recognized that the mechanical, electrical, chemical as well as catalytic properties of zirconia can be improved by using nanocrystalline instead of conventional micron-sized zirconia. Synthesizing nanocrystalline tetragonal- ZrO_2 at room temperature thus plays an important role. Hence, we demonstrate in this investigation, the synthesis

of nanocrystalline tetragonal- ZrO_2 particles, using a sol-gel technique, utilizing hydroxypropyl cellulose (HPC) polymer as a steric stabilizer.

2. EXPERIMENTAL PROCEDURE

2.1. Chemicals

Pure zirconium (IV) n-propoxide, anhydrous ethanol (200 proof), and the HPC polymer (molecular weight 80 000 g/mol) were obtained from Aldrich Co. U.S.A. and used as received.

2.2. Sol-Gel Synthesis of Sterically Stabilized Nanocrystalline ZrO_2 Powder

Nanocrystalline ZrO_2 powder is synthesized in the present investigation via hydrolysis of zirconium (IV) n-propoxide in an alcohol solution. The beakers used in the experiments were cleaned, washed with de-ionized water, dried completely and rinsed with anhydrous 200 proof ethanol before use. During synthesis, two different but equal parts of alcohol solutions were prepared. In the first part, de-ionized water was dissolved into an anhydrous 200 proof ethanol in a specific proportion. An appropriate amount of the HPC polymer was then added and dissolved completely by stirring the solution overnight using a

Corresponding author: S.Seal, e-mail: sseal@pegasus.cc.ucf.edu

magnetic stirrer. The second part of the alcohol solution was then prepared by completely dissolving a specific amount of zirconium (IV) n-propoxide (this amount was kept constant for all experiments involved in this investigation) in anhydrous ethanol under atmospheric conditions. The solution is homogenized using magnetic stirring for few minutes only. After preparing each solution, both the beakers were sealed immediately with paraffin tape. Hydrolysis of zirconium (IV) n-propoxide was then carried out under atmospheric condition by rapidly mixing the two sealed solutions under vigorous stirring. The formation of ZrO_2 particles, due to immediate precipitation, was evident from the white color of the resulting sol. The sol was stirred very slowly for 4 hrs and then held under static condition for 24 hrs to ensure completion of the hydrolysis and the condensation reactions. The sol was subsequently dried at 80 °C using petri dishes in order to remove the solvent completely. The small gel pieces obtained were then crushed to obtain the nanocrystalline ZrO_2 powder.

The nanocrystalline ZrO_2 powder was synthesized using the above method under various processing conditions by varying the ratio of molar concentrations of water and zirconium (IV) n-propoxide (R -value) and the concentration of HPC [HPC]. The concentration of zirconium (IV) n-propoxide was kept constant for all experiments (0.1 M). The amount of water and [HPC] were respectively varied as $R = 5, 15, 30, 60$ and [HPC]=0.0, 1.0, 2.0 g/L. The ZrO_2 powder synthesized under different processing conditions was calcined at 400 in air for crystallization. The samples were heated at a rate of 30 °C/min up to the calcination temperature, held at that temperature for 2 hrs and then furnace cooled to room temperature.

3. CHARACTERIZATION

The as-synthesized ZrO_2 powders were then examined using Phillips EM400 transmission electron microscope (TEM) at 120 kV to determine the nanocrystallite size. The crystalline phases present in the as-synthesized as well as calcined powders were determined using a standard Rigaku x-ray diffractometer (XRD). Line traces were obtained over 2θ values ranging from 10°-80°. The volume fraction of tetragonal (V_T) phase was calculated from the broad scan analysis considering the relative intensity of two monoclinic peaks $(-111)_M$ and $(111)_M$ and one tetragonal $(111)_T$ peak and then using the relationship of the form [1]:

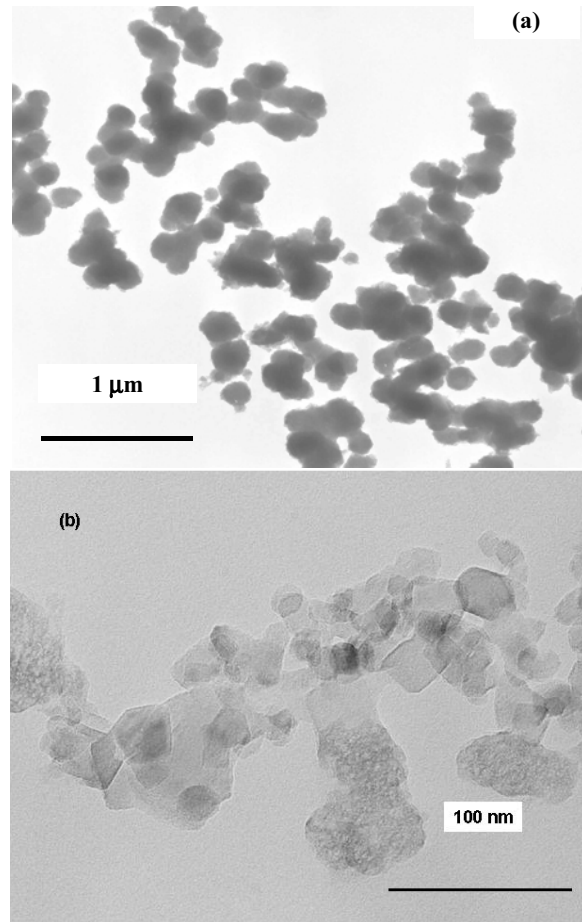


Fig. 1. Submicron-sized (200-300 nm) (a) and nano-sized (15-20 nm) (b) ZrO_2 particles, synthesized under the conditions of $R=5$, [HPC]=0.0 g/L (a) and $R=30$, [HPC]=2.0 g/L (b).

$$V_T = I(111)_T / [I(111)_T + I(-111)_M + I(111)_M]. \quad (1)$$

Narrow scan analysis was conducted in the 2θ range of 27°-32° as it contained the strongest lines for the tetragonal $(111)_T$ phases. This intense peak was then curve-fitted using the peak-fit software (peak-fit, version-4, SPSS Inc.). The average tetragonal (D_T) crystallite size was calculated from the $(111)_T$ diffraction peaks using Scherer's equation [6] as shown below,

$$D_T = (0.9\lambda) / (\beta \cos\theta), \quad (2)$$

where, D_T is the average tetragonal crystallite size in nm, λ the radiation wavelength (0.154 nm), β the corrected half-width at half-maximum intensity, and θ the diffraction peak angle.

4. RESULTS

Typical TEM images of the sol-gel derived nanocrystalline ZrO_2 powder synthesized under the

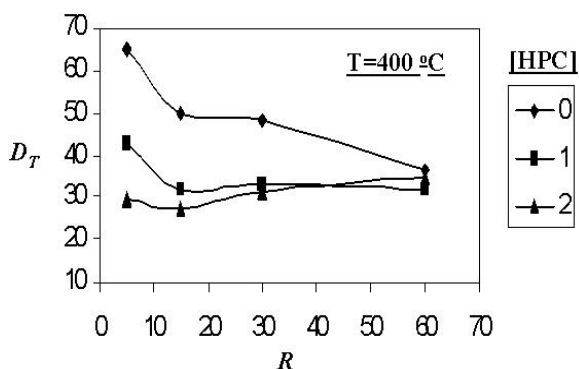


Fig. 2. Variation in tetragonal crystallite size as a function of R and [HPC].

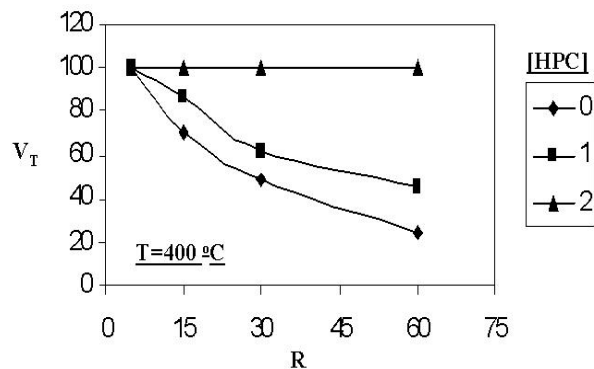


Fig. 3. Variation in volume fraction of tetragonal phase as a function R and [HPC].

processing conditions of $R=5$, [HPC]=0.0 g/L and $R=30$, [HPC]=2.0 g/L are presented in Figs. 1(a) and 1(b) respectively. Submicron-sized ZrO_2 particles of size 200–300 nm are observed under the processing conditions of $R=5$, [HPC]=0.0 g/L, Fig. 1(a). The formation of submicron-sized (>100 nm) particles was also observed at $R=5$, during the synthesis of ZrO_2 particles in the presence of HPC polymer. However, under the processing conditions of $R=30$, [HPC]=2.0 g/L, nanocrystalline ZrO_2 particles of size 15–20 nm were obtained, Fig. 1(b). The aggregation of small ZrO_2 nanocrystallites (which results in the formation of sub-micron sized particles) appears to be prevented due to the presence of HPC polymer during the synthesis.

The variation in the tetragonal- ZrO_2 nanocrystallite size, determined using Eq. 2, after the calcination treatment at 400 °C, is presented in Fig. 2. The ZrO_2 nanocrystallite size is observed to decrease from 65 nm to 45 nm with increasing R -value from 5 to 60 for [HPC]=0.0 g/L. Since, TEM observation indicates the presence of submicron-sized ZrO_2 particles, Fig. 1(a), under the processing conditions of $R=5$, [HPC]=0.0 g/L, it appears that, these particles are composed of small nanocrystallites having tetragonal structure. Hence, the aggregation of ZrO_2 nanocrystallites could not be prevented under $R=5$.

Further, the addition of 1.0 g/L of HPC polymer, significantly reduced the ZrO_2 nanocrystallite size to 32–45 nm, Fig. 2. With increase in the amount of HPC polymer to 2.0 g/L, the ZrO_2 nanocrystallite size is observed to reduce to 28–32 nm. It is also noted from the Fig. 1(b), that with large R -value ($R=30$), the aggregation tendency of ZrO_2 nanocrystallites could be prevented due to the addition of 2.0 g/L of HPC polymer. Hence, $R=30$,

[HPC]=2.0 g/L appears to be the optimum condition for synthesizing nanocrystalline (15–20 nm) ZrO_2 .

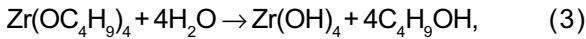
XRD results show that the as-synthesized ZrO_2 powder is amorphous under all processing conditions and crystallizes only at 400 °C. The variation in V_T (determined using Eq. 1) for the sol-gel derived nanocrystalline ZrO_2 powder as a function of ' R ' and [HPC], at the crystallization temperature of 400 °C, is presented in Fig. 3. We observe that, for the [HPC]=0.0 g/L, V_T decreases from 100 % to 20 % with increasing ' R ', within the range of 5–60. For [HPC]=1.0 g/L, V_T is observed to decrease from 100 % to 50 % with increasing ' R ', within the range of 5–60. Increase in V_T is however noted for all R -values due to the addition of 1.0 g/L of the HPC polymer. Further increase in the [HPC] to 2.0 g/L results in the formation of 100 % tetragonal phase. Thus, irrespective of ' R ', high [HPC] of 2.0 g/L appears to be a necessary condition for obtaining 100 % tetragonal phase at the crystallization temperature of 400 °C. Moreover, 100 % V_T is also observed at $R=5$, irrespective of [HPC]. Typically, we note that, the ZrO_2 nanocrystallites synthesized under the processing conditions $R=30$, [HPC]=2.0 g/L exhibit 100 % tetragonal crystal structure.

Thus, nanocrystalline tetragonal- ZrO_2 particles are successfully synthesized under the processing conditions of $R=30$, [HPC]=2.0 g/L. ZrO_2 particles having 100 % tetragonal crystal structure are also synthesized under the processing conditions of $R=5$, [HPC]=0.0 g/L; however, the particles are submicron-sized under these conditions.

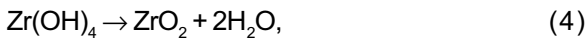
5. DISCUSSION

The sol-gel synthesis of ZrO₂ powder involves hydrolysis and condensation of zirconium (IV) n-propoxide in an alcohol solution. The hydrolysis and condensation reactions, which take place as a result of mixing the two parts of alcohol solutions can be described as,

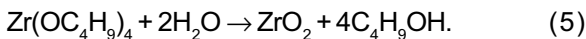
Hydrolysis:



Condensation:



Net reaction:



As a result of hydrolysis and condensation reactions, ZrO₂ particles with surface hydroxyl groups get nucleated in the solution, where the rate of nucleation of particles depends primarily on 'R' [7]. Lower water concentrations are associated with smaller R-values (R=5). As a result, the nucleation rate of ZrO₂ particles is very low under these conditions. Due to very low reaction kinetics, the ZrO₂ nanocrystallites aggregate within the sol, forming submicron-sized ZrO₂ particles. The addition of HPC polymer could not prevent the aggregation of ZrO₂ nanocrystallites under very low reaction kinetics. On the other hand, the higher water concentrations associated with the larger R-value (R=30) result in higher nucleation rate of ZrO₂ nanocrystallites. In the presence of HPC polymer, these ZrO₂ nanocrystallites are sterically stabilized due to the adsorption of the HPC polymer on their surface. The aggregation of ZrO₂ nanocrystallites is thus prevented, resulting in the formation of ZrO₂ nanoparticles. Hence, ZrO₂ nanoparticles of size 15-20 nm is successfully obtained, in the present investigation, under the processing conditions of R=30, [HPC]=2.0 g/L.

Further, we note that the nanocrystalline ZrO₂ nanoparticles synthesized under the processing conditions, R=30, [HPC]=2.0 g/L, crystallize into the tetragonal phase. Thus, the metastable tetragonal phase of ZrO₂ is stabilized at room temperature without doping any di- or tri-valent doping. The stabilization of metastable tetragonal phase in pure-ZrO₂, below 30 nm crystallite size, has been reported earlier [8-10]. In consonance with these earlier investigations, in the present investigation, the stabilization of metastable tetragonal phase within the ZrO₂ nanoparticles of size 15-20 nm is attributed to the minimization of surface energy as a 'nanoparticle-size' effect.

6. CONCLUSIONS

- (1) Nanocrystalline as well as submicron-sized tetragonal-zirconia (ZrO₂) particles have been successfully synthesized using the sol-gel technique utilizing hydroxypropyl cellulose (HPC) as a polymeric steric stabilizer.
- (2) The ZrO₂ particles of size 200-300 nm and 15-20 nm, having tetragonal crystal structure, are obtained under the processing conditions R=5, [HPC]=0.0 g/L and R=30, [HPC]=2.0 g/L respectively. Large R-value and high HPC concentration are observed to be conducive for synthesizing nanocrystalline tetragonal ZrO₂ particles.
- (3) The stabilization of metastable tetragonal phase in nanocrystalline ZrO₂ is the result of minimizing the surface energy.

ACKNOWLEDGEMENTS

Authors acknowledge NSF DMI 0334260 for the NSF workshop on nanotechnology, ONR YIP (Young Investigator Award), and NSF EEC 0136710, EEC 0139614 for funding the nanotechnology research.

REFERENCES

- [1] M.I. Osendi, J.S. Moya, C.J. Serna and J. Soria // *J. Am. Ceram. Soc.* **68** (1985) 135.
- [2] E. Haeefele, K. Kaltenmaier and U. Schoenauer // *Sensors and Actuators B: Chemical* **B4** (1991) 525.
- [3] M. Haruta, T. Kobayashi, H. Sano and N. Yamada // *Chem. Lett.* **829** (1987) 405.
- [4] A. Knell, P. Barnickel, A. Baiker and A. Wokaun // *J. Catal.* **137** (1992) 306.
- [5] R.S. Pavlik Jr., L.C. Klein and R.A. McCauley // *J. Am. Ceram. Soc.* **78** (1995) 221.
- [6] B.D. Cullity, *Elements of X-Ray Diffraction* (Addison-Wesley, MA, 1978).
- [7] S. Shukla, S. Seal and R. Vanfleet // *J. Sol-Gel Sci. Technol.* **27** (2003) 119.
- [8] R.C. Gravie // *J. Phys. Chem.* **69** (1965) 1238.
- [9] R. Nitsche, M. Rodewald, G. Skandan, H. Fuess and H. Hahn // *Nanostruct. Mater.* **7** (1996) 535.
- [10] R. Nitsche, M. Winterer and H. Hahn // *Nanostruct. Mater.* **6** (1995) 679.