Effect of pH Values on the Formation of Magnesia Doped Zirconia by Ball-Mill Assisted Co-precipitation Method

Sukhbayar Gankhuyag and Dong Sik Bae

Department of Convergence Materials Science and Engineering, Changwon National University, Gyeongsangnam-Do 641-773, Republic of Korea

Abstract: We have studied the effect of magnesia (MgO) addition (0, 5, 10, and 20 mol%) in zirconia at pH values (7, 9, 11). The magnesia doped zirconia (MgO-ZrO₂) has been synthesized by a co-precipitation method using ammonium hydroxide as a mineralizer. As-prepared samples were characterized by XRD, FE-SEM, and TG-DSC. The XRD results showed that the quantity of tetragonal phase was increased with increasing pH value during synthesis. On the other hand, a decrease in the crystallite size of tetragonal phase was observed with increasing pH value. Therefore, the FE-SEM micrograph showed a clear decline in the particle size with increasing pH value. As-precipitated at pH~11, the addition of 10 mol% of MgO showed nearly pure tetragonal phase with a crystallite size of ~34.16 nm.

Key words: Zirconia, phase-stabilization, magnesia, co-precipitation, sintering.

1. Introduction

Zirconia (ZrO₂) has attracted much attention due to their fascinating chemical inertness and mechanical properties. Based on these properties, ZrO₂ mainly used in biomaterials, refractories, catalysis, high strength tools, SOFC (solid oxide fuel cell) and thermal barrier coatings [1-7]. The ZrO₂ existed in three well-known structural forms: monoclinic, tetragonal, and cubic phase, which is known as the polymorphic form of the ZrO₂. The monoclinic phase exists up to a temperature of 1,170 °C, the tetragonal phase from 1,170 to 2,370 °C, and the cubic phase from 2,370 to 2,680 °C. The melting point of ZrO₂ is 2,680 °C [8]. The most applicable phase of ZrO₂ is tetragonal and cubic phase because of the stability at high temperature.

The properties of ZrO₂-based materials substantially depend on the type of structural phases. For instance, tetragonal stabilized ZrO₂ used to fabricate high strengthen tools or tough materials, whereas refractory materials needed cubic ZrO₂.

Hence, the most encountering objective is the stabilization of tetragonal or cubic phase of ZrO₂. The most efficient method to make tetragonal or cubic phase stabilized ZrO₂ is using low valence oxides as a dopant material. These dopant including CaO [9], MgO [10], Y₂O₃ [11], CeO₂ [12], Al₂O₃ [13] were used to achieve fully or partially stabilized ZrO₂. Therefore, the properties of the doped ZrO₂ material strongly depend on particle size and surface area which is closely related to the fabrication methods [14].

Besides, synthesis methods are essential to get stabilized ZrO₂ where co-precipitation [15-17], hydrothermal [18-20], sol-gel processing [21-23], and ball-milling are most useful techniques. The co-precipitation method is simplest and costs effective way to obtain partially or fully stabilized ZrO₂. However, the main difficulties in co-precipitation method are controlling the pH value to the phase stabilization of ZrO₂. Davis et al. [24] reported that the tetragonal phase could be made at low (3-5) and high range (13-14) of pH values using pure ZrO₂ by using co-precipitation method. However, they

Corresponding author: Dong Sik Bae, professor, research field: nano materials fabrication and processing.

obtained monoclinic phase in the medium pH (8-11) range. Thus, there is a big challenge to get tetragonal or cubic phase stabilized ZrO_2 in the medium pH levels.

This work is aimed to evaluate the effect of pH level in the basic region of the polymorph transportation in ZrO_2 . In this report, four different concentrations of MgO are utilized to stabilize zirconia. The pH values were controlled by NH_4OH as mineralizer at 7, 9 and 11. In summary, the phase transformation and microstructure changes are characterized using XRD, FESEM instruments.

2. Materials and Methods

2.1 Materials

Zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 99.0%) and Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 99.9%) were used as a precursor of initial solution without further purification. Ammonium hydroxide (NH_4OH , 25-28%) was also used to obtain a precipitate as a mineralizer and distilled water used as a solvent.

2.2 Methods

The typical experimental procedure that is used to obtain MgO-doped ZrO_2 composite material was schematically illustrated in Scheme 1. Briefly, four different concentrations of ZrO_2 and magnesium precursors individually were dissolved in distilled water, and total solution concentration kept at 0.3 moles. Then, the pH value was adjusted at 7, 9, and 11 using NH_4OH . The precipitated solution was ball-milled at milling speed of 160 rpm for 6 h. Hereupon, the precipitated solution was dried in an oven at 100 °C for four days and calcined at 800 °C for 2 h.

TG-DSC analysis was carried out to investigate weight losses and thermal decomposition of powders. As-precipitated at pH value 11 samples were placed in a platinum crucible and heated up to 1,200 °C in atmospheric condition with the rate of 20 °C/min using a STA N-1500 SCINCO equipment. The calcined

Scheme 1. Experimental procedure.

powders were examined by FE-SEM using CZ/MIRA I LMH operated at 20 kV.

Furthermore, X-ray diffraction technique was used to explore the structure of obtained material. The phase quantification analysis was performed by using Eq. (1), and the average crystallite size was estimated using Scherrer's Eq. (2).

$$W_t = \frac{I_{(hkl)t}}{(I_{(hkl)m} + I_{(hkl)t} + I_{(hkl)m})} \quad (1)$$

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

3. Results and Discussion

3.1 Powder Analysis

The weight loss and thermal decomposition was clearly shown as-precipitated at pH value 11 (Figs. 1a and 1b). Weight loss of samples which became constant from 800 °C and the DSC curve shows endothermic and exothermic peaks (Fig. 1a). The endothermic peaks indicated elimination of adsorbed water and hydroxide form at a temperature of 110, 198, and 210 °C. The zirconium hydroxide ($\text{ZrO}(\text{OH})_2$) to ZrO_2 decomposition that was revealed in the endothermic peaks at the range of 230-340 °C. These

Fig. 1 The thermal decomposition analysis of precursor precipitated at pH 11 (a) TG, and (b) DSC.

peaks intensity were slightly distinguished due to the addition of dopant concentration.

The exothermic peak is related to fast crystallization into metastable tetragonal zirconia; it was shown at temperature region of 487.5-514 °C (Fig. 1b). Phase transformation temperature was changed [25], which might be due to the addition of dopant concentration or difference in particle size. Furthermore, it can be possible to cause that in the specific surface area, surface free energy is larger when the particle size of the powder is smaller, which results in a lower transformation temperature that could be formed [26].

3.2 Phase Characterization

Four different concentrations of MgO doped ZrO_2 samples were prepared by controlling the pH values as

7, 9, and 11. XRD analysis was used to analyze the impact of pH values on the phase changes of ZrO_2 , with MgO content of 0, 5, 10, and 20 mol%, respectively (Fig. 2). As for crystal phase determinations, the scans were selected from 10 to 80° in the 2θ region. The pattern exhibits peaks at the 2θ region of 30.2, 34.7, 35.3, 50.38, 59.48, 60.3, 63.1, and 74.78° corresponding to the tetragonal phases of ZrO_2 in all XRD patterns.

The as-precipitated at pH value 7, the fraction of tetragonal phase was increased with increasing MgO dopant concentration (Fig. 2a). Therefore, monoclinic phases are clearly shown at 24.02, 28.26, 31.36, 38.76, 41.04, 45.18, 54.04, and 55.52° of the 2θ region in the XRD pattern, with small peaks. The fraction of monoclinic phase was high at the pure ZrO_2 with the percentage of 67.1% (Fig. 2a). The addition of MgO affected up to 10 mol% of dopant to get nearly pure tetragonal phase. However, at the 20 mol% of MgO, the fraction of monoclinic phase was slightly increased. Perhaps, it is also possible to cause the excess amount of MgO or some contaminants as nitrate ion or chlorine from starting material. These findings suggest that the 10 mol% of MgO might be the proper way to obtain purely tetragonal phase as-precipitated at pH value 7.

The samples are precipitated at pH value 9 which shows increased tetragonal phase, with all samples but slightly for MgO dopant compared to pH value 7 (Fig. 2b). Besides, the monoclinic peak was revealed in the 2θ region of 24.02 on all samples. This may have been caused by the excess amount of ammonium hydroxide. As for MgO-doped ZrO_2 , their fraction of tetragonal was tended to increase compared to that was precipitated at pH value 7.

Remarkably, most of the ZrO_2 materials were purely tetragonal as-precipitated at pH value 11. Although the pure ZrO_2 precipitated at pH value 11, produces a material with 10.71 % or less of the tetragonal phase. Moreover, the 10 mol% of MgO showed extremely pure tetragonal phase without any

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Fig. 2 The XRD pattern of samples calcined at 800 °C for 2 hours (a) pH~7, (b) pH~9, (c) pH~11.

monoclinic peaks, as depicted in Fig. 2c. These results provide further support for the hypothesis that is increasing the pH values affected to get the pure tetragonal phase of ZrO_2 with the addition of magnesia. Particularly, the pure tetragonal phase was obtained as-precipitated at pH value 11, with the addition of 10 mol% magnesia. As reported by Davis et al. that the monoclinic phases are formed in the

medium pH region (8-11). However, in this study, the purely tetragonal phases are obtained in the medium pH region (7-11). Probably, this is due to the effect of dopant concentration and ball-milling.

The effect of the pH value on the crystallite size and phase quantity was plotted and (Fig. 3). The crystallite size was calculated from the peak width at the half maximum intensity of the total quantity of tetragonal peaks. As for each prepared sample, the pH values affected and crystallite size decreased from 61.5 to 31.6 nm, with increasing pH values. When the fraction of tetragonal phase was less the crystallite size was bigger. The material derived from precipitation in either the 7 or 11 shows similar crystallite sizes approximately 33-34 nm, with the addition of 10 and 20 mol% magnesia. As for 10 mol% of magnesia, the crystallite size was slightly bigger than 20 mol% MgO

Fig. 3 Effect of the pH values on the (a) crystallite size and (b) phase transformation of Mg- ZrO_2 samples.

Fig. 4 The morphology of the pure zirconia sample calcined at 800 for 2 h, (a) pH~7, (b) pH~9, (c) pH~11.

while precipitated at pH value 9 (Fig. 3a).

3.3 Morphology

Fig. 4 shows the FESEM micrographs of pure ZrO_2 particles prepared at different pH values as 7, 9, and 11. The average particle size was decreased with increasing pH values and agglomeration takes place as indicated in Figs. 4a-4c. The micrographs showed spherical and agglomerated particles. The powders precipitated at pH 7; the average particles size was approximately 80 nm sized. However, as precipitated at pH values 9 and 11, the average particle size was substantially decreased approximately 40 nm and less than 20 nm sized, as indicated in Figs. 4b and 4c.

4. Conclusion

In summary, MgO-stabilized ZrO_2 was prepared by ball-mill assisted co-precipitation method. The pH values are being effected on the tetragonal stabilized zirconia. The fraction of tetragonal phase was increased with increasing pH value and also increasing dopant concentration.

Particularly, the relatively pure tetragonal phase was formed as-precipitated at pH value 11, with the addition of 10 mol% of magnesia. As for pure zirconia, the fraction of tetragonal phase was substantially increased with increasing pH value. It is the most appropriate result to show the effect of pH values on the phase transformation. On the other hand, the crystallite size tended to decrease with increasing pH values as for pure zirconia and 5 mol% of magnesia.

Besides, the crystallite size became stable, with the addition of 10 and 20 mol% magnesia.

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References

- [1] Lyon, D., Chevalier, J., Gremillard, L., and Cam, C. D. 2011. "Zirconia as a Biomaterial." *Compr. Biomater.* 20: 95-108.
- [2] Jamali, H., Mozafarinia, R., Shoja Razavi, R., and Ahmadi-Pidani, R. 2012. "Comparison of Thermal Shock Resistances of Plasma-Sprayed Nanostructured and Conventional Ytria Stabilized Zirconia Thermal Barrier Coatings." *Ceram. Int.* 38: 6705-12.
- [3] Furuta, S., Matsushashi, H., and Arata, K. 2006. "Biodiesel Fuel Production with Solid Amorphous-Zirconia Catalysis in Fixed Bed Reactor." *Biomass and Bioenergy* 30: 870-3.
- [4] Peck, D. H. et al. 2007. "Fabrication of Porous Structure with Scandia Stabilized Zirconia Electrolyte for Solid Oxide Fuel Cells." In *ECS Transactions* 7: 2187-95.
- [5] Mandal, N., Doloi, B., and Mondal, B. 2011. "Development of Flank Wear Prediction Model of Zirconia Toughened Alumina (ZTA) Cutting Tool Using Response Surface Methodology." *Int. J. Refract. Met. Hard Mater.* 29: 273-80.
- [6] Zhao, X. et al. 2014. "Structural and Optical Properties of Zirconia Thin Films Deposited by Reactive High-Power Impulse Magnetron Sputtering." *Thin Solid Films* 570: 404-11.
- [7] Lee, J. H. et al. 2001. "Electrical Conductivity and Defect

- Structure of Yttria-Doped Ceria-Stabilized Zirconia.” *Solid State Ionics* 144: 175-84.
- [8] Huang, R. T. et al. 2014. “Characterization of the Irradiation-Induced Phase Transition in the Monoclinic Polymorph of Zirconia.” *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* 332: 293-7.
- [9] Broda, M., and Müller, C. R. 2014. “Sol-Gel-Derived, CaO-Based, ZrO₂-Stabilized CO₂ Sorbents.” *Fuel* 127: 94-100.
- [10] Tian, X. et al. 2011. “Fabrication and Stabilization of Nanocrystalline Ordered Mesoporous MgO-ZrO₂ Solid Solution.” *Microporous Mesoporous Mater.* 143: 357-61.
- [11] Dell’Agli, G., Mascolo, G., Mascolo, M. C., and Pagliuca, C. 2005. “Crystallization-Stabilization Mechanism of Yttria-Doped Zirconia by Hydrothermal Treatment of Mechanical Mixtures of Zirconia Xerogel and Crystalline Yttria.” *J. Cryst. Growth* 280: 255-65.
- [12] Raju, V., Jaenicke, S., and Chuah, G. K. 2009. “Effect of Hydrothermal Treatment and Silica on Thermal Stability and Oxygen Storage Capacity of Ceria-Zirconia.” *Appl. Catal. B Environ.* 91: 92-100.
- [13] Sommer, F., Landfried, R., Kern, F., and Gadow, R. 2012. “Mechanical Properties of Zirconia Toughened Alumina with 10-24vol.% 1Y-TZP Reinforcement.” *J. Eur. Ceram. Soc.* 32: 4177-84.
- [14] Dell’Agli, G., and Mascolo, G. 2001. “Agglomeration of 3 mol% Y-TZP Powders Synthesized by Hydrothermal Treatment.” *J. Eur. Ceram. Soc.* 21: 29-35.
- [15] Chu, H.-L. et al. 2014. “Thermal Behavior and Phase Transformation of ZrO₂-10%SiO₂ Precursor Powder Prepared by a Co-precipitation Route without Adding Stability Agent.” *J. Alloys Compd.* 616: 413-9.
- [16] Li, L., Mao, D., Yu, J., and Guo, X. 2015. “Highly Selective Hydrogenation of CO₂ to Methanol over CuO-ZnO-ZrO₂ Catalysts Prepared by a Surfactant-Assisted Co-precipitation Method.” *J. Power Sources* 279: 394-404.
- [17] Wang, S., Zhai, Y., Li, X., Li, Y., and Wang, K. 2006. “Coprecipitation Synthesis of MgO-Doped ZrO₂ Nano Powder.” *J. Am. Ceram. Soc.* 89: 3577-81.
- [18] Duran, C., Sato, K., Hotta, Y., Gocmez, H., and Watari, K. 2015. “Ball Milling Assisted Hydrothermal Synthesis of ZrO₂ Nanopowders.” *Ceram. Int.* 41: 5588-93.
- [19] Liu, X. L. et al. 2010. “Solvothermal Synthesis and Characterization of ZrO₂ Nanostructures Using Zirconium Precursor.” *Mater. Lett.* 64: 1591-4.
- [20] Uchiyama, H., Matsumoto, K., and Kozuka, H. 2012. “Solvothermal Synthesis of Micron-Sized Spherical Particles in TiO₂-ZrO₂ Binary System.” *J. Cryst. Growth* 338: 201-7.
- [21] Sajjadi, S. M., Haghighi, M., and Rahmani, F. 2015. “Sol-Gel Synthesis of Ni-Co/Al₂O₃-MgO-ZrO₂ Nanocatalyst Used in Hydrogen Production via Reforming of CH₄/CO₂ Greenhouse Gases.” *J. Nat. Gas Sci. Eng.* 22: 9-21.
- [22] Mamana, N., Ortiz, A. L., Sánchez-Bajo, F., and Caruso, R. 2014. “A Comparative Study of the Pressureless Sinterability of 3 mol% Y₂O₃-Stabilized ZrO₂ Powders Prepared by the Sol-Gel Method under Different Synthesis Conditions without Modifiers.” *Ceram. Int.* 40: 16829-34.
- [23] Kumar, S., Bhunia, S., and Ojha, A. K. 2015. “Effect of Calcination Temperature on Phase Transformation, Structural and Optical Properties of Sol-Gel Derived ZrO₂ Nanostructures.” *Phys. E Low-dimensional Syst. Nanostructures* 66: 74-80.
- [24] Burtron H. D. 1984. “Effect of pH on Crystal Phase of ZrO₂ Precipitated from Solution and Calcined at 600 °C.” Communication of the American Ceramic Society.
- [25] Chevalier, J., Gremillard, L., Virkar, A. V., and Clarke, D. R. 2009. “The Tetragonal-Monoclinic Transformation in Zirconia: Lessons Learned and Future Trends.” *J. Am. Ceram. Soc.* 92: 1901-20.
- [26] Settu, T. 2000. “Characterization of MgO-ZrO₂ Precursor Powders Prepared by In-situ Peptization of Coprecipitated Oxalate Gel.” *Ceram. Int.* 26: 517-21.