

Effect of solvents on the properties of co-precipitated MgO-ZrO₂ nano powders

Lei Yuan, Dong Xiang and Jing-kun Yu*

School of Materials and Metallurgy, Northeastern University, Shenyang 110004, P. R. China

8 mol% MgO-ZrO₂ nano-sized powders have been synthesized through the coprecipitation route using ammonia as precipitant. In order to investigate the agglomeration of the nano powders during synthesis, water, butyl alcohol, and a mixture of butyl alcohol and ethanol were utilized as the solvents to precipitate and wash. The characteristics of the different powders were estimated by FT-IR, TG-DSC, XRD and SEM. It has been demonstrated that uniformly dispersed and soft agglomerates containing MgO-ZrO₂ nano-sized powders can be obtained when the butyl alcohol, especially the butyl alcohol and ethanol mixture are used. It has been found that the hydroxyl group on the particle surface is replaced by the alkoxy group to alleviate the hard agglomerate.

Key words: MgO-ZrO₂, Nano powder, Butyl alcohol, Ethanol, Solvent.

Introduction

Partially stabilized zirconia (PSZ) materials have been widely used in industry due to their high temperature strength, excellent thermal shock resistance and electrical properties [1, 2]. The main stabilized additives are MgO, CaO, Y₂O₃, etc. Among them, MgO partially stabilized zirconia has been selected as an oxygen sensor to measure the oxygen of molten steel because of its stabilized properties and relatively low cost [3].

In order to obtain high performance oxygen sensor, most researchers focused on the synthesis of nano-sized MgO-doped ZrO₂ powders, since nanocrystalline-stabilized zirconia has homogeneous microstructure and low-temperature sinterability. Various methods, such as coprecipitation, sol-gel, combustion synthesis, hydrothermal method, ball milling, and others have been used to prepare nano-sized zirconia powders [4-9]. In which, the coprecipitation method has been widely used because of its easiness to control and low cost, but the agglomeration is unavoidable. Consequently, the minimization of agglomeration is the key subject of using this method. Generally, soft agglomerations are accepted and do not impede the densification of the subsequent sintering process. However, in the precipitation processing, water molecules can bridge the neighboring hydroxyl groups, thus resulting in hard agglomerations by forming solid necks among particles when the hydroxide is calcined into the oxide [10]. Hard agglomerations are not easy to break down, worsening the sintering behavior.

Many efforts have been paid to remove the water to avoid the formation of hard agglomerations, including azeotropic distillation (AD), ethanol washing, ultrasonic treatment, citrate synthesis and spray drying, etc [11-15]. Among them, ethanol washing are commonly used due to its simple and effective to suppressing hard agglomeration [10, 16]. Furthermore, ethanol is also employed as reaction solvent in the solvothermal and sol-gel method [17, 18]. Generally, butyl alcohol is also used as a medium in AD, but the equipment is complex. However, it has not been reported that the butyl alcohol or a mixture of butyl alcohol and ethanol was used as precipitating and washing medium to prepare ZrO₂ nano powders.

For these reasons, to prepare uniformly dispersed MgO-doped ZrO₂ powder with soft agglomerations in this work, butyl alcohol and ethanol were employed as the precipitating and washing medium in coprecipitation method. And the effect of solvents on properties of MgO-ZrO₂ powder was presented.

Experimental Procedure

ZrOCl₂ · 8H₂O and Mg(NO₃)₂ · 6H₂O were used as raw materials. Distilled water, butyl alcohol, and a mixture of butyl alcohol and ethanol at a volume ratio of 1 : 1 were selected as precipitating and washing solvents, respectively. Appropriate amounts of ZrOCl₂ · 8H₂O and Mg(NO₃)₂ · 6H₂O were dissolved respectively in the solvents mentioned above to form 0.5 mol/L Zr⁴⁺ solution and yield powders of final composition 8 mol/L MgO. A little amount of water was added into butyl alcohol or ethanol solvents to dissolve the raw materials. 4 mol/L NH₃ · H₂O was used as precipitant which diluted with the same solvents. The NH₃ · H₂O solution was added dropwise to the constantly stirred Mg(NO₃)₂ and ZrOCl₂ solution. Much care should be paid to ensure

*Corresponding author:
Tel : +86-24-83686526
Fax: +86-24-83681576
E-mail: yujk@smm.neu.edu.cn

that the pH value of the terminal precipitation was about 10 to prepare white, flocculent precipitates. After the centrifugal filtration, the precipitates were washed with the same corresponding solvents by three times. Washed gels were dried at 60 °C for 72 hrs, and calcined at 800 °C for 2 hrs. The samples which were precipitated and washed with water labeled as sample 1 (S1), with butyl alcohol labeled as S2, and with a mixture of butyl alcohol and ethanol labeled as S3.

Fourier transform infrared spectrum (FT-IR, PerkinElmer Co.) and thermogravimetric-differential scanning calorimetry (TG-DSC 6300, PerkinElmer Co.) were employed to characterize the hydroxide precursor. Phase compositions of MgO-doped ZrO₂ powders were identified by X-ray diffraction (XRD, Model D500, Siemens) using Cu K_α as the radiation source. The microstructure and morphology of powders were observed by scanning electron microscopy (SEM, Model S-3400N, Hitachi).

Results and Discussion

TG-DSC analyses of the precursors

After drying, the thermal analyses of three precursors were performed using TG-DSC under air atmosphere at a heating rate of 10 °C/min, as shown in Fig. 1. The results from TG show that the weight losses are 13.91%, 25.04% and 20.33% for S1, S2 and S3, respectively. It is attributed to the liberation of physisorbed water and the decomposition of zirconium hydroxide. The reason about more weight loss of S2 and S3 than S1 may be due to the absorption of alkoxy groups on zirconium hydroxide particles [10].

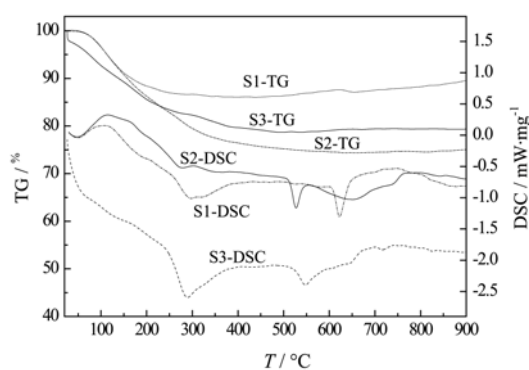


Fig. 1. TG-DSC curves of the precursors.

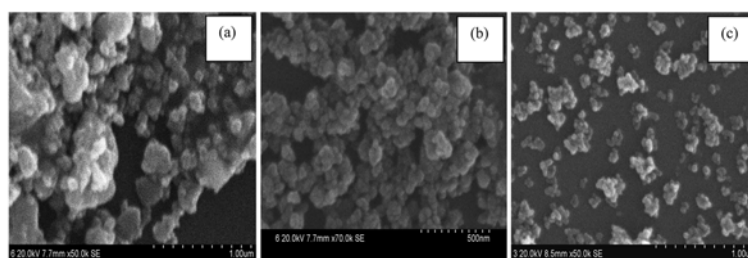


Fig. 2. SEM images of the powders by (a) water, (b) butyl alcohol, and (c) a mixture of butyl alcohol and ethanol for precipitating and washing medium.

It can be seen from DSC curves that the dehydration of three precursors all occurs below 400 °C (Fig. 1). This is also indicated from the TG results. There are exothermic peaks appeared at around 623 °C and 527 °C for S1 and S2, and 548 °C for S3. The exothermic peaks are attributed to the crystallization of amorphous zirconia. The phase-transform temperature is different among each series of samples may be due to the difference of particle size. It can be explained that the specific surface area is larger and surface free energy is bigger when the particle size of powder is smaller, which results in a lower transform temperature [12].

Microstructure of MgO-ZrO₂ powder

In order to investigate the effect of different precipitating and washing mediums on the microstructural features of 8 mol% MgO-ZrO₂ powder, SEM images was carried out in this research, as showed in Fig. 2. It has been found that the agglomeration was formed and the particle size was larger when water was used as solvent for precipitating and washing medium (Fig. 2(a)). There is hard agglomeration and unavoidable.

However, when butyl alcohol or a mixture of butyl alcohol and ethanol was used, uniformly dispersed and soft agglomerates containing MgO-ZrO₂ powders were obtained (Figs. 2(b) and 2(c)). The powders exhibit much looser, and the particles are nano-sized. This indicates that the solvents such as butyl alcohol and ethanol had obvious effect on the alleviation of the agglomeration.

Phase of the powder

Fig. 3 shows the X-ray diffraction patterns of MgO-doped ZrO₂ powders of S1, S2 and S3, which both calcined at 800 °C for 2 hours. A large amount of tetragonal phase and little traces of monoclinic phase are observed in MgO-ZrO₂ powders of S1, which synthesized in water. When butyl alcohol or a mixture of butyl alcohol and ethanol was used, the amounts of monoclinic phase of S2 and S3 are increased. This indicates that the MgO-doped ZrO₂ powder has a lower phase transition temperature using butyl alcohol or a mixture of butyl alcohol/ethanol than water. Generally, the smaller the particle size, the higher the surface free energy, thus the temperature of phase transition is lower. The results are in close agreement with the SEM results.

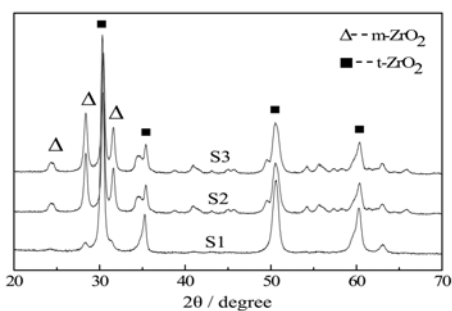


Fig. 3. X-ray diffraction patterns of powders calcined at 800 °C.

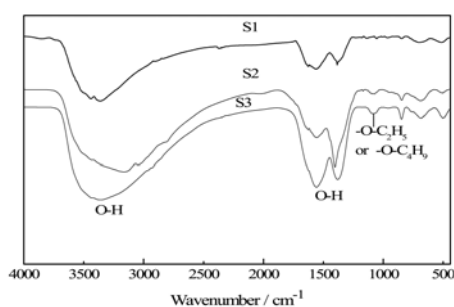


Fig. 4. Infrared spectrometer spectrum of the precursors treated with different solvents.

Discussion

The agglomeration was reduced by ethanol washing since hydroxyl groups were replaced by ethoxy groups [16]. Lee proposed that ethanol was just postulated to hydrogen bond to surfacial hydroxyls that could not cause particle-particle interaction [19]. Kaliszewski suggested that partial hydroxyls of Zr(OH)₄ had been also replaced by ethoxy groups, not just surfacial hydroxyls [10]. Our results are in agreement with Kaliszewski's, since chemi-sorbed alkoxy bond is also found from FTIR spectra in this work (Fig. 4). The broad absorption bands are 3000 ~ 3800 cm⁻¹ due to the O-H stretching. The weaker absorption bands are 1350 ~ 1630 cm⁻¹ corresponded to the hydrogen bonding among various hydroxyl groups in the Zr(OH)₄. The difference among S1, S2 and S3 precursors is that the absorption band occurs at 1095 cm⁻¹, due to the C-O stretching in the terminal zirconium alkoxide. When butyl alcohol or a mixture of butyl alcohol and ethanol was used, the chemical bond of -O-C₂H₅ or -O-C₄H₉ could be found, which result in forming Zr(OH)₂(OC₂H₅)₂ or Zr(OH)₂(OC₄H₉)₂ groups.

It can be explained by the models in Fig. 5. Model (A) shows the formation of the agglomeration using water as the precipitating and washing solvents. In this case, particle bridging by hydrogen bonds of water molecules would occur in the gels. After drying, water molecules were lost and hydrogen bonding occurred among terminal hydroxyl groups of the different particles, resulting in the hard agglomeration. Model (B) is proposed for the case using the butyl alcohol as the precipitating and washing solvents. Excess butyl

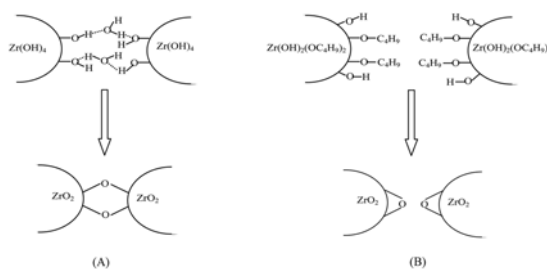


Fig. 5. Proposed models for agglomeration formation treated in (A) water and (B) butyl alcohol. The dotted lines indicate hydrogen bonds.

alcohol could not form hydrogen bonds between butoxy groups on the surface, and could not link particles together. As the drying of the gels, the hydrogen bonding would not occur between terminal butoxy groups of different particles. Thus, the formation of chemical bonds between particles is avoided, resulting in soft and loose nano powders.

Conclusions

Butyl alcohol and a mixture of butyl alcohol and ethanol for precipitating and washing medium in coprecipitation synthesis have obvious influence on the formation of the agglomeration in MgO-doped ZrO₂ powder. Butoxy or ethoxy groups were formed in this synthesis, which would inhabit the close approach between particles. After the removal of those butoxy or ethoxy groups, the hard agglomeration would not be formed. Consequently, soft and loose nano MgO-doped ZrO₂ powders could be obtained.

Acknowledgments

The authors would like to express their gratitude for the financial support from the Fundamental Research Funds for the Central Universities of China (N100302011) and the National Natural Science Foundation of China (No. 51274059).

References

1. J.R. Kellya, I. Denry, Dent. Mater. 24 [3] (2008) 1-10.
2. B. Smuk, M. Szutkowska, J. Walter, J. Mater. Process. Tech. 133 [1-2] (2003) 195-198.
3. J. W. Fergus, J. Mater. Sci. 38 [21] (2003) 4259-4270.
4. R. Septawendar, B.S. Purwasasmita, S. Sutardi, N. Sofyaningsih and W. Kristanto, J. Ceramic Processing Research. 13 [3] (2012) 343-348.
5. F. Heshmatpour, Z. Khodaiy, R.B. Aghakhanpour, Powder Technol. 224 (2012) 12-18.
6. I.O. Fábregas, A.F. Craievich, M.C. Fantini, R.P. Millen, M.L.A. Temperini, D.G. Lamas, J. Alloy. Compd. 509 [16] (2011) 5177-5182.
7. R. Septawendar, B.S. Purwasasmita, Suhanda, L. Nurdiwijayanto and F. Edwin, J. Ceramic Processing Research. 12 [1] (2011) 110-113.
8. G. Dell'Agli, G. Mascolo, J. Europ. Ceram. Soc. 20 [2] (2000) 139-145.

9. A. Sekulic, K. Furic, M. Stubicar, *J. Mol. Struct.* 410-411 (1997) 275-279.
10. M. Kaliszewski, A. Heuer, *J. Am. Ceram. Soc.* 73 [6] (1990) 1504-1509.
11. G. Zheng, X. Cui, W. Zhang, Z. Tong and F. Li, *Particuology* 10 [1] (2012) 42-45.
12. T. Settu, *Ceram. Int.* 26 [5] (2000) 517-521.
13. Y.H. Chiou, S.T. Lin, *Ceram. Int.* 23 [2] (1997) 171-177.
14. S. Vivekanandhan, M. Venkateswarlu, H.R. Rawls and N. Satyanarayana, *Mater. Chem. Phys.* 120 [1] (2010) 148-154.
15. Z. Chen, R.W. Trice, M. Besser, X. Yang and D. Sordelet, *J. Mater. Sci.* 39 [13] (2004) 4171-4178.
16. S. Wang, Y. Zhai, X. Li, Y. Li and K. Wang, *J. Am. Ceram. Soc.* 89 [11] (2006) 3577-3581.
17. X. Wang, G. Lorimer, P. Xia, *J. Am. Ceram. Soc.* 88 [4] (2005) 809-816.
18. A. Diaz-Parralejo, A. Macias-Garcia, E. M. Cuerda-Correa and R. Caruso, *J. Non-Cryst. Solids* 351 [24-26] (2005) 2115-2121.
19. M.J. Readey, R.R. Lee, J.W. Halloran and A.H. Heuer, *J. Am. Ceram. Soc.* 73 [6] (1990) 1499-1503.