Synthesis and electrical field-assisted sintering behaviour of yttria-stabilized tetragonal ZrO₂ nanopowders by polyacrylamide gel method

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Abstract. The tetragonal ZrO₂ nanopowders stabilized with 3 mol% Y₂O₃ (3YSZ) were synthesized using a polyacrylamide gel method. The mean particle size of the 3YSZ nanopowders was found to decrease with increasing molecular ratio of monomer to the precursor salt. The 3YSZ nanopowders with mean particle size of 12 nm can be densified in 1 h at 800°C, by the application of a d.c. electrical field. Under a constant d.c. electrical field, the current density through the specimen of 3YSZ rose rapidly when the temperature increased to a certain value. In the sintering process, the current density was restricted when the sharp increase occurred. By limiting current density to different values for one hour, it was found that current density was the most important factor in electrical field-assisted sintering process. The grain size of 3YSZ bulk increased with the enhanced current density. The stable stage of electrical field-assisted sintering process can be explained by Joule heating. Corresponding real temperature of specimens is estimated by applying black body radiation theory.

Keywords. Yttria-stabilized ZrO₂; electrical field-assisted sintering; current density; Joule heating.

1. Introduction

Zirconia (ZrO₂) is a functional material with many unique properties, such as high performance in mechanical, thermal, optical, catalytic properties and high ionic conductivity at elevated temperatures [1–3]. At atmospheric pressure, pure ZrO₂ has three solid polymorphs: monoclinic, i.e., thermodynamically stable at the temperatures below 1175°C, tetragonal, stable at the temperature range of 1175–2370°C, and cubic, stable above 2370°C [4,5]. The tetragonal form can be retained in a metastable state at room temperature by adding various oxides, in particular yttria or by decreasing the particle size below a certain critical size [6–8]. Tetragonal phase ZrO₂ has been applicable to a number of technologies. Yttria-stabilized tetragonal ZrO₂ are promising candidates for fuel cell electrolytes [9,10], oxygen sensors [11], oxide conducting component of mixed ionic–electronic conducting composite electrodes and oxygen separation membranes [12,13], structural ceramics [14,15].

Several different methods have been investigated as routes for the synthesis of ZrO₂ nanopowders, such as sol–gel process [16–19], pyrolysis [20–22], hydrothermal synthesis [23–25], polymerized complex [26,27], precipitation [28] and glycothermal synthesis [29]. However, most of these methods are complicated and not suitable for large-scale preparations. A large-scale synthetic procedure should be developed for the extensive applications of ZrO₂ nanopowders.

In addition to the preparation of ZrO₂ nanopowders, sintering is important for the preparing bulk ZrO₂ ceramics. The conventional sintering process is not only time consuming, but also oppressively required of energy and equipment. Recently, some novel techniques in applying electrical fields in densification of ceramics termed flash sintering have obvious improvement in terms of reducing the sintering temperature and the sintering time [30–38]. These electrical techniques for densification provides us with an opportunity to prepare bulk ZrO₂ ceramics at low temperature in short time.

Sintering techniques applying electrical fields termed flash sintering and is characterized by a remarkable observation: a sharp increase in current when the temperature reaches a certain value known as the onset of flash sintering [32]. Because of the sudden surge of the current, ceramics can be densified at lower temperatures and in shorter times. Raj [39] first reported the flash sintering in a d.c. electrical field and explained this phenomenon by the local Joule heating. They proposed that local Joule heating generated at grain boundaries promotes grain boundary diffusion, while at the same time restricts grain growth which also enhances the rates of sintering of ceramics [32,39]. Other possible mechanisms have been proposed, such as the nucleation of Frenkel pairs [40], the intervention of oxygen and oxide ion [30] and the selective Joule heating caused by defect segregation [41]. However, the fundamental mechanism remains obscure and further investigation is still in demand.

This paper describes a polyacrylamide gel route for producing weakly agglomerated tetragonal ZrO₂ nanopowders stabilized with 3 mol% Y₂O₃ (3YSZ). The process is quite

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simple, so that the production rate is expected to be much higher upon scale-up than those of many other methods. The stoichiometric ratio of Y_2O_3 to ZrO_2 can be easily controlled, simply by adjusting the composition of the solution containing the precursors. In addition, the sintering behaviour of the 3YSZ nanopowders under a direct current electrical field (d.c.-sintering) is investigated. The effect of current density has been stressed in this paper. Finally, the mechanism of d.c.-sintering process was discussed and an interpretation with Joule heating theory was proposed.

2. Experimental

2.1 Preparation of 3YSZ nanopowders

3YSZ nanopowders were prepared using a polyacrylamide gel method. Zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (Aladdin Chemical, China, purity: 99.99%) were used as starting materials. The Zr and Y mixed salts were dissolved into deionized water to obtain solution, and the Zr^{4+} concentration was adjusted to 0.01 mol l^{-1} with an yttrium molar ratio of 3%. The monomers, acrylamide and *N,N'*-methylene-bis-acrylamide (Macklin Chemical, China, purity: 98%) were dissolved in the solution. The concentration of acrylamide was adjusted to 0.2, 0.5, 0.8, 1.2 mol l^{-1} , respectively. The polymerization was initiated by free radicals afforded by ammonium persulphate (Aladdin Chemical, China, purity: 99.99%). In all experiments, the molecule ratio of acrylamide/*N,N'*-methylene-bis-acrylamide/ammonium persulphate was kept as 24/2/1. The mixed solution was successively stirred until a transparent solution was obtained. By heating the solution at 80°C , a white gel was obtained. The gel was dried at 80°C in air for several days to allow the formation of xerogel. Finally, the 3YSZ nanopowders were obtained by a calcination of the xerogel at 800°C for 2 h in air at a heating rate of 5°C min^{-1} .

2.2 Direct current electrical field-assisted sintering process

The prepared 3YSZ nanopowders were mixed with 5 wt% PVA binder in aqueous solution. Then the mixture was uniaxially pressed into a bar-shaped die under a pressure of 300 MPa. The bar had a length of 11 mm and a rectangular cross-section of $1 \text{ mm} \times 5 \text{ mm}$. The bar was bounded with the platinum wire at each end as electrodes. Platinum paste was coated on each end to make sure a good contact between the bar and the platinum wires, and to achieve a constant electrical field through the bar. Sintering was performed in a tubular furnace under the application of a constant d.c. voltage with a heating rate of 8°C min^{-1} . The power supply was switched to current control when the current reached a preset value. Then the state was maintained for 1 h at 800°C . Dividing current value by cross-sectional area which was 0.05 cm^2 , the corresponding current density was calculated. In this experiment, the current value was controlled to 0.4, 0.5, 0.6 A,

respectively. Correspondingly, the current density was 8, 10, 12 A cm^{-2} . The applied electrical field was 160, 300, 500, 630 V cm^{-1} , respectively.

2.3 Characterization

The phase transformation analysis of the nanopowders was conducted by X-ray diffraction (XRD) on an X-ray diffractometer (Bruker D8 Davinci, Germany) with $\text{CuK}\alpha$ radiation (40 kV, 60 mA) in the $2\theta = 10\text{--}80^\circ$ range. The scan was performed at a scan rate of 5°min^{-1} with the step size of 0.02° . The microstructure and morphology of the nanopowders were examined by a transmission electron microscope (TEM, Hitachi H-600, Tokyo, Japan) with a voltage of 80 kV. The samples for the TEM analysis were prepared by suspending powders in ethanol, dropping the suspensions on a carbon film supported on a copper grid, and drying. The surface morphology of the d.c.-sintered specimens was characterized by field emission scanning electron microscopy (SEM, Hitachi S-4800, Tokyo, Japan). The bulk densities of the specimens sintered with different current densities were measured by the Archimedes' method. The relative density was calculated with respect to the theoretical density of YSZ (5.958 g cm^{-3}).

3. Results and discussion

Figure 1 shows the XRD patterns of powders by calcining the xerogel at various temperatures for 2 h. For the powders calcined at 700°C , the XRD diffraction pattern shows the strong diffraction peaks of tetragonal ZrO_2 (JCPDS card no. 80-0784), together with the diffraction peaks of monoclinic ZrO_2 (JCPDS card no. 37-1484). When the powders calcined at 800°C , the diffraction peaks of monoclinic ZrO_2 disappear completely and XRD diffraction pattern contains only the

Figure 1. XRD patterns of powders obtained by calcining the xerogel at various temperatures for 2 h.

diffraction peaks of tetragonal ZrO_2 . The intensities of these tetragonal ZrO_2 diffraction peaks become more intense and sharper with further calcination to 1200°C . The XRD analysis indicates that the single-phase 3YSZ can be obtained at 800°C .

The TEM micrographs of the 3YSZ nanopowders obtained by calcining the xerogel with the different molecule ratios of acrylamide to $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (abbreviated as A:Zr) at 800°C for 2 h are shown in figure 2. The 3YSZ nanopowders obtained from the A:Zr molecule ratio of 20 have comparatively larger and heavier agglomerates, and the mean particle size is about 45 nm (figure 2a). When the A:Zr molec-

ular ratio increases to 120, the obtained 3YSZ nanopowders are weakly agglomerated have a mean particle size of about 12 nm, and a narrow size distribution (figure 2b). The mean particle sizes of the 3YSZ nanopowders obtained with different molecular ratio of A:Zr are shown in figure 3. It is showed that the polymer network from a higher molecule proportion of A:Zr not only prevents the agglomeration but also limits the growth of the 3YSZ particles. Therefore, 3YSZ nanopowders with various particle sizes can be successfully prepared by polyacrylamide gel method

The polyacrylamide gel method has the advantage of the polymerization of acrylamide, which is initiated by free radicals afforded by persulphates. The polyacrylamide chains are linked by the two functional groups of *N, N'*-methylene-bis-acrylamide. A biacrylamide molecule can be incorporated into two chains simultaneously and forms a permanent link between them. As a result, the polyacrylamide grows into a complex web of interconnected loops and branches [42]. The gel constituted by the polyacrylamide polymer network immobilizes the precursor solution of zirconium oxychloride. The xerogel has to be calcinated to produce 3YSZ nanopowders. The prepared 3YSZ nanopowders are white loose powders, which can be easily ground. The polymer network effectively limits grain growth and agglomeration of the 3YSZ nanopowders, depending on the A:Zr molecular ratio in the polyacrylamide gel, as indicated in figures 2 and 3. In this work, weak agglomeration, well-controlled 3YSZ nanopowders were prepared by polyacrylamide gel method. However, this method involves expensive and highly carcinogenic organic chemicals such as acrylamide, *N, N'*-methylene-bis-acrylamide. Therefore, large-scale production cost will be high. A comparison of various synthesis methods is illustrated in table 1.

The direct current electrical field-assisted sintering (d.c.-sintering) behaviour of 3YSZ nanopowders with mean particle size of 12 nm is studied. Figure 4 illustrates the current density of sample using electric fields between 160 and 630 V cm^{-1}

Figure 2. TEM micrographs of the 3YSZ nanopowders obtained by calcining the xerogel with (a) the A:Zr molecule ratio of 20 and (b) the A:Zr molecule ratio of 120 at 800°C for 2 h.

Figure 3. Mean particle size as a function of the A:Zr molecule ratio (calcinated at 800°C for 2 h).

Table 1. Comparison of various synthesis methods.

Synthesis method	Advantages	Disadvantages
Sol-gel [17,19]	Obtain high purity, weak agglomeration nanopowders.	Complicated, difficult to control.
Pyrolysis [20,22]	Simple. Obtain weak agglomeration nanopowders.	Expensive starting materials.
Hydrothermal [24,25]	Obtain well crystalline, weak agglomeration nanopowders.	Complicated, expensive equipment.
Polymerized complex [26,27]	Obtain weak agglomeration nanopowders.	Expensive. Environment polluted.
Precipitation [28]	Convenient and cost-effective.	Severe agglomeration.
Our method	Simple. Obtain weak agglomeration, well controlled nanopowders.	Expensive, carcinogenic starting materials.

Figure 4. Current density as a function of temperature in d.c.-sintering process.

during the heating ramp. It can be seen that the current density in 3YSZ bulk increases suddenly when the furnace's temperature reaches a certain value which is known as the onset of flash-sintering process [35]. The onset temperature for the 3YSZ bulks under the electrical field of 160, 300, 500, 630 V cm⁻¹ is 898, 768, 662 and 613°C, respectively. Obviously, the onset temperature decreases when the electrical field is increased. This result is consistent with previous reports [35,43].

To investigate the effect of the current density on d.c.-sintering process, the current density is limited to a certain value (8, 10, 12 A cm⁻²) after the onset temperature under the initial electrical field of 30 V cm⁻¹. By holding on each current density for 1 h at 800°C, the 3YSZ bulks are sintered. 3YSZ bulks sintered under different current densities are compared in terms of microstructure. Figure 5 shows the SEM surface micrographs of the sintered specimens. It is noted that 3YSZ bulk without applying any direct current electrical field mainly consists of raw particles (figure 5a) because 800°C is far below the densification temperature of 3YSZ. When the current density increases to 8 and 10 A cm⁻², the SEM micrograph indicates a well-densified structure with only few pores, as shown in figure 5b and c. As the current density is enhanced to 12 A cm⁻², the SEM observations demonstrate that 3YSZ bulks are nearly fully dense. The Archimedes density and the relative density of

specimens are summarized in table 2. It shows that the density increases with the increasing current density. And the SEM micrographs also reveal an interesting finding that with the increase of current density in d.c.-sintering, the average grain size increases correspondingly, as shown in figure 6. Evidently, current density plays a dominating role in d.c.-sintering. The change in grain size and densification with current density can be attributed to Joule heating at grain boundaries because electrical energy can be converted to thermal energy and a current density corresponds to a real sintering temperature of 3YSZ bulks.

The phenomenon of flash-sintering can be explained by Joule heating theory, though some previous researches point out that the estimated temperature by this theory is far below the temperature that would be required to sinter the specimen in a few seconds [39,40]. However, it is important to note that the presumption of the theory is that the system is in thermal equilibrium. It is unconvincing to apply this theory during the first few seconds in flash sintering, because system is not in equilibrium yet. Therefore, based on the observation in the present work, when the current control sintering stage is stable, Joule heating by power dissipation and black body radiation is probably the most appropriate theory.

When applying an electrical field to a sample in a furnace, the sample is heated not only by the furnace, but also by electrical power. Thus, the temperature is different between specimen and furnace. The rise in temperature may be calculated by equating black body radiation to the power dissipation in the specimen by the applied electrical field. The analysis leads to the following equation [39]:

$$T = \left[T_0^4 + \frac{W}{A\sigma} \right]^{1/4}. \quad (1)$$

In equation (1), T_0 (1073.15 K) is the temperature of the furnace, A the total surface area of the specimen (assumed to be the gage section), σ the black body radiation constant equal to $5.67 \times 10^{-8} \text{ Wm}^2 \text{ K}^{-1}$, W the power supplied by electrical energy and $A = 1.3 \times 10^{-4} \text{ m}^2$. Substituting the range of values from the experiments, the real specimen temperature T is obtained. The results are reported in figure 7. It can be seen that as the current density rises, corresponding power dissipation increases. Consequently, the estimated temperature increases. When the current density is 8, 10 and 12 A cm⁻², the estimated temperature of 3YSZ bulk is 1486, 1523, 1552°C, respectively. These estimated temperatures are

Figure 5. SEM micrographs of the surface of specimens sintered with different current densities. (a) No current applied, (b) 8 A cm^{-2} , (c) 10 A cm^{-2} and (d) 12 A cm^{-2} .

Table 2. Density of specimens sintered with different current densities.

Current density (A cm^{-2})	Archimedes density (g cm^{-3})	Relative density (%)
0	4.659	78.2
8	5.696	95.6
10	5.797	97.3
12	5.863	98.4

Figure 6. Average grain size as a function of current density at 800°C .

Figure 7. Estimated temperature and power dissipation as a function of current density.

high enough to close the densification temperature of 3YSZ. Notably, the estimated temperature refers to the specimen in thermal equilibrium condition, and the temperature of initial stage of d.c.-sintering process can even be higher.

4. Conclusions

Weakly agglomerated nanoparticles of 3 mol% Y_2O_3 stabilized zirconia (3YSZ) were synthesized by polyacrylamide gel method. The polymer network effectively limits grain growth and agglomeration of the 3YSZ nanopowders,

depending on the A:Zr molecular ratio in the polyacrylamide gel. The mean particle sizes of the as-prepared 3YSZ nanopowders were 12 nm, for the powders obtained from the A:Zr molecular ratio of 120. The 3YSZ nanopowders with mean particle sizes of 12 nm can be densified at 800°C in 1 h by applying a direct current electrical field-assisted sintering technique. The grain size of 3YSZ bulk increased with the rising current density, which implies the dominating role of current density in d.c.-sintering process. Meanwhile, the electrical field had an effect on the onset temperature in flash-sintering. And the d.c.-sintering process was explained by Joule heating. Electric field-assisted sintering is a most attractive technology for promoting densification of oxide ceramic, in contrast to conventional sintering which requires relatively high temperature and long dwell time. Furthermore, by adjusting the current density and dwell time, the 3YSZ bulk ceramic with designed grain size can be prepared.

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References

- [1] Wang Z, Yang B, Fu Z, Dong W, Yang Y and Liu W 2005 *Appl. Phys. A—Mater.* **81** 691
- [2] Rhee S J, White J O, Lee S and Chen H 2001 *J. Appl. Phys.* **90** 6110
- [3] Merino R I, Orera V M, Povill O, Assmus W and Lomonova E E 1997 *J. Phys. Chem. Solids* **58** 1579
- [4] Shukla S and Seal S 2004 *J. Phys. Chem. B* **108** 3395
- [5] Salavati-Niasari M and Dadkhah M 2009 *Polyhedron* **28** 3005
- [6] Borchers L, Stiesch M, Bach F W, Buhl J C, Hübsch C, Kellner T, Kohorst P and Jendras M 2010 *Acta Biomaterialia* **6** 4547
- [7] Chraska T, King A H and Berndt C C 2000 *Mater. Sci. Eng. A* **286** 169
- [8] Chen L, Mashimo T, Omurzak E, Okudera H, Iwamoto C and Yoshiasa A 2011 *J. Phys. Chem. C* **115** 9370
- [9] Shim J H, Chao C C, Huang H and Prinz F B 2007 *Chem. Mater.* **19** 3850
- [10] Zhu Q and Fan B 2005 *Solid State Ionics* **176** 889
- [11] Tan O K, Cao W, Hu Y and Zhu W 2004 *Ceram. Int.* **30** 1127
- [12] Minh N 1993 *J. Am. Ceram. Soc.* **76** 563
- [13] Ji Y, Kilner J A and Carolan M F 2005 *Solid State Ionics* **176** 937
- [14] Mayo M J, Seidensticker J R, Hague D C and Carim A H 1999 *Nanostruct. Mater.* **11** 271
- [15] Garvie R C, Hannink R H and Pascoe R T 1975 *Nature* **258** 703
- [16] Mamana N, Ortizb A L, Sánchez-Bajo F and Caruso R 2014 *Ceram. Int.* **40** 16829
- [17] Mamana N, Díaz-Parralejo A, Ortiz A L, Sánchez-Bajo F and Caruso R 2014 *Ceram. Int.* **40** 6421
- [18] Davar F, Hassankhani A and Loghman-Estarki M R 2013 *Ceram. Int.* **39** 2933
- [19] Joo J, Yu T, Kim Y W, Park H M, Wu F, Zhang J Z and Hyeon T 2003 *J. Am. Chem. Soc.* **125** 6553
- [20] Ksapabutr B, Gulari E and Wongkasemjit S 2004 *Mater. Chem. Phys.* **83** 34
- [21] Eslamian M, Ahmed M and Ashgriz N 2006 *Nanotechnology* **17** 1674
- [22] Heine M C, Mädler L, Jossen R and Pratsinis S E 2006 *Combust. Flame* **144** 809
- [23] Tahir M N, Gorgishvili L, Li J, Gorelik T, Kolb U, Nasdala L and Tremel W 2007 *Solid State Sci.* **9** 1105
- [24] Wang H, Li G, Xue Y and Li L 2007 *J. Solid State Chem.* **180** 2790
- [25] Hayashi H, Ueda A, Suino A, Hiro K and Hakuta Y 2009 *J. Solid State Chem.* **182** 2985
- [26] Zhang Y W, Yan Z G, Liao F H, Liao C S and Yan C H 2004 *Mater. Res. Bull.* **39** 1763
- [27] Roy S 2007 *J. Sol–Gel Sci. Technol.* **44** 227
- [28] Garg N, Mittal V K, Bera S, Dasgupta A and Sankaralingam V 2012 *Ceram. Int.* **38** 2507
- [29] Ryu J H, Kil H S, Song J H, Lim D Y and Cho S B 2012 *Powder Technol.* **221** 228
- [30] Muccillo R, Kleitz M and Muccillo E N 2011 *J. Eur. Ceram. Soc.* **31** 1517
- [31] Cordier A, Kleitz M and Steil M C 2012 *J. Eur. Ceram. Soc.* **32** 1473
- [32] Cologna M, Rashkova B and Raj R 2010 *J. Am. Ceram. Soc.* **93** 3556
- [33] Hao X, Liu Y, Wang Z, Qiao J and Sun K 2012 *J. Power Sources* **210** 86
- [34] Zapata-Solvas E, Bonilla S, Wilshaw P R and Todd R I 2013 *J. Eur. Ceram. Soc.* **33** 2811
- [35] Cologna M, Prette A L G and Raj R 2011 *J. Am. Ceram. Soc.* **94** 316
- [36] Prette A L G, Cologna M, Sglavo V and Raj R 2011 *J. Power Sources* **196** 2061
- [37] Muccillo R, Muccillo E N S and Kleitz M 2012 *J. Eur. Ceram. Soc.* **32** 2311
- [38] Jiang T, Liu Y, Wang Z, Sun W, Qiao J and Sun K 2014 *J. Power Sources* **248** 70
- [39] Raj R 2012 *J. Eur. Ceram. Soc.* **32** 2293
- [40] Francis J S C, Cologna M and Raj R 2012 *J. Eur. Ceram. Soc.* **32** 3129
- [41] Narayan J 2013 *Scripta Mater.* **69** 107
- [42] Wang H, Gao L, Li W Q and Li Q 1999 *Nanostruct. Mater.* **11** 1263
- [43] Schmerbauch C, Gonzalez-Julian J, Röder R, Ronning C and Guillon O 2014 *J. Am. Ceram. Soc.* **97** 1728