

POROUS ALUMINA-ZIRCONIA COMPOSITES PREPARED WITH STARCH AS A PORE FORMING AGENT

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Abstract

In this paper microstructure and mechanical properties of porous oxide ceramics prepared by pressing have been investigated. In the laboratory study, alumina-zirconia composite powders containing various types and amounts of alumina, m-ZrO₂, MgO and corn starch were prepared, shaped by dry pressing, dried, sintered at different temperatures: 1300, 1400, 1460 and 1550°C for two hours, and characterized. It is shown that maximum values of the total porosity of porous ceramics prepared with starch as a pore-forming agent were approx. 60 %. In MgO-doped alumina-zirconia composites, m-ZrO₂ did not transformed to t-ZrO₂ after sintering. Starch doping enhanced the total porosity of the composites, which increased with an increase in the starch content. The maximum total porosity was 60.65 % and was observed when the starch amount was 30 % and sintering temperature was 1400°C.

Keywords: ALUMINA, ZIRCONIA, POROSITY, ZTA

Introduction

Porous ceramics are essential for a wide range of engineering applications including separation membranes [1], filters [2], piezoelectric [3] and pyroelectric ceramics [4], lightweight structural materials [5], biomaterials [6], battery separators [7] and solid oxide fuel cell (SOFC) electrodes [8–10]. Controlling the features of the porosity in ceramic microstructures is crucial to satisfy the requirements of desired applications. For instance, uniform distribution of pores gives rise to the electrochemical performance of SOFC electrodes while their connectivity/percolation allows transport of the reactant and product gases efficiently [11–13].

For thermal or acoustic insulators materials with closed porosity are preferred, whereas membranes and filters require open pores with exactly defined pore size. The same can be said about gas burners and about certain bioceramics applications, where important criteria can be open porosity and sufficient pore size (e.g. minimum pore size aperture for tissue ingrowth, especially for bone tissue, is above 100 µm). In the case of catalyst supports a large specific surface area is desired, again in connection with sufficient open porosity and suitable pore size. Very specific are the requirements for functional ceramics with controlled porosity, e.g. membranes for solid oxide fuel cells (SOFCs) and piezoelectric PZT ceramics for hydrophones. One of the preparation methods of porous ceramics is using pore-forming agents (PFAs). Over the last 15 years there has

been an increasing interest in PFAs and the development of new preparation methods of porous ceramics [14].

In this paper we report on the characterization of porous oxide ceramics prepared with starch as a pore-forming agent, in particular the porosity, pore size distribution and SEM investigation of sintered bodies. Porous composite Al₂O₃-ZrO₂ ceramics are prepared by traditional dry pressing, and the resulting microstructures are investigated and discussed. As a pore-forming agent starch (corn) is used.

2. Experimental

2.1. Starting Chemicals and Samples Preparation

The following materials were used in the present study: submicrometer α-Al₂O₃ powder (HTM30, Indian Alumina), monoclinic zirconia (m-ZrO₂) (d₉₀ = 45 µm, DVS Inc., Ukraine), light magnesia (Sigma Aldrich Co., Spain), and corn starch (Dr. Oetker, median particle size 14 µm and density 1.5 g/cm³ respectively).

Before shaping, as received alumina powder was washed five times by distilled water by the aim of reducing the Na₂O amount. Dried powder was sieved minus 50 mesh and dry pressing was employed to prepare specimens for mechanical and physical tests. It is observed that the main phase is monoclinic (m) for DVS zirconia powder.

M-ZrO₂ (10, 20 and 30 vol. % of m-ZrO₂) doped alumina samples were used in the experiments. As a stabilizing agent 10 mole % of magnesia was added to all powder mixtures. Various amounts of corn starch were added to the powder mixtures (10, 20 and 30 wt. %). Throughout this paper, the nomenclature AXXYY is employed. A, XX and YY represent alumina, the volume fraction of zirconia and the weight fraction of starch in the specimens, respectively.

Alumina/zirconia/magnesia/starch powder mixtures were prepared by mixing the dry powders by ball-milling for 2h.

The samples were pressed uniaxially into bars with a stress of 100 MPa. Pressed specimens were released from the mold and dried at 110°C until a constant weight was achieved. Finally, the specimens were sintered at temperatures of 1300, 1400, 1460 and 1550°C in air at a constant heating rate of 300 °C/h for 2 h.

Characterization Techniques

The density, closed and open porosity of sintered samples were determined according to the Archimedes method. The bending strength, σ_f , was determined by three-point bending test. The specimens were tested at room temperature using a three point support with a span of 40 mm in a universal testing machine (Schimadzu AG-IS). The specimens were loaded to failure with a cross-head speed of 0.05 mm/min. Reported strengths represented the mean of at least eight specimens and were calculated according the equation:

$$\sigma_f = \frac{3.Q.L}{2.l.h^2}$$

where Q is the failure load, L is the span, l is the width and h is the height. Crystalline phases were analyzed by X-ray diffraction (XRD) on a Panalytical X-Pert diffractometer equipped with Cu-K α radiation. A scan speed of 0.1 2 θ /min was employed in the 20–70° 2 θ range. A scanning electron microscope (SEM) (Jeol JSM 6400) equipped with an energy dispersive X-ray spectrometer (EDS) was used to characterize the microstructure of the sintered specimens.

3. Results and Discussions

3.1. Phase analysis of sintered composites

Composition of phases of alumina and zirconia powders were investigated by means of XRD and the respective patterns are illustrated in Fig. 1 and Fig. 2. It is observed that the main crystalline phase of alumina powder is corundum (α -Al₂O₃) and the main phase is monoclinic (m) corresponding to reflections 2 θ = 28° and 2 θ = 31° present in zirconia powder.

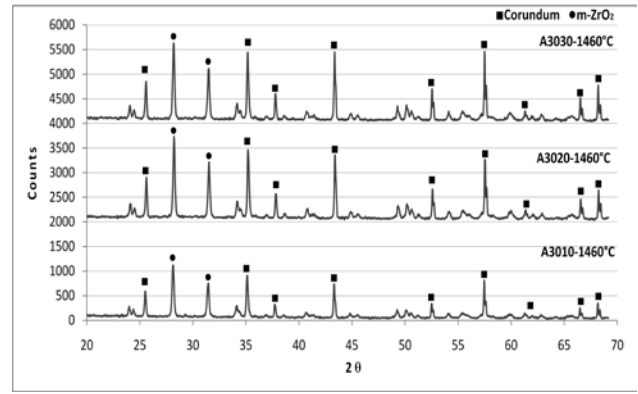


Figure 1. XRD Patterns of composites after sintering at 1460°C.

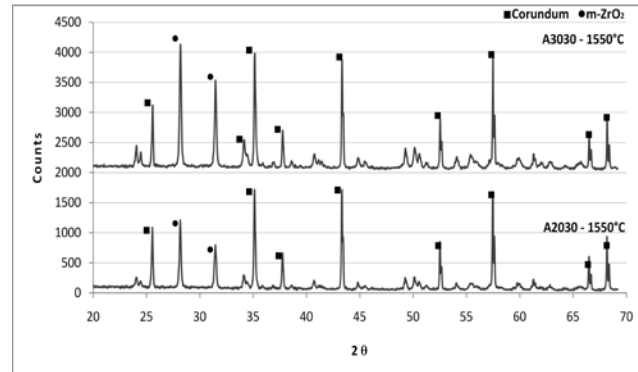


Figure 2. XRD Patterns of composites after sintering at 1550°C.

The diffractograms of all samples sintered at 1460 and 1550 °C showed corundum and m-zirconia as the principal crystalline phases. Upon cooling alumina-m-ZrO₂ composites from 1460 and 1550°C to room temperature, the tetragonal→monoclinic transformation occurred. Magnesia doping did not effect the stabilization of tetragonal zirconia at room temperature.

3.2. Water absorption tests

The effect of the sintering temperature on the water absorption, bulk density, porosity and relative density of alumina-zirconia composites are shown in Table 1. and Table 2. respectively.

Table 1. Water absorption test results of the samples

Sample Code	Sintering Temperature (°C)	Apparent Porosity (%)	Closed Porosity (%)	Total Porosity (%)
A1010	1300	48,352	1.503	49,532
	1400	45,848	1.535	47,383
	1460	45,611	0,919	46,529
A2010	1300	44,624	1.660	46,284
	1400	44,444	1.904	46.348
	1460	43,243	0,906	44,612
A3010	1300	45,869	0,795	46,664
	1400	42,985	2,075	45,059
	1460	43,285	1,328	43,613

Sample Code	Sintering Temperature (°C)	Apparent Porosity (%)	Closed Porosity (%)	Total Porosity (%)
A1020	1300	52,046	3,682	55,728
	1400	54,337	1,065	55,403
	1460	52,402	1,803	54,205
A2020	1300	53,214	1,642	54,856
	1400	53,767	0,384	54,151
	1460	51,059	1,640	52,699
A3020	1300	52,487	3,360	55,847
	1400	50,352	2,822	53,174
	1460	48,680	2,337	51,017

Sample Code	Sintering Temperature (°C)	Apparent Porosity (%)	Closed Porosity (%)	Total Porosity (%)
A1030	1300	58,099	1,555	59,654
	1400	58,214	0,437	58,651
	1460	56,944	1,591	58,536
A2030	1300	51,835	6,863	58,709
	1400	58,799	1,846	60,645
	1460	53,938	5,529	59,467
A3030	1550	46,000	1,664	47,664
	1300	52,593	6,700	59,293
	1400	56,004	3,832	59,836
	1460	55,833	0,748	56,582
	1550	46,000	4,676	50,676

Table 2. Water absorption test results of samples

Sample Code	Sintering Temperature (°C)	Apparent Density (gr/cm ³)	Bulk Density (gr/cm ³)	Water Absorption (%)
A1010	1300	4,026	2,079	23,291
	1400	4,004	2,168	21,160
	1460	4,051	2,203	20,762
A2010	1300	4,153	2,299	19,411
	1400	4,133	2,296	19,355
	1460	4,211	2,371	18,476
A3010	1300	4,375	2,368	19,391
	1400	4,280	2,439	17,623
	1460	4,337	2,504	16,912

Sample Code	Sintering Temperature (°C)	Apparent Density (gr/cm ³)	Bulk Density (gr/cm ³)	Water Absorption (%)
A1020	1300	3,813	1,824	28,628
	1400	4,026	1,837	29,630
	1460	3,965	1,887	27,806
A2020	1300	4,130	1,932	27,542
	1400	4,244	1,962	27,400
	1460	4,142	2,024	25,224
A3020	1300	4,120	1,960	27,418
	1400	4,193	2,079	24,217
	1460	4,240	2,175	22,396

Sample Code	Sintering Temperature (°C)	Apparent Density (gr/cm ³)	Bulk Density (gr/cm ³)	Water Absorption (%)
A1030	1300	3,969	1,662	34,956
	1400	4,077	1,704	34,172
	1460	3,968	1,708	33,333
A2030	1300	3,676	1,767	29,364
	1400	4,089	1,684	34,970
	1460	3,804	1,735	31,100
A3030	1550	4,148	2,240	20,536
	1300	3,813	1,807	29,098
	1400	4,053	1,783	31,415
	1460	4,365	1,928	28,971
	1550	4,056	2,190	21,005

As shown in the tables, total porosity values of the samples decreased with the increasing sintering temperatures for both alumina-zirconia composites. Although there are numerous techniques to fabricate porous ceramics such as combustion synthesis [15,16], foaming [17], reactive infiltration [18], freeze drying [19] pyrolysis of polymeric precursors [20], electrophoretic deposition [21] and gel-casting [22], partial sintering of ceramic tapes [23,24] and incorporation of pyrolyzable pore formers to tape casting slurries [8,25,26] are commonly employed methods to fabricate tape-cast porous ceramics. In partial sintering, densification is retarded in order to obtain a certain amount of porosity. However, partial sintering has fundamental difficulties in controlling the essential features of porosity such as shape, size, distribution and connectivity of the pores. Moreover, a desired dense ceramic matrix cannot be formed since the ceramic particles are allowed only to form neck and create a skeleton. Thus, porous ceramics fabricated by partial sintering are poor in mechanical strength [8,27].

Total porosity values of the higher amount of zirconia containing samples are lower than that of higher amount of alumina containing samples. This effect is related to the different relative density of green body (after drying).

In all cases of oxide ceramics prepared by dry pressing with corn starch it was found that below certain values of starch contents the porosity in the ceramic bodies remains essentially open (i.e. apparent) and above this “critical” value the fraction of closed porosity increases more or less abruptly. This effect can be interpreted as percolative in the sense, that from a certain value of total porosity mutual pore contact occurs, and with increasing total porosity a connected pore network is formed throughout the ceramic body.

Water absorption values of samples were given in Table 1. As shown in Table 1, water absorption values of the samples decreased with the increasing sintering temperatures for both samples. Water

absorption values of higher amounts of starch containing samples are higher than that of other samples. These results are expected.

Bulk density versus sintering temperature of the samples were given in Table 2. As shown in Table 2 bulk density values of the samples increased with the increasing sintering temperature for both samples. As expected, starch addition decreased the bulk density values.

From these graphs it can be concluded, that the total porosity of ceramics (after burnout) can be generally controlled by the nominal starch content in the powder mixture.

3.3. Bending strength

The results of the three point bending strength tests of the samples after sintering at 1300, 1400, 1460 and 1550 °C for 2 h are showed in Fig. 3, 4, and 5.

As shown in Figs. 3, 4 and 5 bending strength values of the samples increased with the increasing sintering temperature for both samples. At low amount of starch contents (10 %) the higher the zirconia content the higher the bending strength values. But when starch amount of the composites increases the strengthening effect of zirconia disappears. This can be a result of high porosity of the composites. Finally as expected, the higher the starch content the lower the bending strength for all composites.

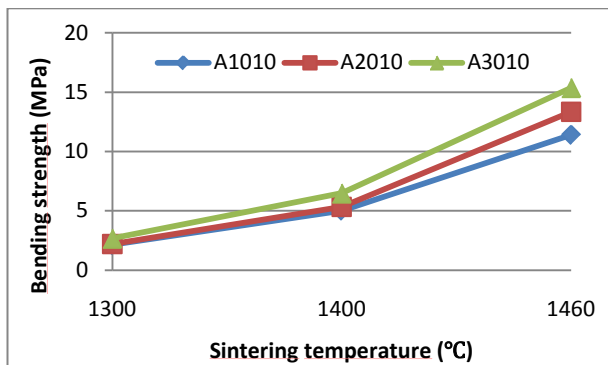


Fig.3. Three point bending strength tests of A1010, A2010 and A3010 samples after sintering at 1300, 1400 and 1460 °C for.

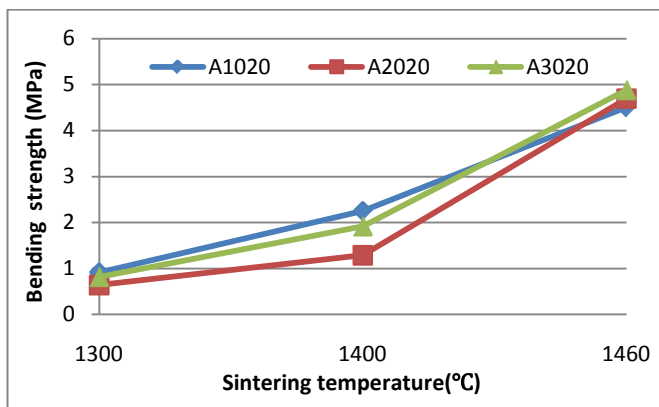


Fig.4. Three point bending strength tests of A1020, A2020 and A3020 samples after sintering at 1300, 1400 and 1460 °C.

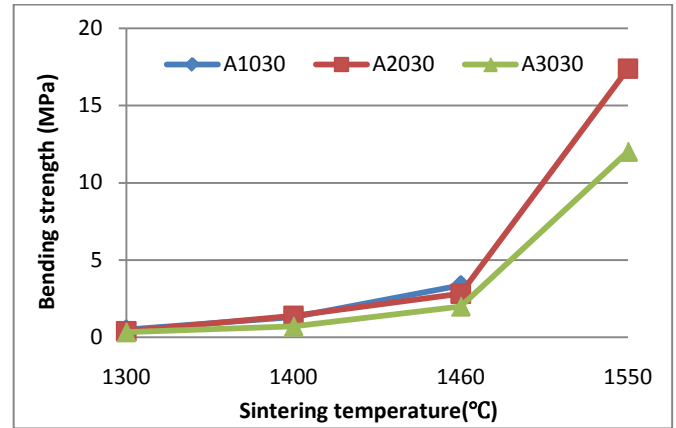


Fig.5. Three point bending strength tests of A1030, A2030 and A3030 after sintering at 1300, 1400, 1460 and 1550 °C

3.4. SEM Analysis

Fig. 6 shows the microstructure of A3030 sample sintered at 1550°C. As shown in Fig. 7, plate-like grains formed in the sintered body of the composite. Wang et al. (2001) indicated that plate-like grains of Al_2O_3 are observed when the matrix contains small amount of impurities, especially when SiO_2 is present with other oxides. However Koyama et al. reported that, to form plate-like grains, higher temperatures ($\geq 1500^\circ\text{C}$) and longer holding times are typically required [28]. In the present work, plate-like grains formed at 1550°C

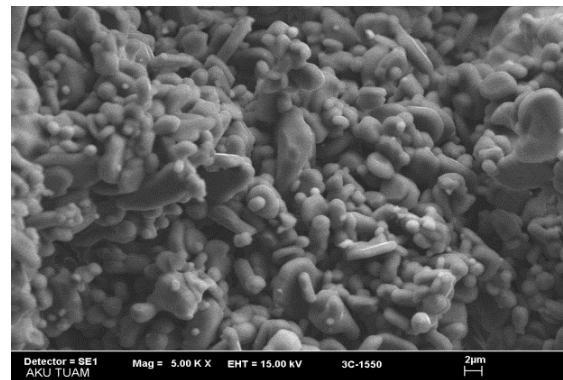


Fig 6. SEM micrograph of A3030 sample sintered at 1550°C.

4. Conclusions

Maximum values of the total porosity of porous ceramics (Al_2O_3 , ZrO_2 and ZTA composite ceramics) prepared with starch by dry pressing was approx. 60 %. The total and open (apparent) porosity in the ceramics after firing depends on the amount of starch added to the suspension. Above a total porosity value of approx. $18 \pm 5\%$ (percolation threshold) the fraction of open porosity increases steeply, and at total porosity values of approx. 50% practically all pores are open. Generally it can be said that the porosity of ceramics can be controlled by the amount (nominal content) of starch added to the suspension and the pore size can be controlled by the type of pore-forming agent. Total porosity values of the higher amount of zirconia containing samples are lower than that of higher amount of alumina containing samples. This effect is related to the different relative density of green body. Finally as expected, the higher the starch content the lower the bending strength for all composites.

5. Literature

- [1] T. Tsuru, Inorganic porous membranes for liquid phase separation, *Separation & Purification Reviews* 30 (2001) 191–220.
- [2] J. She, T. Ohji, Z.-Y. Deng, Thermal shock behavior of porous silicon carbide ceramics, *Journal of the American Ceramic Society* 85 (2002) 2125–2127.
- [3] M.L. Dunn, M. Taya, Electromechanical properties of porous piezoelectric ceramics, *Journal of the American Ceramic Society* 76 (1993) 1697–1706.
- [4] C.P. Shaw, R.W. Whatmore, J.R. Alcock, Porous, functionally gradient pyroelectric materials, *Journal of the American Ceramic Society* 90 (2007) 137–142.
- [5] L. Yin, H.X. Peng, L. Yang, B. Su, Fabrication of three-dimensional inter-connective porous ceramics via ceramic green machining and bonding, *Journal of the European Ceramic Society* 28 (2008) 531–537.
- [6] A.R. Walpole, Z. Xia, C.W. Wilson, J.T. Triffitt, P.R. Wilshaw, A novel nano-porous alumina biomaterial with potential for loading with bioactive materials, *Journal of Biomedical Materials Research Part A* 90 (2009) 46–54.
- [7] X. Huang, Separator technologies for lithium-ion batteries, *Journal of Solid State Electrochemistry* 15 (2011) 649–672.
- [8] S.F. Cobin, P.S. Apte, Engineered porosity via tape casting, lamination and the percolation of pyrolyzable particulates, *Journal of the American Ceramic Society* 82 (1999) 1693–1701.
- [9] G.T. Chandrappa, N. Steunou, J. Livage, Macroporous crystalline vanadium oxide foam, *Nature* 416 (2002) 702.
- [10] Z. Zivcova, E. Gregorova, W. Pabst, Low- and high-temperature processes and mechanisms in the preparation of porous ceramics via starch consolidation casting, *Starch/Stärke* 62 (2010) 3–10.
- [11] J.R. Wilson, S.A. Barnett, Solid oxide fuel cell Ni-YSZ anodes: effect of composition on microstructure and performance, *Electrochemical and Solid-State Letters* 11 (2008) B181–B185.
- [12] D. Simwonis, F. Tietz, D. Stöver, Nickel coarsening in annealed Ni/8YSZ anode substrates for solid oxide fuel cells, *Solid State Ionics* 132 (2000) 241–251.
- [13] A. Sarikaya, V. Petrovsky, F. Dogan, Effect of the anode micro-structure on the enhanced performance of solid oxide fuel cells, *International Journal of Hydrogen Energy*, doi: 10.1016/j.ijhydene.2012.05.007, in press.
- [14] Zuzana Zivcová-Vlčková, Janis Locs, Melanie Keuper, Ivona Sedlářová, Michaela Chmelíčková, Microstructural comparison of porous oxide ceramics from the system $\text{Al}_2\text{O}_3\text{--ZrO}_2$ prepared with starch as a pore-forming agent, *Journal of the European Ceramic Society* xx(2012).
- [15] D. Chen, B. Zhang, H. Zhuang, W. Li, Combustion synthesis of network silicon nitride porous ceramics, *Ceramics International* 28(2003) 363–364.
- [16] K. Maca, P. Dobsak, A.R. Boccaccini, Fabrication of graded porous ceramics using alumina–carbon powder mixtures, *Ceramics International* 27(2001) 577–584.
- [17] X. Mao, S. Wang, S. Shimai, Porous ceramics with tri-modal pores prepared by foaming and starch consolidation, *Ceramics International* 34(2008) 107–112.
- [18] J.-M. Qian, Z.-H. Jin, X.W. Wang, Porous SiC ceramics fabricated by reactive infiltration of gaseous silicon into charcoal, *Ceramics International* 30(2004) 947–951.
- [19] T. Fukasawa, M. Ando, T. Ohji, S. Kanzaki, Synthesis of porous ceramics with complex pore structure by freeze-dry processing, *Journal of the American Ceramic Society* 84(2001) 230–232.
- [20] Y.-W. Kim, S.-H. Kim, C. Wang, C.B. Park, Fabrication of micro cellular ceramics using gaseous carbon dioxide, *Journal of the American Ceramic Society* 86(2003) 2231–2233.
- [21] A. Nakahira, F. Nishimura, S. Kato, M. Iwata, S. Takeda, Green fabrication of porous ceramics using an aqueous electrophoretic deposition process, *Journal of the American Ceramic Society* 86 (2003) 1230–1232.
- [22] Y. Gu, X. Liu, G. Meng, D. Peng, Porous YSZ ceramics by water-based gel casting, *Ceramics International* 25(1999) 705–709.
- [23] A. Mortensen, S. Suresh, Functionally graded metal–ceramic composites: part 1—processing, *International Materials Reviews* 40(1995) 239–265.
- [24] J.F. Yang, G.J. Zhang, T. Ohji, Porosity and micro structure control of porous ceramics by partial hot pressing, *Journal of Materials Research* 16(2001) 1916–1918.
- [25] S. Zhu, S. Ding, H. Xi, Q. Li, R. Wang, Preparation and characterization of SiC/cordierite composite porous ceramics, *Ceramics International* 33(2007) 115–118.
- [26] L. Hu, C.-A. Wang, Y. Huang, Porous yttria-stabilized zirconia ceramics with ultra-low thermal conductivity, *Journal of Materials Science* 45(2010) 3242–3246.
- [27] H.L. Zhang, J.-F. Li, B.-P. Zhang, Micro structure and electrical properties of porous PZT ceramics derived from different pore-forming agents, *Acta Materialia* 55(2007) 171–181.
- [28] Koyama, T., Nishiyama, A., Niihara, K., 1993. Effect of a small amount of liquid-forming additives on the microstructure of Al_2O_3 ceramics, *J. Mater. Sci.* 28 (21) 5953–5956.