VERSITA

Cent. Eur. J. Chem. • 6(3) • 2008 • 482–487
DOI: 10.2478/s11532-008-0047-y

Central European Journal of **Chemistry**

Preparation and characterization of alumina-zirconia composite material with different acid ratios by the sol-gel method

Research Article

Ozgecan Barlay Ergu, Metin Gürü*, Canan Cabbar

Department of Chemical Engineering, Gazi University, 06570 Ankara, Turkey

Received 13 December 2007; Accepted 28 May 2008

Abstract: Alumina-zirconia composite materials were produced with different acid ratios by the sol-gel method using aluminum isopropoxide and zirconium chloride. The composites were produced by changing acid/alkoxside ratio in alumina. The composite materials were calcinated at 600°C, 900°C and 1300°C. The effects of acid concentration and calcination temperature on the surface area and pore radius were determined from the nitrogen adsorption isotherm at 77 K. The density of the composites was also measured. The minimum density of produced material was recorded as 1.35 g cm^{-3} at an acid/alkoxside ratio of 0.2. The highest specific surface area and pore diameter of the lightest material are 191.86 m^2 g^{-1} and 18.4 Å, respectively. Although pore diameter and specific surface area are not changed at any of the experimental temperatures which were tested by decreasing acid/alkoxside ratio, the density is slightly increased. However, it was observed that the calcination temperature significantly affects the surface area and density of the material.

Keywords: *Alumina-zirconia composite material • Sol-gel method • BET • Porosity*

1. Introduction

High technology ceramics have different crystal phases as well as superior characteristics such as high temperature resistance and high chemical stability. Among high technology ceramics, Al_2O_3 and ZrO_2 ceramic oxides have wide usage possibilities as filters, membranes and catalysts, due to their porous structures [1,2].

Alumina is one of the widely used structural ceramics [3]. Additive interactions can modify and achieve tailor-made properties of alumina ceramics. Zirconia is one such additive which can increase the strength and toughness of the alumina matrix either by stress-induced transformation toughening or microcrack toughening [4].

Several methods of preparing the alumina / zirconia powders and composites have been reported [5-8]. Sol-gel processing technology has been developed for the fabrication of high quality ceramic-based composites. The processing conditions such as composition, retention of the t-phase of zirconia and the calcination temperature strongly influence the morphology of the powder and sintering behavior [8,9].

This study intends to get a composite structure from Al_2O_3 and ZrO_2 through the use of the sol-gel method. The ZrO_2-Al_2O_3 calcinated at different temperatures were analyzed by means of X-ray diffraction, and thus the temperature dependence of the phase structure was determined. In addition, alumina-zirconia composite materials were produced by changing the acid/alkoxside ratio in alumina and the effects of this change on BET surface area pore radius distribution of the composite material were determined.

2. Experimental Procedures

The ZrO_2-Al_2O_3 composite materials were prepared using the sol-gel method. To prepare beohmite sols, aluminium iso-propoxide ($Al(C_3H_7O)_8$, Aldrich) was hydrolyzed in excess water (113:1 H_2O/Al^{3+} mol) at

* *E-mail: mguru@gazi.edu.tr*

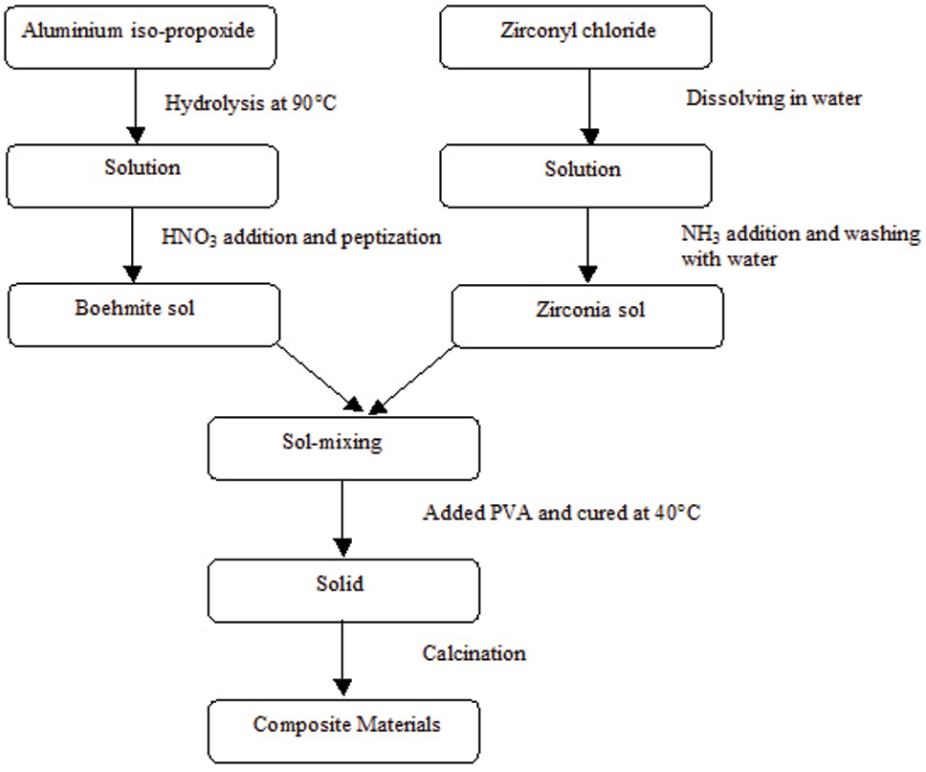

Figure 1. Flow diagram of the processing of alumina-zirconia composite materials.

90°C, followed by peptization with different amounts of HNO_3 (Merck) (0.2:1, 0.02:1, 0.03:1 H^+/Al^{3+} mol) to form a stable colloid sol. The sol was kept at about 90°C for 12 h under reflux condenser, at which time, most of the alcohol was evaporated. Then the clear beohmite sol with pH values of about 3.7, 4.1, 4.2 were obtained.

Zirconia sol was prepared from zirconyl chlorite ($ZrOCl_2$-$8H_2O$, Aldrich) in aqueous solution. While stirring, 8g zirconyl chloride was dissolved in 50 ml deionized water to form a clear solution. Concentrated NH_4OH (Merck) solution was then added to obtain the desired pH values (3.7, 4.1, 4.2)

The prepared beohmite sol and zirconia sol were mixed at molar ratio of 1:1 of Al:Zr to prepare the composite sol. A solution of polyvinyl alcohol (PVA, Aldrich) with an average molecular weight of 72,000 (3g/100 ml H_2O) was then added to the composite sol at room temperature. The sol was dried and cured at 40°C in an oven. Then different samples were sintered at 600°C, 900°C and 1300°C. Fig. 1 shows the typical flow chart of the processing of the ZrO_2-Al_2O_3 composite material.

2.1. Characterization

The phase structures of ZrO_2-Al_2O_3 composite materials, pure zirconia and pure alumina were determined by X-ray diffraction (XRD, Bruker D8). The surface morphology was examined with a scanning electron microscope equipped with EDS (SEM, JSM 6360, JOEL). The pore size distribution (PSD) was measured using the nitrogen isothermal adsorption technique (Nova Quantachorome). Thermal properties of the ZrO_2-Al_2O_3 dried gel sample were specified simultaneously by thermogravimetric analysis and a differential scanning calorimetry system (Seteram SETSYS Evolution 1750) in air at a heating rate of 10°C/min. Furthermore the densities of the produced materials were measured using a helium pycnometer (Quantochrome Stereopycnometer).

3. Results and Discussion

3.1. Phase structure of composite materials

X-ray diffraction (XRD) data of pure alumina and pure zirconia calcinated at different temperatures (600°C, 900°C, 1300°C) for 2 h, were in agreement literature values [10-12].

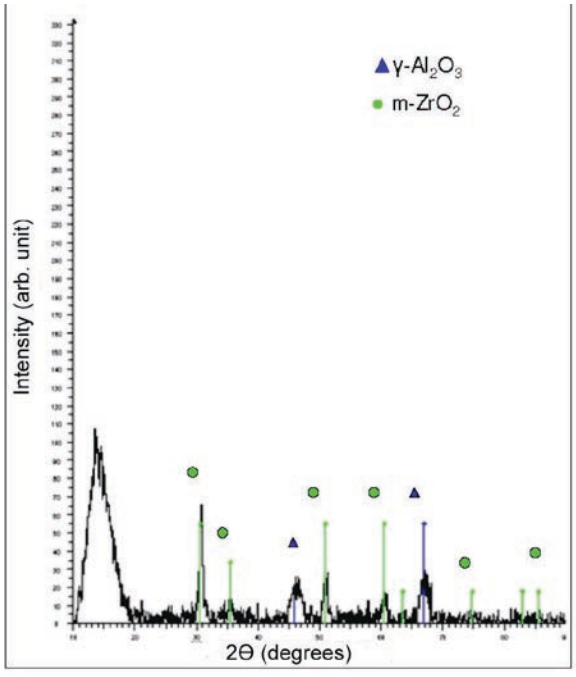

Figure 2. XRD pattern of the alumina-zirconia composite material calcinated at 600ºC at an acid concentration of 0.2 for the alumina matrix of the material.

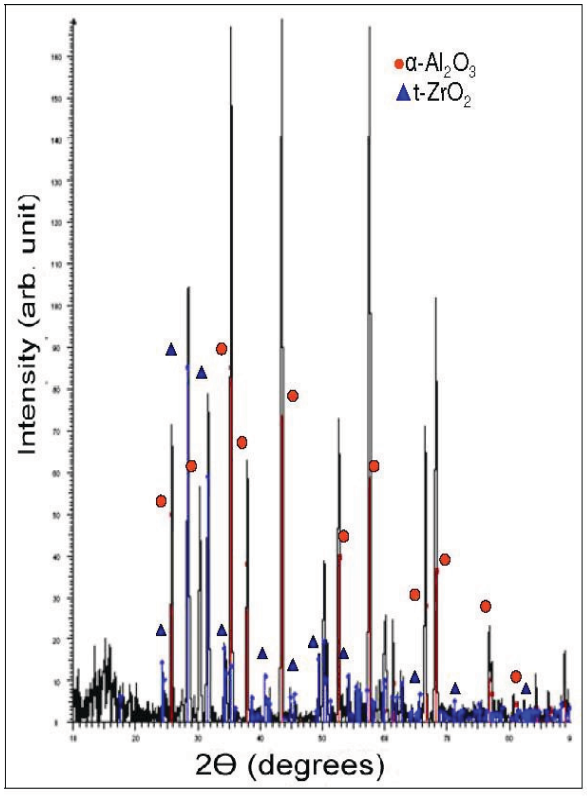

Figure 4. XRD pattern of the alumina-zirconia composite material calcinated at 1300ºC at an acid concentration of 0.2 for the alumina matrix of the material.

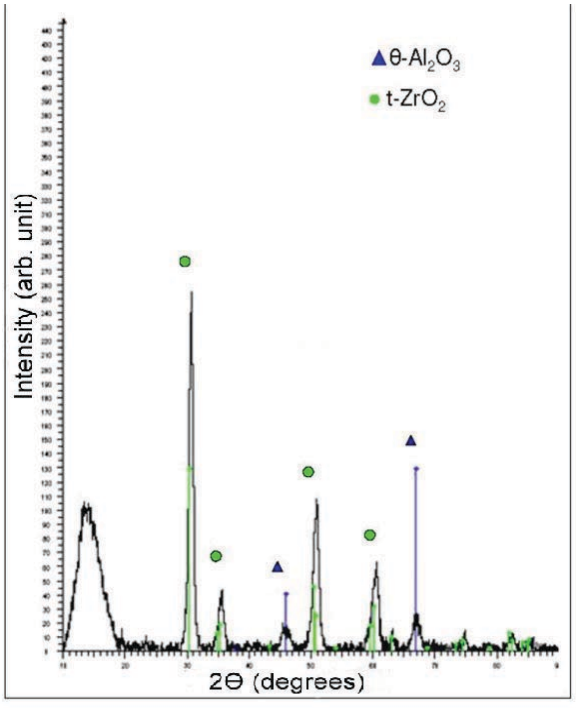

Figure 3. XRD pattern of the alumina-zirconia composite material calcinated at 900ºC at an acid concentration of 0.2 for the alumina matrix of the material.

Figs. 2-4 show the XRD patterns of the ZrO_2-Al_2O_3 composite materials produced at different calcination temperatures (600°C, 900°C and 1300°C (0.2:1 H^+/Al^{3+} mol)).

After calcination at 600°C, zirconia does not transform into the tetragonal form but alumina transforms into the γ-Al_2O_3 phase. After further heat treatment at 900°C, zirconia exists in two phases of tetragonal and monoclinic modifications, and alumina transforms into the θ-Al_2O_3 form. With increasing temperature, zirconia transforms completely to the monoclinic structure after calcination at 1300°C and alumina transforms to the α-Al_2O_3 form. Increasing the sinterization temperature from 900°C to 1300°C gradually leads to a rise in the diffraction peak intensity and a decrease in diffraction peak width. This indicates that, gradually, the crystal structure becomes homogenous and the grain sizes increase. The main crystal phase observed for the composite material heated up to 1300°C was t-ZrO_2 and α-Al_2O_3.

3.2. PSD and density of the composite materials

The effects of acid concentration and calcination temperature in the alumina matrix on the surface area and pore radius were observed from its nitrogen adsorption isotherm. The pore size distribution computed from the adsorption isotherm using the BET

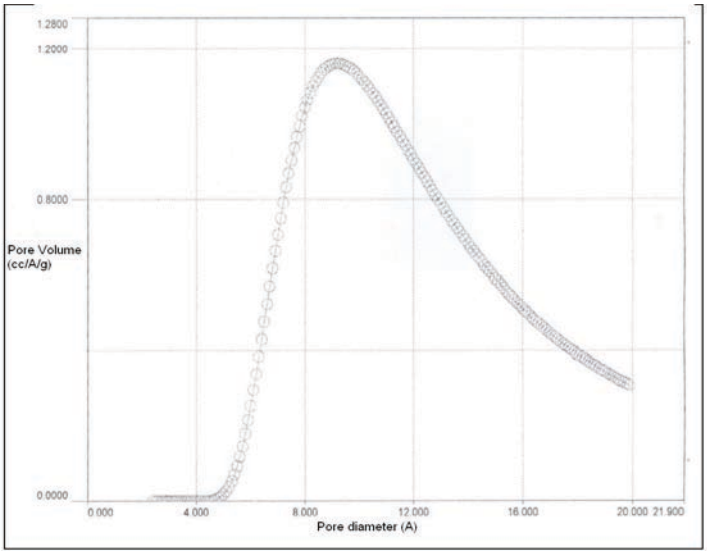

Figure 5. Porosity volume versus porosity diameter of the alumina-zirconia composite material calcinated at 600ºC and an acid concentration of 0.2 in the alumina matrix of the material.

Table 1. Data of PSD and density of composite materials.

Calcination Temperature (°C)	Acid/alkoxside ratio	Specific surface area (m^2 g^{-1})	Pore diameter (Å)	Density (g/cm^3)
600	0.2	191.86	18.4	1.35
900	0.2	105.29	18.2	1.62
1300	0.2	Can not measured	9.6	2.15
600	0.03	191.52	18.2	1.41
900	0.03	118.27	18	1.89
1300	0.03	2.13	9.6	2.16
600	0.02	192.29	18.2	1.48
900	0.02	125.39	18	1.92
1300	0.02	2.21	9.6	2.24

method is shown in Fig. 5. The pore size distribution graphs obtained at different acid concentrations and calcination temperatures resemble the pattern in Fig. 5. Surface areas and pore radii are tabulated in Table 1. The densities of produced materials measured using a helium pycnometer are also given in the same Table. The change in acid concentration did not significantly affect the surface area and pore radius. However, changes in the calcination temperature had a strong effect on these parameters. With increasing crystallization and the structure converting to shrunk form, the specific surface area of material was observed to be about 2 m^2 g^{-1}. From these experimental results, it was concluded that the pore diameter decreased and the density increased with increasing syntherization.

3.3. EDS-equipped SEM analysis

Microstructures of the produced composite materials and their surface morphologies were examined by SEM equipped with EDS. SEM images and EDS mappings of alumina-zirconia composite material calcinated at 600ºC with an acid ratio of 0.2 in the alumina matrix are given in Fig. 6 and Fig. 7, respectively. Despite the good quality of the SEM photographs, porosities of the material could not be observed at x1000 magnification, since the pores in the structure are very small. However, as can be seen from the image, zirconia was uniformly dispersed in the alumina. Also, EDS mappings of the same material which are shown in Fig. 7, support this conclusion. It was observed from the mappings that oxygen, alumina and zirconia particulates had not grown.

Since the EDS mappings were imaged from the surface of the structure, compositions of elements correspond to the surface composition of the structure. The highest assay is oxygen which was originated from alumina and zirconia compounds. The second and third components were aluminum and zirconium according to the EDS analysis. Since mol fractions of alumina and zirconia were equal, the results suggest that a large quantity of zirconia might be embedded in the internal structure.

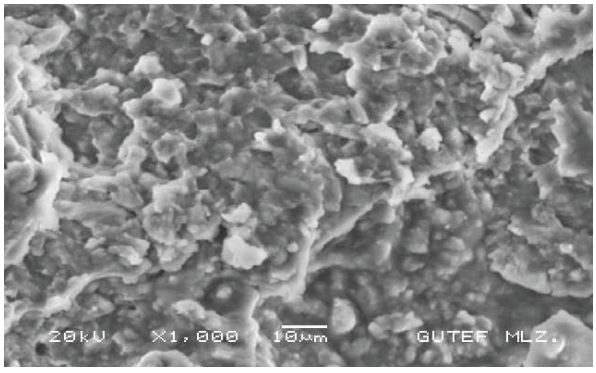

Figure 6. SEM image of the alumina-zirconia composite material calcinated at 600ºC with an acid concentration of 0.2 in the alumina matrix.

3.4. TGA analysis

The DSC and TG analyses of dried gel for acid/alkoxside ratio of 0.2 are shown in Fig. 8. The endothermic peak at 200ºC is due to the expulsion of physically bonded water and some organics [3]. Another endothermic peak at 400ºC corresponds to the transformation of pseudo boehmite [$Al(OH)_3$ and γ-AlOOH] into γ-alumina. The exothermic peak at 600ºC is attributed to the crystallization of t-zirconia. The formation of α-Al_2O_3 is completed at 1290ºC with a small exothermic peak [3,6,13]. The phase transformation from γ-AlOOH to α-Al_2O_3 follows the path reported previously [13,14].

$$\gamma\text{-}Al_2OOH \xrightarrow{400ºC} \gamma\text{-}Al_2O_3 \xrightarrow{800ºC} \delta\text{-}Al_2O_3 \xrightarrow{1000ºC} \theta\text{-}Al_2O_3 \xrightarrow{1200ºC} \alpha\text{-}Al_2O_3$$

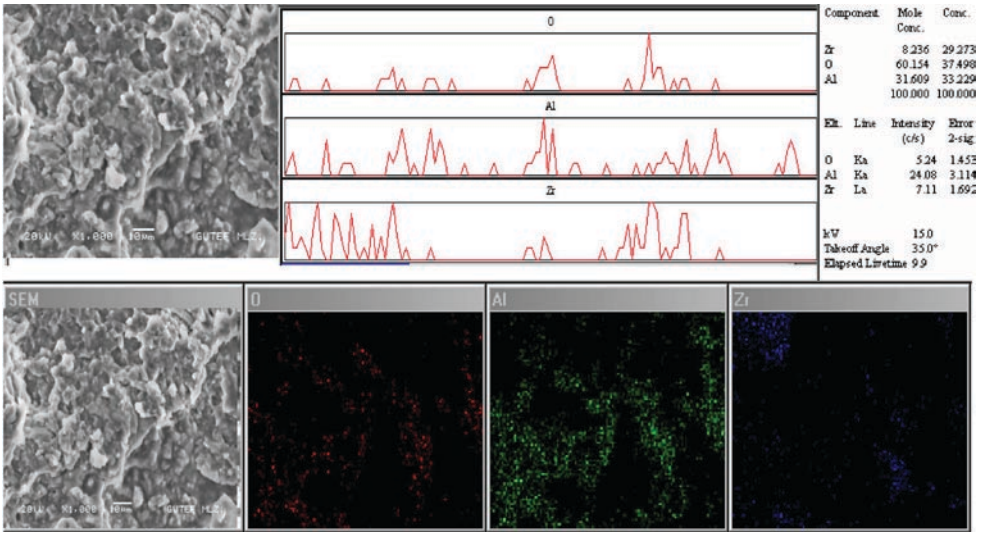

Figure 7. EDS mappings of the alumina-zirconia composite material calcinated at 600ºC with an acid concentration of 0.2 in the alumina matrix.

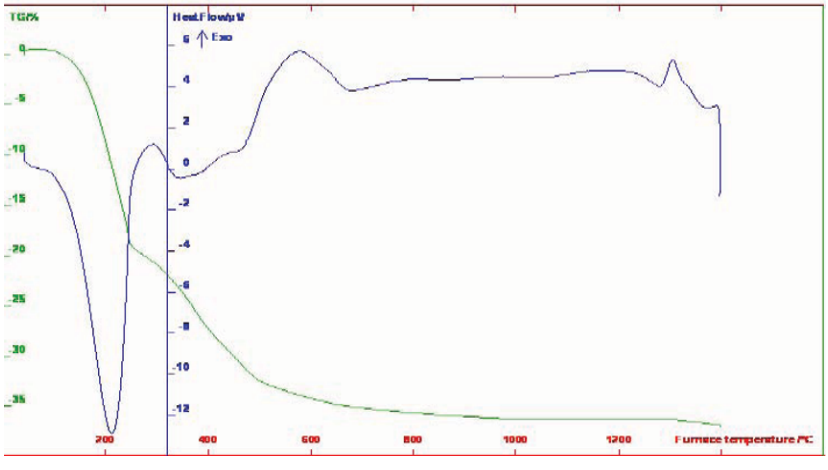

Figure 8. TG/DSC plot for the Al_2O_3-ZrO_2 precursor powders with 0.2 acid/alkoxside ratio.

4. Conclusion

Alumina zirconia composite material were produced with different acid ratios using the sol-gel method. Acid ratios were obtained by changing the acid-alkoxside ratio in alumina. The produced materials were calcinated at 600ºC, 900ºC and 1300ºC. The change in the acid concentration did not affect surface area, pore radius and density of produced materials, but different calcination temperatures strongly affected these parameters.

Acknowledgements

This study was supported by 06/2007-22 Gazi University. Scientific Research Project and 2001K120590 State Planning Authority Project.

References

[1] M. Schwartz, " Composite Material Handbook" (Mc Graw Hill, New York, 1984) 1-7
[2] D. Hull, " An Introduction to Composite Materials" (Cambridge University Press, UK, 1981)
[3] K. Wefers, C. Misra, " Oxides and hydroxides of aluminium", Alcoa Technical Paper No.19 (Alcoa Laboratories, Pittsburgh, PA, 1987)
[4] D. Sarkar, D. Mohapatra, S. Ray, S. Bhattacharyya, S. Adak, and N. Mitra, " Synthesis and characterization of sol-gel derived ZrO2-doped Al203 nanopowder", Ceramics International, (2006)
[5] M. Balasubramanian, S.K. Malhotra, C.V. Gokularathnam, Materials Processing Technology 67, 67 (1997)
[6] D. Jayaseelan, T. Nishikawa, H. Awaji, F.D. Gnanam, Materials Science and Engineering A256, 265 (1998)
[7] B. Kerkwijk, A.J.A. Winnubst, H. Verweij, E. J. Mulder, H.S.C. Metsalaar, D. J. Schipper, Wear 225-229, 1293 (1999)
[8] H.Y. Lee, W. Rieheman, B.L. Mordike, J Eur Ceram Soc 10, 245 (1992)
[9] X. W. Huang, S. W. Wang, X. X. Huang, Ceram Int 29, 765 (2003)
[10] H. Cheong, W. Cho., J. Ha., C. Kim, D. Choi, D. Cheong, J Alloys and Com 290, 304 (1999)
[11] D.D. Jayaseelan, D.A. Rani, T. Nishikawa, H. Awaji, F.D. Gnanam, J Europ Ceram Society 20, 267 (2000)
[12] Y. Hao, J. Li, X. Yang, X. Wang, L. Lu, Materials Science and Engineering A 367, 243 (2004)
[13] D. Sarkar, S. Adak, N.K. Mitra, Composites: Part A. 38, 124 (2007)
[14] B. B. Roger, G. L. Messing, J Am Ceram Soc, 82, 825 (1999)