Key Engineering Materials Vols. 264-268 (2004) pp. 403-406
online at http://www.scientific.net

Preparation and Characterization of Sol-Gel Derived 4%La_2O_3- Al_2O_3 Ceramic Membrane on Clay-Based Supports

B. Ersoy[1], V. Gunay[2]

[1] Afyon Kocatepe University, Mining Engineering Dept., AFYON-TURKEY
[2] TUBITAK-MRC, MCTRI, P.O. Box 21, 41470, Gebze-KOCAELI / TURKEY

Keywords: Sol-gel coating, clay support, γ-Al_2O_3, porosity, ceramic membranes.

Abstract. In this work, γ-Al_2O_3 membrane layer (4 wt % La_2O_3 + 96 % Al_2O_3) was coated on the clay based porous support by using the sol-gel coating. The coating solution was prepared by using boehmite (AlOOH), La-nitrate ($La_2(NO_3)_3.6H_2O$), PVA, distilled water and HNO_3. The thickness of the γ-Al_2O_3 membrane layer was between 5-7 µm. Two unprocessed clay samples which were supplied from Kutahya and Balıkesir regions, were used to produce supports for the membranes. Porosities of the supports were varied from 25 to 40% depending on sintering temperatures. Mean pore diameter of the supports were between 0.01-1µm. The mean pore diameter of 4wt%La_2O_3 – Al_2O_3 membrane layer was around 11 nm and total pore area was 113 m^2 / g at 1000^0C for 1 hour.

Introduction

Ceramic membranes are used to separate two phases (gas-liquid, solid-liquid, liquid-gas) and gas mixtures (H_2, N_2, CO_2, O_2, etc.), and to filtrate impurities with very fine size in a phase [1]. Polymeric materials are generally used as membrane but polymeric membranes are chemically and thermally unstable for some applications, which require high temperature and drastic chemical conditions.

Most ceramic membranes have a composite structure, consisting of two or more layers. One of the layers is the support, which usually gives the required strength to the membrane and also should have certain separation ability with appropriate pore size and pore-size distribution. The porosity in each membrane layer consists of a well-controlled size range to provide the desired separation selectivity. Although ceramic membranes can be used in fine filtration (2-10µm), most of them are used in micro-filtration (0.02-2µm) and ultra-filtration (0.001-0.02µm) applications. The top layers of the membrane are usually prepared by coating the substrate using the sol-gel technique [2].

Commercial and local alumina powders are widely used for the preparation of porous supports and these were used in the preparation of ceramic membranes by our group and the results were reported elsewhere [3]. Clay based porous supports can also be used for this purpose since the availability and the prices of natural clay samples, give them advantages over other materials [4].

In this work ceramic membranes were prepared by coating of Al_2O_3-4wt%La_2O_3 top layer on the clay based porous supports using the sol-gel technique. Then, the membranes were characterized and tested under 2-10 bars pressure for mechanical stability by water flux test.

Experimental procedure

Preparation of porous supports. Two different clays obtained from Kütahya (Turkey) region were used as received without any processing. First, clays were reduced to powder size (mean particle diameter was around 100μm) and then moisturized with water to 6 wt %. These moist clay powders were pressed by applying 1 ton/cm^2 pressure as disk-shaped supports with 40 mm diameter and 3 mm thickness. Supports were sintered at 1000 ^oC for 1 hour and characterized by employing XRD, SEM and Hg-porosimeter techniques. More details on the clays and preparation were given elsewhere [4].

Membrane Preparation

Böehmite sol with $La_2(NO_3)_3.6H_2O$ addition were prepared in hot water (80^0C) by dispersing the böehmite powders (Keith Ceramics, UK), La-nitrate solution and PVA (72000 g.mol^{-1}), (the weight ratio of PVA:H_2O was 3 %) solution used as a binder and HNO_3 was added for adjusting the pH to 2. Al_2O_3 gels were prepared with 4wt% La_2O_3 and without La_2O_3 additions. The clay supports were dip coated with the sol for 5 seconds. Then, these coated supports were dried first at 35 ^oC in 70% humidity for 12 hrs, then at 45^0C in 60% humidity for 12 hrs, and at 55^0C in 50% humidity for 6 hrs in a humidity chamber. The dried membranes were sintered at 1000^0C for 3 h, with an heating and cooling rate of 1^0C/min.
The morphology of membrane layer was examined using scanning electron microscope (SEM) and tested for its mechanical stability under 2-10 bar pressure by water flux method. Pore size, pore size distribution and phases of the γ-Al_2O_3 membrane layers were measured by using calcined gels.

Results and Discussion

Supports. Clay based supports have large (0.01-10 μm) and non-homogeneous pore size distribution. This was an expected result and related to crystalline structure of clays and occurrence of impurities. The clay samples were named as Clay-1 and Clay-2. The chemical compositions and crystalline phases were different in each clay samples. Clay-1 was an alunitic clay containing; alunite (3 Al_2O_3. 4 SiO_2. 8 H_2O), quartz (SiO_2), and kaolinite ($Al_2Si_2O_5(OH)_4$) with the main oxides as 65wt% Al_2O_3, 27wt% SiO_2. Clay-2 contained; quartz, dolomite ($CaMg(CO_3)_2$), kaolinite with the main oxides as 9wt% Al_2O_3, 80wt% SiO_2 and 4.5wt% CaO. The mean pore diameters of the supports were around 1μm at 1000^0C for 1 hour. The content of porosities were 45% and 25% for Clay-1 and Clay-2, respectively.

γ-Al_2O_3 gels. XRD, pore size and total pore area results of alumina gels from 700 to1200^0C for 1 hour, were given in Table 1.

Table 1. Phases, pore sizes and total pore areas of alumina gels

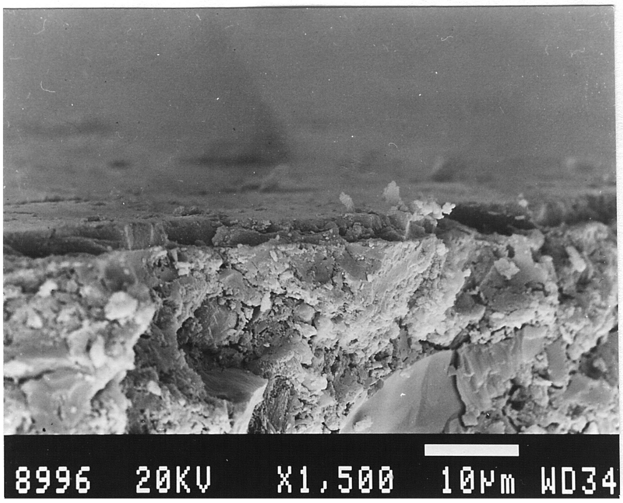
Temp. (^oC)	Al-0 Phases	Al-0 P.Size (nm)	Al-0 T.P.A. (m^2/g)	Al-4 Phases	Al-4 P.Size (nm)	Al-4 T.P.A (m^2/g)
700	γ,θ	7.4	179	γ,θ	7.2	180
900	γ,θ	7.7	165	γ,θ	7.9	139
1000	γ,θ,α	10.8	105	γ,θ,	11.0	113
1100	γ,θ,α	13.2	55	γ,θ,	12.2	79
1200	α	58.7	9	γ,θ	14.8	37

Al-0: 100 % Al_2O_3, Al-4: 4 wt % La_2O_3 - Al_2O_3 T.P.A: Total Pore Area, P: Pore

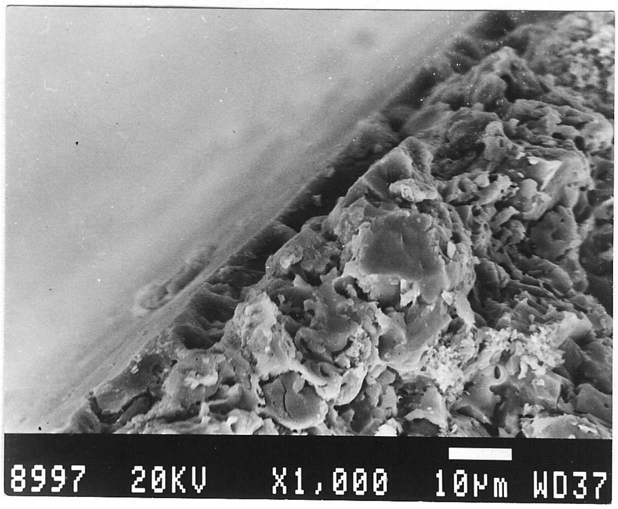
According to XRD results, crystalline phases of all alumina gels up to 900^0C with and without La_2O_3 addition were γ-Al_2O_3 (mixture of γ-Al_2O_3 and θ-Al_2O_3 phases). At 1000°C, alumina gel without La_2O_3 addition (Al-0) showed some transformation of γ-Al_2O_3 phase to α-Al_2O_3 phase. But in alumina gel with 4 wt% La_2O_3 addition (Al-4) this phase transformation was inhibited. Even at 1200^0C, there was only γ-Al_2O_3 present in Al-4 gel. These results clearly support the hypothesis that the phase transformation from γ-Al_2O_3 to α-Al_2O_3 proceeds via a nucleation and growth mechanism[5]. Some alkaline earth or rare earth oxides have been reported to suppress the phase transformation and thermal stability of γ-Al_2O_3 by inhibiting the nucleation of α-phase[6].
The specific surface area of γ-Al_2O_3 membrane layers must be high and pore size distribution should be very narrow with small pore diameters in order that the gel layer can use for membrane applications. According to Table 1, the mean pore diameter of Al-0 and Al-4 gels were 10.8 nm and 11 nm respectively. The main differences in mean pore diameter and in total pore ares of the gels started above 1000^0C. Total pore area of Al-0 gel at 1200 ^{o}C was 9 m^2/g and that of Al-4 was 37 m^2/g. Mean pore diameters of Al-0 and Al-4 at 1200^0C, were 58.7 and 14.8 nm, respectively. This is an important parameters for membranes to use them at high temperatures. Thermal stability of γ-Al_2O_3 were increased to 1200^0C with the addition of 4wt% La_2O_3.

Membrane characterization

The SEM micrographs of γ-Al_2O_3 membrane layer (Al_2O_3 – 4wt% La_2O_3) is shown in Figure 1 . The thickness of gel layer is 5-7 µm and the coatings have homogeneous structure. Coarse structure of the substrates can be seen clearly.



a)



b)

Figure 1**.** SEM micrographs of membranes with supports **a**)Clay-1, **b**)Clay-2.

The results of water flux test of membranes are shown in Figure 2. The membranes were stable under 10 bars pressure. The amount of water flux were different in membrane with two different clay-based substrates. Water flux was higher in membrane with Clay-2 than Clay-1. In Clay-2 the amount of porosity at 1000^0C was around 25% and that was 45% in Clay-1. The mean pore diameter in Clay-2 was smaller than Clay-1. This showed that capillary sunction of water in the water flux test was more effective with smaller pore size substrate.

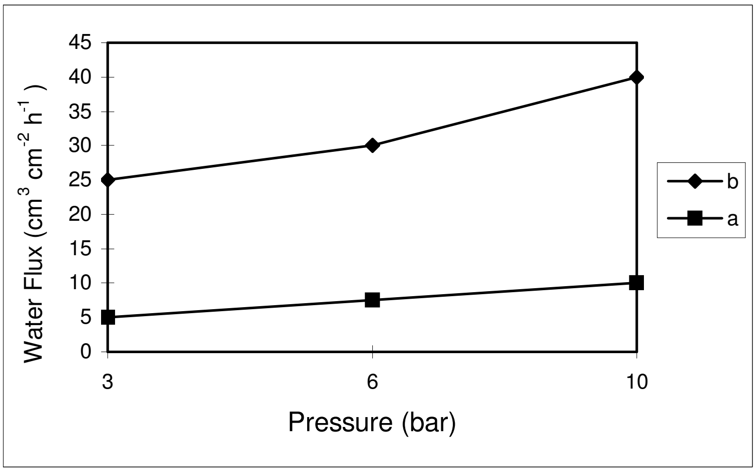


Figure 2. Water flux tests of membranes with supports **a**)Clay-1, **b**)Clay-2.

Conclusions

γ-Al_2O_3 (4%La_2O_3 -Al_2O_3) membranes top layers were coated on clay based support and ceramic membranes were prepared. Ceramic membranes retained their thermal and mechanical stabilities at high temperature (at 1200 °C) and 10 bars pressure.

The addition of La_2O_3 inhibited the γ- to α-phase transformation in alumina gels resulting with high thermal stability.

It was shown in this study that, clay based supports can be used in ceramic membrane preparation.

References

[1] H. Strathmann, "Membranes and Membrane Separation Processes", Ullman's Encylopedias of Industrial Chemistry, vol.A16, p. 187

[2] V. Gunay, et al., Proc. Third Euro-Ceramics, Vol.1, pp :651-656, Eds. P. Duran, J.F. Fernandez, Faenza Editrice Iberica S.L., 1993, Madrid, Spain.

[3] G.G. Avci, Z. Mısırlı, V. Günay, Ceramic International, 22 (1996), p. 42

[4] B. Ersoy, MSc Thesis, Dumlupınar University, Turkey, September 1996.

[5] Y. S. Lin, et al., J. Materials Sci., 26, (1991), p. 715

[6] V. Gunay et al., Proc.Third Euro-Ceramics, Vol.1, pp :267-272, Eds. P. Duran, J.F. Fernandez, Faenza Editrice Iberica S.L., 1993, Madrid, Spain.