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Fabrication and Microstructure of Al_2O_3–TiO_2 Composite Membranes with Ultrafine Pores

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Abstract: A ceramic membrane consisting of an α-Al_2O_3 support and an Al_2O_3–TiO_2 top layer, which is thermally stable up to 900°C, was prepared by the sol–gel method. The supported Al_2O_3–TiO_2 top layer was made by dip-coating the support in a mixed sol. The microstructure of the composite membranes was studied by SEM and TEM after calcination at 850–1000°C. After sintering at 850°C for 1 h, the average particle diameter of the Al_2O_3–TiO_2 top layer was about 15 nm. The supported Al_2O_3–TiO_2 composite membranes exhibited much higher heat resistance than the TiO_2 membranes. Although significant grain growth was observed for the TiO_2 membrane after heating above 700°C due to phase transformation, the Al_2O_3–TiO_2 composite membrane retained a crack-free microstructure and narrow particle size distribution even after calcination up to 900°C. © 1997 Elsevier Science Limited and Techna S.r.l.

Keywords: composite membrane; Al_2O_3–TiO_2; sol–gel method; thermal stability.

1 INTRODUCTION

Ceramic membranes are technically important in separation and filtration, as well as in catalytic reactions, because of some unique characteristics in comparison with polymeric membranes. They have high thermal and chemical stability, long life and good defouling properties in their application, and they can have catalytic properties.[1] These properties have made these membranes desirable for industrial applications in food, pharmaceutical and electronic industries currently utilizing polymeric, organic and metal membranes.[2]

The potential application of the ceramic membranes at elevated temperatures requires more study and further improvement in the ceramic membrane preparation, the sol–gel approach[3] is considered to be the most practical one for ceramic membrane synthesis.

A ceramic membrane being thermally stable at a certain temperature means that the properties of the membrane remain unchanged or change negligibly at that temperature for a period of time comparable to the actual application time.[4]

For the ceramic membranes which were prepared by the sol–gel approach, the smallest possible pore size is determined by the primary particle size in the colloid suspension.[5] Depending on the desired pore size of the membrane, the membrane precursor particles may be prepared by the sol–gel method, etc.[6] In the sol–gel technique, ultrafine particles of a few nanometres in diameter can be prepared by polycondensation or redox reactions of hydrolysis and condensation of metal alkoxides. After treatment with a peptizing agent, such as acid, and optionally with a viscosity modifier, the slip is deposited on the porous support by the dipping or slip casting procedure.[7] The smallest pore size is formed by drying and calcining the gel at a relatively low temperature. In most cases the pore

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size of a membrane top layer increases with the firing temperature. The pore growth with the temperature increase has been confirmed in the top layers of γ-Al_2O_3, TiO_2 and ZrO_2.[8–11] Consequently, it is difficult to keep the pore diameter of a ceramic membrane top layer smaller than 50 nm at firing temperatures higher than 1000°C. In the limited studies related to the thermal stability of ceramic membranes, Burggraaf *et al.*[6] and Qunyin and Marc[8] determined the pore size of some ceramic membrane top layers at different sintering temperatures. Kumar *et al.*[12] studied the phase transformation behaviour of both unsupported and supported titania membranes. For a sintering time of 8 h (in air), the titania membranes underwent anatase to rutile phase transformation in the temperature range of 550–600°C.

The objective of the study is to report the fabrication and microstructure analysis of Al_2O_3–TiO_2 composite membranes with improved thermal stability in the Al_2O_3–TiO_2 top layers. The microstructural changes of mixed-oxide membranes with firing will also be studied. In particular, we investigate the effect of the second component on the thermal stability of mesoporous membranes. The thermal stability of the membranes was evaluated by measuring the change in the mean particle diameter of membranes after sintering at different temperatures from 850°C to 1000°C.

2 EXPERIMENTAL PROCEDURE

The supported Al_2O_3–TiO_2 mixed-oxide membranes were prepared using the sol–gel method. Figure 1 shows the preparation procedures. These sols were prepared via hydrolysis and condensation of mixed-alkoxide precursors. $Ti[OCH(CH_3)_2]_4$ and $Al[OCH(CH_3)_2]_3$ were used as starting materials. The boehmite sol (0.25 mole) was prepared by adding aluminium tri-*sec* butoxide (Aldrich) to water and peptizing the solution with hydrogen chloride (HCl/alkoxide = 0.14 mole ratio) at ~80°C under refluxing conditions. The titania sol (0.16 mole) was prepared by adding titanium tetra-isoproproxide (Aldrich) to water and peptizing the solution with hydrogen chloride (HCl/alkoxide = 0.34 mole ratio) at ~50°C under refluxing conditions. This solution was stirred for 2 h to ensure complete mixing. The percentage of aluminium in total metals was varied from 25 mol% to 70 mol%. A PVA solution, prepared by dissolving 5 g of PVA (Aldrich, *M*w = 72 000) in 95 ml water, was used as a DCCA (drying control chemical additive) for making supported ceramic membranes. The ceramic support was prepared by slip casting. The average pore diameter of the support was 0.125 μm. The support was immersed in mixed sol for 5–60 s. The concentration of the sol increased as absorbing water and mixed gel were deposited in the pores near the surface of the support. After drying at 45°C in a dry oven for 24 h, the samples were calcined at 850–1000°C for 1 h and then they were furnace cooled. The particle sizes were examined by the dynamic light scattering method (Ar laser, Nicomp 370). The surface morphology and thickness of the membranes after heat treatment at 850–1000°C were observed with a scanning electron microscope (SEM, Hitachi S-4200). The linear intercept method was used to determine the mean particle diameter. The structural changes were analysed by X-ray diffraction (Phillips, PzW 1825/00) with CuKα radiation: voltage 30 kV and current 40 A. Transmission electron microscopy (TEM) measurements were performed to study the dispersion of particles and pore structures of the top layers.

3 RESULTS AND DISCUSSION

The important parameters in the formation of a gel layer are sol concentration, coating time, the pore size of the support and the type and amount of the acid used to peptize the sol.[8]

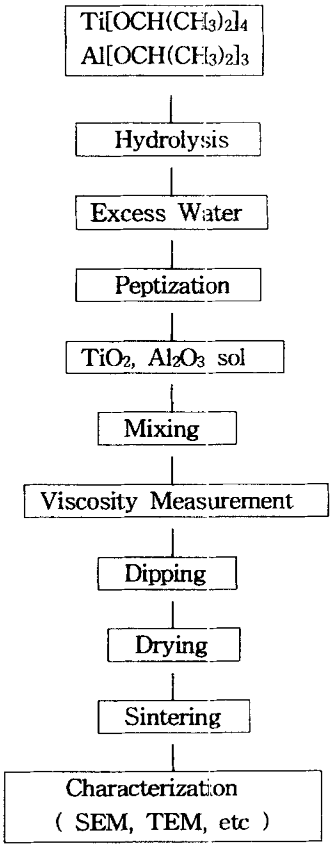

Fig. 1. Preparative procedure of the supported Al_2O_3–TiO_2 composite membranes by destabilization colloidal solution process.

Since particle size and pore size are directly related, the slip used as the membrame precursor needs to contain well-dispersed particles of a uniform size.

The formation of clear solutions in the titania and alumina systems requires the presence of HCl acids.[13,14] The stability of these clear solutions is a function of the acid/alkoxide ratio and there is a window for the most stable solution at 0.14–0.34 mol of acid per mole of alkoxides. The mean particle diameter of mixed sols was less than about 15 nm. There was no significant increase in the particle diameter after 7 days aging and the sols were transparent for the whole time, so the sols were stable. Transmission electron microscopy (TEM) measurement was performed to study the dispersion of particles in the mixed sol. Figure 2 shows that the boehmite and anatase particles are well dispersed in the solution.

All characterization results are obtained from a multi-layer supported membrane. The sol–gel coating is very sensitive to the support characteristics and frequently yields a defective film. In the slip casting method, a porous support is usually made by a conventional ceramic processing technique to provide a rigid structure with relatively large pore size for slip deposition. The pore size distribution of the α-Al_2O_3 support can be obtained by such methods as capillary flow analysis. The average pore diameter of the support was about 0.125 μm and the shape of the particles seems to be spherical.

The influence of PVA on the forming mechanism of the supported thin films was investigated. Polyvinylalcohol is added to the mixed-oxide precursor to improve the sol–gel coatings. The effect of PVA on film formation in mixed gels has also been investigated. Figure 3 shows the differences between the microstructures of the Al_2O_3–TiO_2 composite membranes made with and without PVA. If PVA is not added, the gel layer could not form because the sol went through the supports. The addition of PVA is necessary to deposit the Al_2O_3–TiO_2 membranes on the supports.

For mixed sols, the forming mechanism of supported thin films could be described by slip casting.[15] Due to capillary forces, water is sucked into the pores of the support. The concentration of the mixed sol increases and gelation of the sol occurs. After a certain period (of the order of seconds), the support is taken out and the gel layer is dried and calcined. This mechanism is characterized by a linear increase of the layer thickness, L, as a function of the square root of dipping time, t, according to:[15]

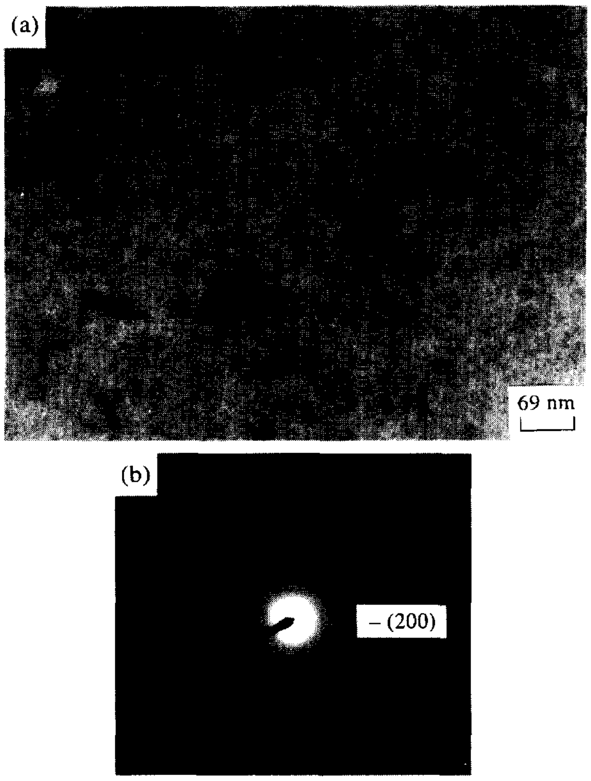

Fig. 2. TEM micrograph and diffraction pattern of the Al_2O_3–TiO_2 mixed sol with 45 mol% Al_2O_3.

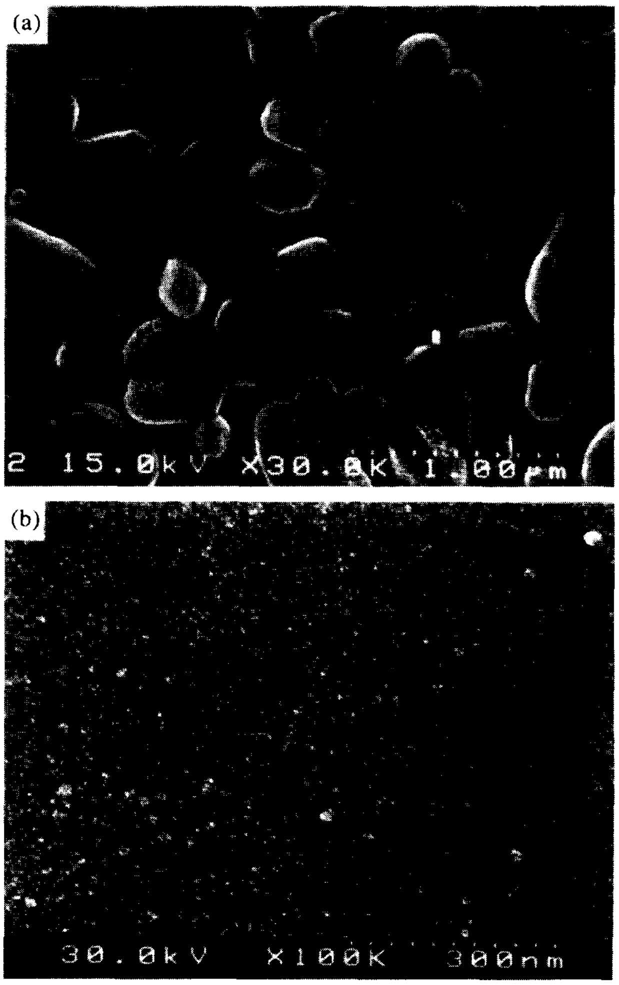

Fig. 3. SEM of the 25 mol% Al_2O_3–TiO_2 top layers sintered at 700°C for 1 h: (a) without PVA and (b) with 2.5 wt% PVA.

$$L = 2\gamma \cos\beta/\eta C(t)^{1/2} + L_a \quad (1)$$

where γ is the surface tension (in Nm^{-1}), β is the contact angle between the liquid and the solid surface, C is a constant, η is the viscosity of the solution and L_a is the adhering layer thickness. The viscosity of the dipping solution increases with the addition of PVA, leading to a lower slip casting rate. Figure 4 shows that the thickness of the calcined membrane layers increased linearly from 1.4 to 2 μm with the square root of the dipping time (5–60 s).

The effect of Al_2O_3 on the microstructure of TiO_2 gels with temperature during the pre-sintering process has been investigated. It should be noted here that the addition of Al_2O_3 into the TiO_2 gel was conducted at the first stage of mixing of the two alkoxides, so that after the sol–gel transformation, Al_2O_3 should be distributed uniformly throughout the TiO_2 network. No other local concentration of Al_2O_3 in the TiO_2 gel has been assumed.

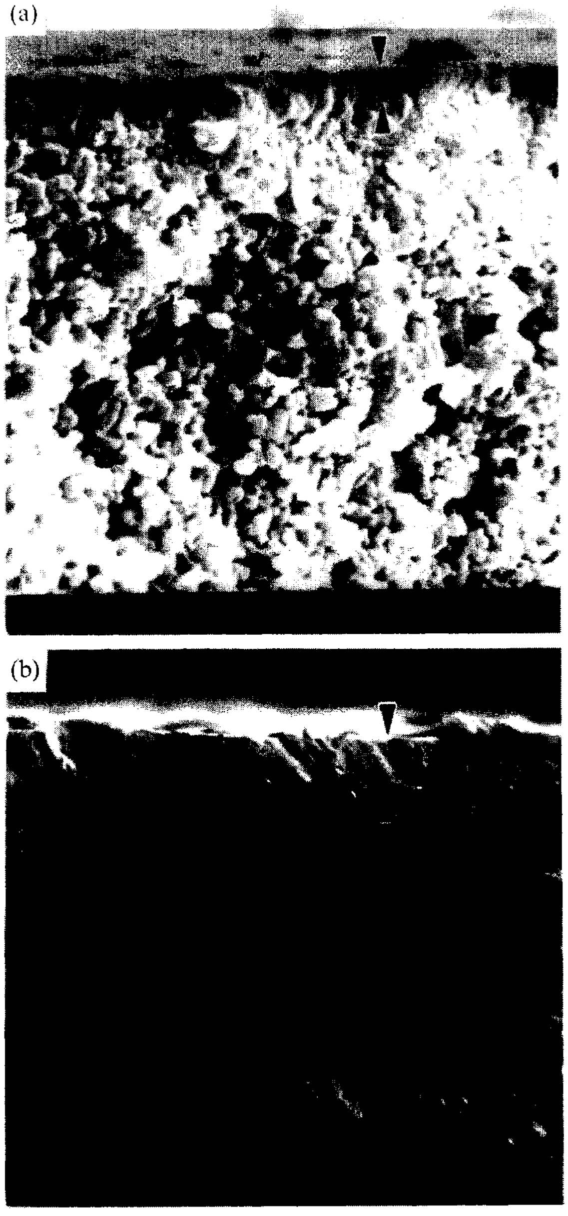

Fig. 4. SEM of the cross-section of the Al_2O_3–TiO_2 membrane with (a) 5 s dipping time and (b) 60 s dipping time.

Figure 5 shows how the microstructure of the Al_2O_3–TiO_2 composite membranes varies with Al_2O_3 concentration. After calcination at 900°C for 1 h, the mean particle diameter of the Al_2O_3–TiO_2 composite membranes decreased from ~30 nm to ~20 nm with an increase of Al_2O_3 concentration from 25 mol% to 70 mol%. Whether it is sintering-caused or crystallization-induced, particle growth has been retarded by mixing Al_2O_3 into the TiO_2 membrane.

Figure 6 illustrates the particle size increase with firing temperature occuring in the Al_2O_3–TiO_2 composite membranes. The shape and size of the particles were studied by SEM. The surface of as-deposited membranes is smooth and flat, i.e. neither cleavages nor cracks are observed. The mean particle size was determined by counting the number of particles in a given area of the membrane. The average mean particle diameter increased and the particle size distribution became broader with increasing calcination temperature. This grain

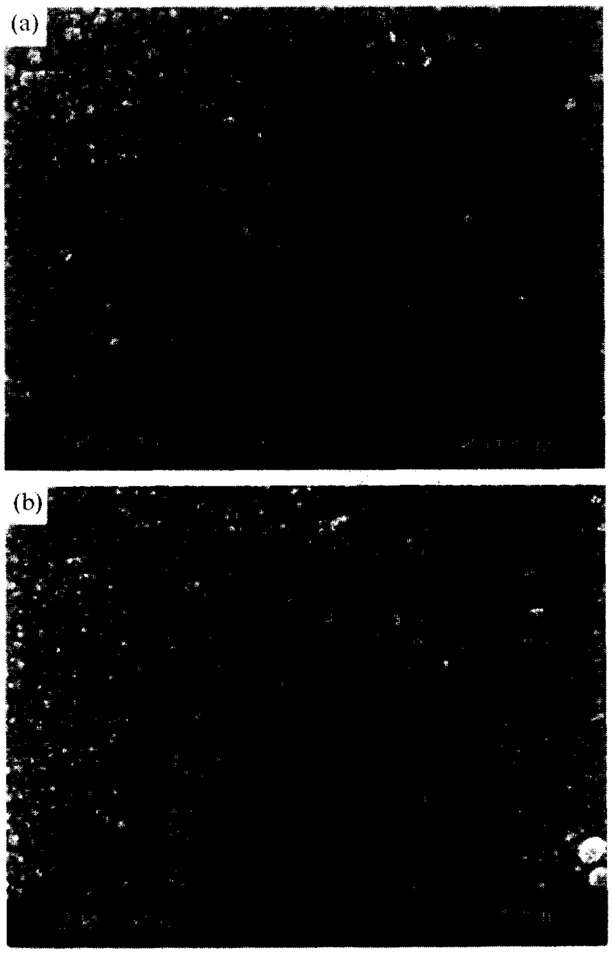

Fig. 5. SEM of the Al_2O_3–TiO_2 composite membranes sintered at 900°C for 1 h with (a) 25 mol% Al_2O_3 and (b) 70 mol% Al_2O_3.

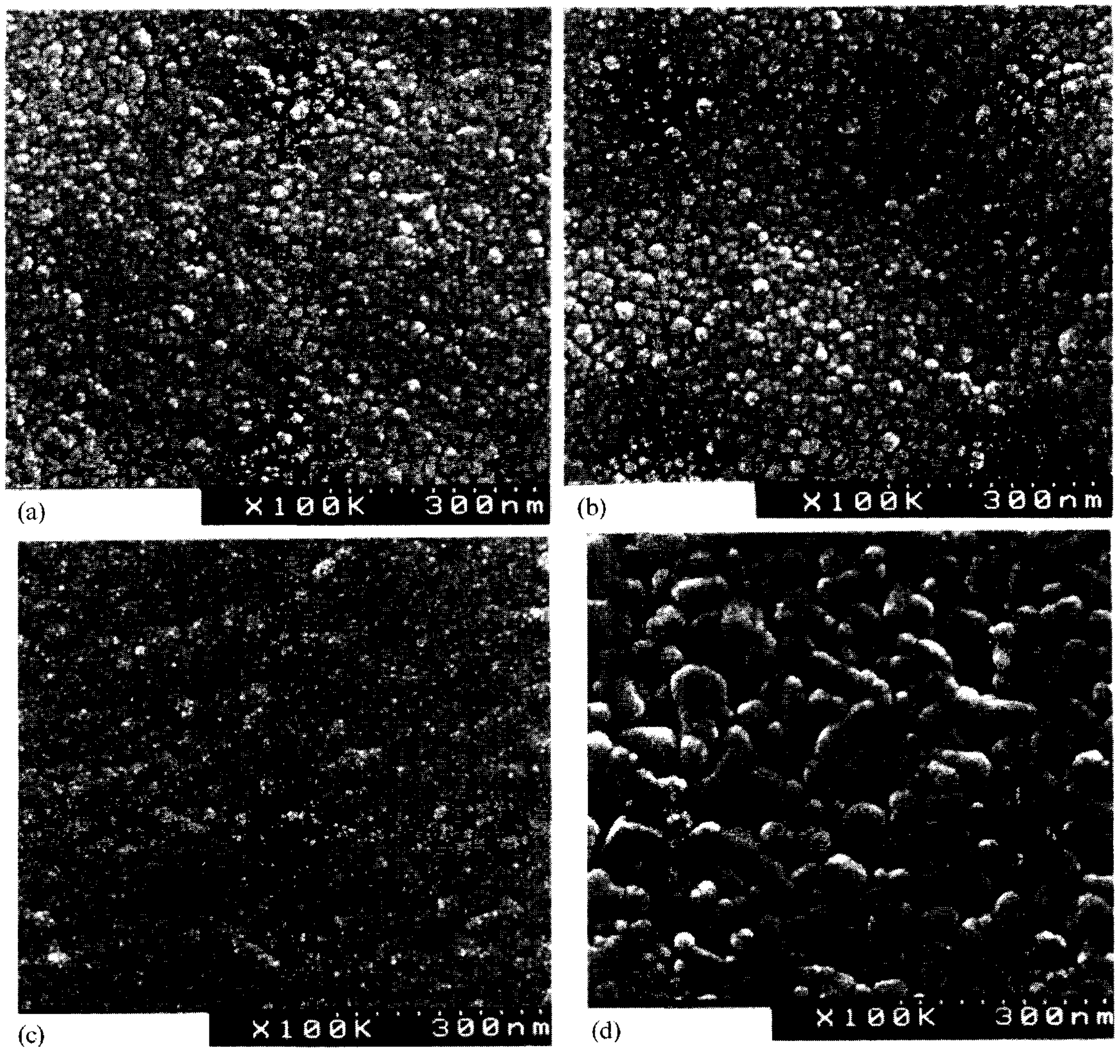

Fig. 6. Microstructure of the 25 mol% Al_2O_3–TiO_2 composite membrane sintered at (a) 850°C, (b) 900°C, (c) 950°C and (d) 1000°C.

growth at low temperatures may still be caused by the surface energy reduction due to the extremely small particle size ($\leq$15 nm).[16] The mean particle diameter of the TiO_2 membrane with 25 mol% Al_2O_3 was increased from 20 to 85 nm with an increase in calcination temperature from 850 to 1000°C. To characterize membranes with ultrafine pores in the nanometre range, TEM may prove to be useful in examining the supported membrane film (Fig. 7). TEM measurement was performed to study the pores structure and to perform elemental analysis of the Al_2O_3–TiO_2 top layers after calcination for 1 h at 850°C. Due to its mode of operation, TEM could not reveal the morphological features of a relatively thick composite membrane. The pore size of the Al_2O_3–TiO_2 composite membranes was less than 10 nm.

The mean pore diameter of the TiO_2 membrane increases beyond the mesoporous region at temperatures higher than 600°C for pure TiO_2. This can be increased to 900°C for the TiO_2 membranes doped with 25–70 mol% Al_2O_3. This ~300°C increase in critical temperature is very important in the application of mesoporous ceramic membranes in high temperature applications.

4 SUMMARY

Two-component mixed oxide (Al_2O_3–TiO_2) membranes have been synthesized through the entire range of the composite. Thin layers of Al_2O_3–TiO_2, 1–3 μm in thickness, could be coated on the porous α-Al_2O_3 support tubes by the dip-coating method. The membrane consists of an alumina support with a mean pore diameter of about 0.125 μm and Al_2O_3–TiO_2 top layers with a mean particle diameter of 15–100 nm. The sols were prepared by destabilization of colloidal solutions, in which the hydrolysed precipitates of $Ti[OCH(CH_3)_2]_4$ and $Al[OCH(CH_3)_2]_3$ were nanoparticle sols with an average particle size of less than 15 nm. The forming mechanism of the supported Al_2O_3–TiO_2 composite membranes can be

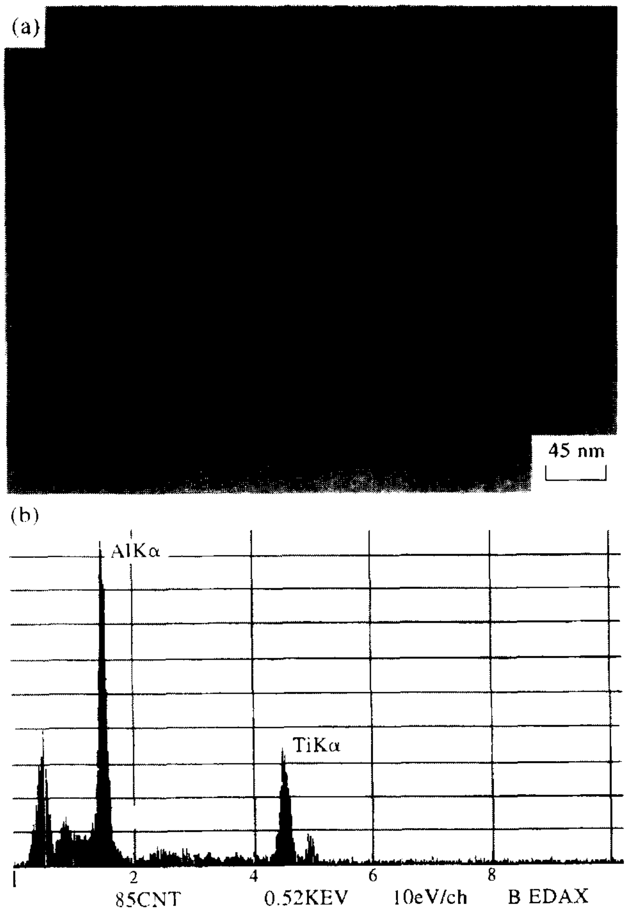

Fig. 7. TEM micrograph and EDS of the 70 mol% Al_2O_3–TiO_2 composite membrane sintered at 850°C for 1 h.

described by the slip casting mechanism. With addition of PVA, mixed oxide gels can be dried and calcined to form an Al_2O_3–TiO_2 composite membrane. The mean particle size of the Al_2O_3–TiO_2 composite membranes increases with firing temperature. The mean particle diameter increases during heat treatment, which is consistent with the typical phenomenon observed for a sintering process. The mean particle diameter of the Al_2O_3–TiO_2 composite membranes decreased with increasing Al_2O_3 concentration. Whether it is sintering-caused or crystallization-induced, particle growth has been retarded by mixing 25–70 mol% Al_2O_3 into the TiO_2 membrane. The critical temperature of the TiO_2, at which the mean pore size of the membrane shifts from the mesoporous region to marcroporous region, increases by about 300°C as a result of introduction 25–70 mol% Al_2O_3. The Al_2O_3–TiO_2 composite membranes retained a crack-free microstructure and narrow particle diameter distribution even after calcination up to 900°C.

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