Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 37 (2011) 1161–1168

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Manufacture and characterization of ultra and microfiltration ceramic membranes by isostatic pressing

Roberta Del Colle *, Carlos A. Fortulan, Sergio R. Fontes

Department of Mechanical Engineering, Engineering School of Sao Carlos - University of Sao Paulo, Av. Trabalhador Sancarlense, 400, 13566-590 São Carlos, SP, Brazil

Received 23 June 2010; received in revised form 29 September 2010; accepted 14 November 2010

Abstract

This paper describes the manufacture of tubular UF and MF porous and supported ceramic membranes to oil/water emulsions demulsification. For such a purpose, a rigorous control was realized over the distribution and size of pores. Suspensions at 30 vol.% of solids (zirconia or alumina powder and sucrose) and 70 vol.% of liquids (isopropyl alcohol and PVB) were prepared in a jar mill varying the milling time of the sucrose particles, according to the pores size expected. The membranes were prepared by isostatic pressing method and structurally characterized by SEM, porosimetry by mercury intrusion and measurements of weight by immersion. The morphological characterization of the membranes identified the formation of porous zirconia and alumina membranes and supported membranes. The results of porosimetry analysis by mercury intrusion presented an average pore size of 1.8 μm for the microfiltration porous membranes and for the ultrafiltration supported membranes, pores with average size of 0.01–0.03 μm in the top-layer and 1.8 μm in the support. By means of the manufacture method applied, it was possible to produce ultra and microfiltration membranes with high potential to be applied to the separation of oil/water emulsions.

Keywords: Ceramic membranes; Isostatic pressing; Sucrose; Micro and ultrafiltration

1. Introduction

A large amount of liquid waste in the form of oil/water (o/w) or water/oil(w/o) emulsions is generated in petrochemical, metallurgical and food process industries. Membrane technology can be an inexpensive and efficient alternative method for the separation of emulsions; therefore several papers describing the separation of o/w emulsions via ceramic membrane have been published [1–3]. The use of ceramic membranes instead of polymeric membranes has generated continuous interest due to their numerous advantages, such as stability at high temperature and pressure, good chemical stability, high mechanical resistance, long life, and good defouling properties. Alumina membranes have been widely applied, but more recently other porous membrane materials, such as zirconia, titania and silica, have been considered.

Plenty of research on manufacturing techniques and their costs, microstrutural properties, filtration efficiencies, etc., should be conducted for commercial applications of the membrane technology. In this sense, many techniques to prepare ceramic membranes, such as sol–gel method, phase inversion, extrusion and slip-casting have been developed in recent years [4–7]. Other methods have been also reported in the literature. For example, Cui et al. [8] prepared zeolite/ceramic microfiltration membranes on an α-alumina tube by in situ hydrothermal synthesis method for the treatment of oil contaminated water. Zhang et al. [9] used the solid state sintering method to prepare TiO_2-doped Al_2O_3 composite microfiltration membranes, which were applied to separate oily wastewater, and Zhou et al. [10] prepared a TiO_2 membrane supported on a planar porous Ti–Al alloy by combining electrophoretic deposition and dip-coating processes.

Isostatic pressing has also been used as a manufacturing method for the production of automotive components, electrical and thermal insulators, coating materials, ceramic scaffolds in the tissue engineering field [11] and, membranes [12,13].

---

* Corresponding author. Tel.: +55 16 3373 9557; fax: +55 16 3373 9402.
E-mail addresses: beta@sc.usp.br (R. Del Colle), cfortula@sc.usp.br (C.A. Fortulan), srf@sc.usp.br (S.R. Fontes).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2010.11.039

However, isostatic pressing has not been considered in current researches as a manufacturing method of ceramic membranes for the micro or ultrafiltration of oil–water emulsions.

This paper reports on the application of isostatic pressing as a forming method to obtain non-supported and supported ceramic membranes for oil–water separation by micro and ultrafiltration processes. This method was chosen due to its several advantages, such as high quality and uniformity of the ceramic units, possibility of making multilayers, flexibility to the design and economy of material (in terms of research) in comparison to other methods.

To manufacture ceramic materials, like filters or membranes, a porogenic agent is mixed in the suspension or slurry (precursor of the ceramic granule). Agents, like sucrose, are substances that decompose during the sintering generating pores. In addition, sucrose allows producing a structure with certain volume and size of pores (open and close), which directly influence the porosity and permeability of the membrane. Thus, some factors, as the milling time of the porogenic agent and temperature of sintering are of extreme importance [14].

The key to the successful application of ceramic membranes lies in the production of membranes that provide larger permeate flux and high selectivity. Therefore, researches on the preparation of membranes have been accomplished focusing on the control of the size and distribution of the pores, as those factors influence the membrane's selectivity and determine its application. To manufacture ultra and microfiltration ceramic membranes, the processing must be controlled so that the pores diameter is between 0.1 and 10 μm for microfiltration membranes, and between 0.01 and 0.1 μm for ultrafiltration membranes [15].

In this respect, developing a method able to control both size of pores and porosity of membranes is appreciable, so that membranes become suitable to certain applications.

This paper describes the manufacture process of microfiltration (MF) and ultrafiltration (UF) ceramic membranes for oil/water emulsions separation using isostatic pressing as a forming method and sucrose as a porogenic agent. The manufacture method was evaluated as a function of the expected characteristics (porosity and pores size) for the proposed application.

2. Materials and methods

The use of sucrose as a porogenic agent and isostatic pressing as a forming method for the manufacture of tubular MF and UF ceramic membranes is proposed in this paper. The choice of sucrose as a porogenic agent was based on its several qualities: relatively low cost with high purity, possibility of being partially removed by lixiviation with water and totally removed by thermal degradation, non-toxicity, and little modification of the crystals' format after pressing.

2.1. Preparation of the ceramic slurry

Calcined alumina A1000 SG (ALMATIS, Inc.) and tetragonal zirconia TOSOH-3Y (Tosoh Corporation) were used as structural components of the ceramic membranes both with average diameter of 0.5 and 0.3 μm and superficial area of 8.4 and 7.7 m^2/g, respectively. The composition of the commercial alumina is described in Table 1. Sucrose for analysis (Synty) with level impurity of 0.08% was utilized as a porogenic agent. Polyvinyl Butyral resin (PVB) (Butvar B-98) in powder form, with density of 1.1 g/cm^3 and Butyral content of 80% (approximately) and isopropyl alcohol (Labsynty Ltda.) with density of 0.782 g/mL and 0.2% of water were used as ceramic binder and binder's solvent, respectively.

Table 1
Composition of the commercial alumina.

% Al_2O_3	% SiO_2	% Fe_2O_3	% Na_2O	% CaO	% B_2O_3	% MgO
99.8	0.03	0.02	0.07	0.02	0.001	0.04

Table 2
Composition of prepared ceramic slurry.

Composition	Slurry	
	A formulation (alumina)	Z formulation (zirconia)
Structural component (A or Z)	15 vol.%	15 vol.%
PVB	3 vol.%	1.5 vol.%
Isopropyl alcohol	67 vol.%	68.5 vol.%
Sucrose	15 vol.%	15 vol.%
Milling time of sucrose to obtain the porous and supported membranes	20 min (to obtain the porous alumina membrane and the alumina support of the supported zirconia–alumina membrane) 2 h (to obtain the porous alumina membrane)	20 min (to obtain the porous zirconia membrane and the zirconia support of the supported zirconia–zirconia membrane) 2 h (to obtain the top layer of the supported membranes)
Sieves' size range to classify the sucrose	177–600 μm (for 20 min of sucrose's milling) 177–300 μm (for 2 h of sucrose's milling)	177–600 μm (for 20 min of sucrose's milling) 177–300 μm (for 2 h of sucrose's milling)

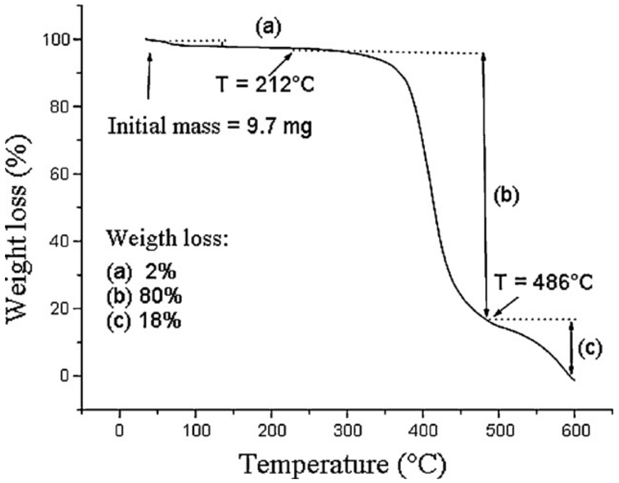

Fig. 1. The percentage of weight loss of the PVB over a range of temperature.

Particles of sucrose were initially submitted to macerating with mortar and pistil and classified into a sieves system (177–300 μm and 177–600 μm sieves). After that, PVB and isopropyl alcohol were introduced into a polyethylene jar (volume of 400 mL) containing 900 g of ceramic milling elements (regular alumina cylinders of 1/2 in.), and mixed in a jar mill for 2 h. Then, the ceramic powder (alumina or zirconia) and sucrose (classified) were added to the jar and mixed in order to realize the sucrose's milling (during 2 h or 20 min) and homogenization of the mixture, resulting in a suspension at 30 vol.% of solids (sucrose and alumina or zirconia) and 70 vol.% of liquids (alcohol and PVB). The quantity (in volume) used for each component of the ceramic slurry is presented in Table 2.

Later, the solvent was evaporated with an air flow heat gun (temperature around 80 °C in order to avoid the burn of sucrose) and the ceramic–sucrose agglomerates were manually granulated until passing through a 250.0 μm sieve. The drying of the ceramic granules was performed for 2 h in an oven at 80 °C.

The glass transition temperature of the PVB B-98 is between 72 and 78 °C. Temperatures around 80 °C will provide higher plasticity to the polymeric film decreasing the stresses concentration and favoring the forming and surface finish of the membranes. Besides, the thermogravimetric analysis (TGA) in Fig. 1 testifies that PVB will not degrade at 80 °C, as its thermal degradation begins at 212 °C.

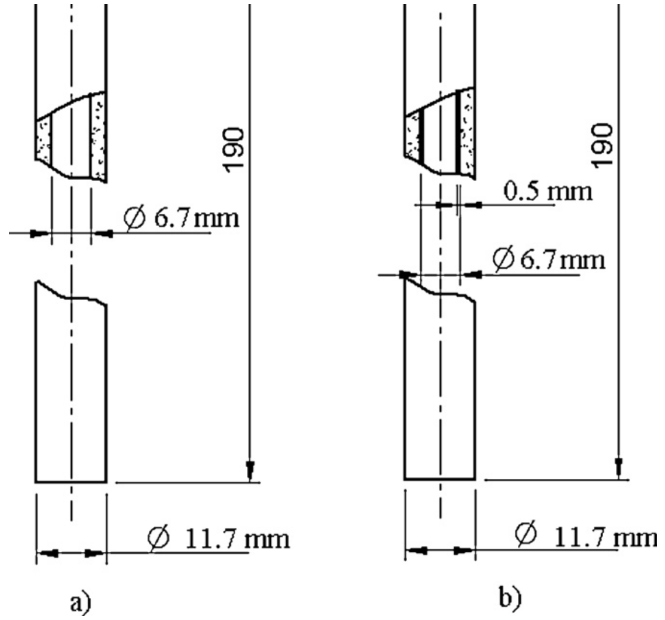

Fig. 2. Design of the ceramic membranes and their respective dimensions. Porous membrane (a) and supported membrane (b).

2.2. Manufacture of the membranes

The ceramic processing was employed to obtain two types of membranes—porous and supported. The dimensions of the tubular ceramic membranes are shown in Fig. 2.

In order to prepare the porous zirconia and alumina membranes, the isostatic mould was filled with ceramic granules or fine-grains powder from Z and A formulation slurry (Table 2) and pressed until 100 MPa, according to Fig. 3.

In the manufacture of supported membranes (zirconia top layer on zirconia or alumina support), the nucleus was first dipped in the test tube with Z formulation slurry (Table 1) and later emerged and dried with an air flow heat gun to evaporate the solvent. This proceeding was realized twice to obtain a zirconia thin film (selective layer) on the nucleus. Finally, the nucleus was inserted in the mould, which was filled with the powder from A or Z formulation (Table 2) to obtain the support of the membranes and then isostatically pressed at 100 MPa. Thus, top layer and support were obtained simultaneously, i.e., they were conformed together by co-pressing. Fig. 4 illustrates the proceeding described above.

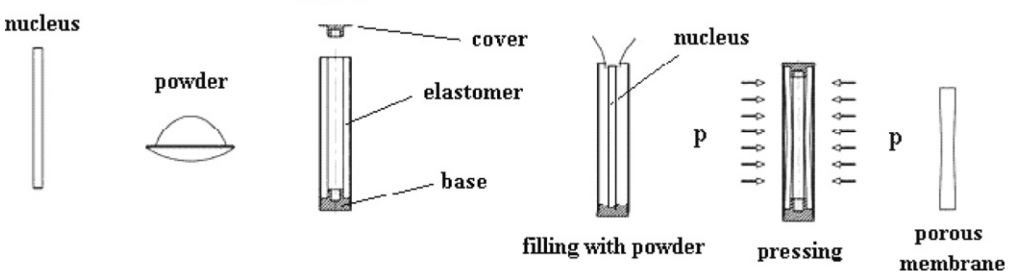

Fig. 3. Materials and proceeding to obtain the porous zirconia and alumina membranes.

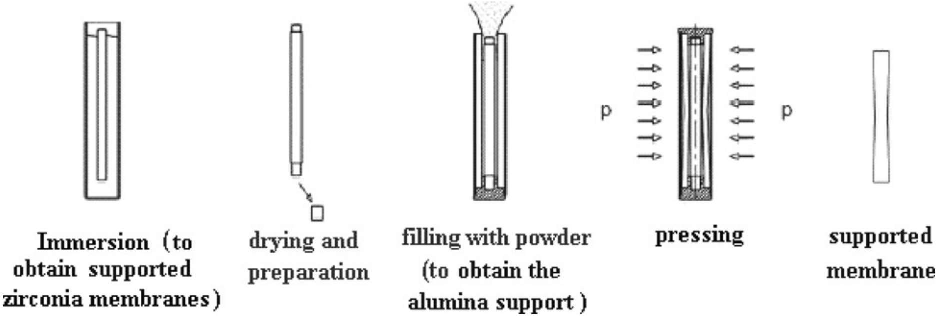

Fig. 4. Proceeding for the manufacture of the supported membranes.

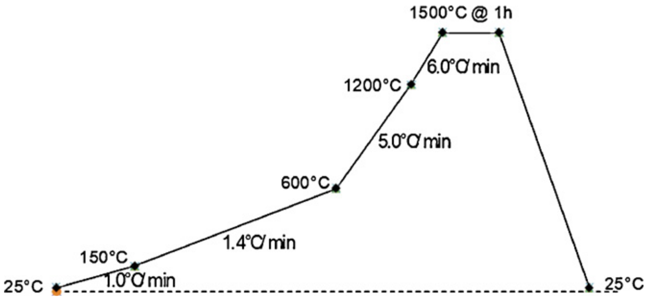

Fig. 5. Sintering profile of ceramic membranes.

In the next stage a thermal treatment was realized in the system (support + zirconia top-layer). The membranes were placed in a refractory container and covered with manioc starch (to absorb the melted sucrose). They were burned in an oven at temperatures ranging from 100 °C to 160 °C. There was a 20 °C rise in the temperature every 24 h for the partial removal of sucrose, diminishing the risk of fractures in the tubes during the sintering, due to a thermal expansion of the sucrose. After that, the tubular membranes were sintered in an electric chamber box furnace (Lindberg/Blue M) in a controlled manner using a sintering profile, as shown in Fig. 5. The cooling was realized in furnace up to room temperature.

The structural characterization of the ceramic membranes was realized by tests of immersion in water (Arquimedes' principle) to determinate the apparent density and porosity of the membranes, porosimetry by mercury intrusion and scanning electronic microscopy (SEM). Four samples were used for the tests of immersion in water and to the other analyses two samples were used of each membrane. For the porosimetric analysis a mercury poresizer model PORESIZER 932 (Micrometrics Instruments Corporation) was used. The immersion tests were accomplished according to the American Society for Testing and Materials standard [16]. The morphological analysis of the membranes was realized by a LEO1430 scanning electronic microscope with OXFORD detector, operating with a 20 kV electron sheaf.

3. Results and discussion

3.1. Structural characterization of ceramic membranes

Different sizes of pores were obtained for the porous alumina membranes, according to the sieves' size utilized to classify the sucrose and its milling time. Fig. 6 presents the pores size distribution for these membranes in relation to the milling time of sucrose.

The porosimetry analysis shows that the average diameter distribution of the pores is more homogeneous for the alumina membrane manufactured with longer milling time of sucrose,

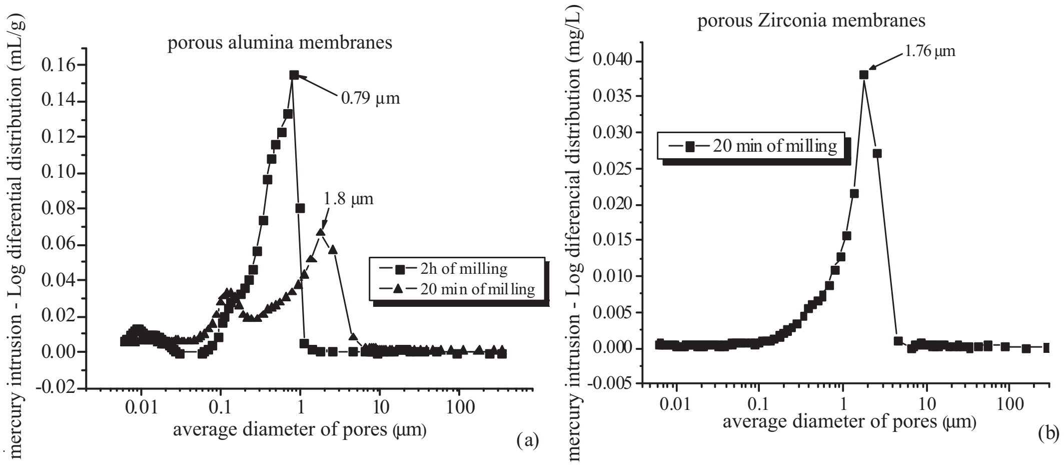

Fig. 6. Pores size distribution for porous alumina membranes with different milling times of the sucrose (a) and pores size distribution for porous zirconia membrane (b).

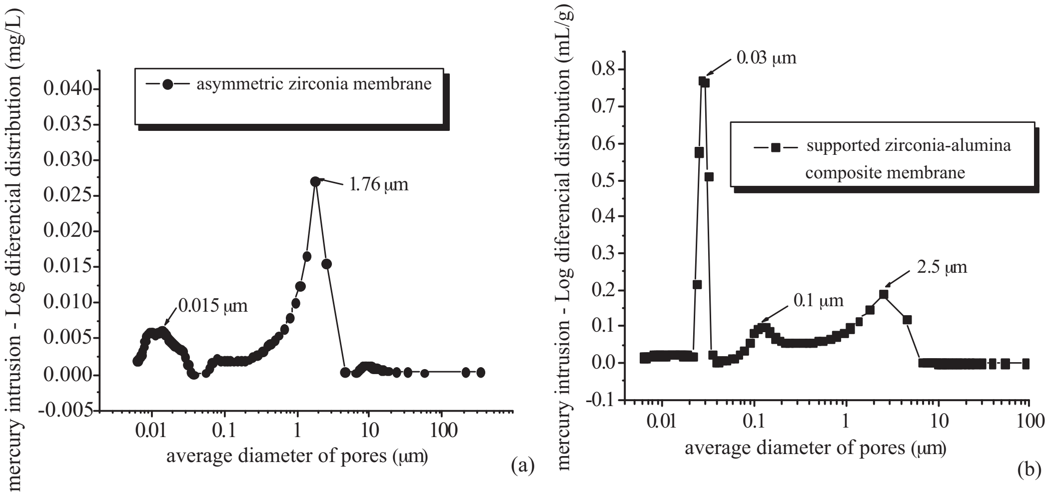

Fig. 7. Porosimetric analysis of the zirconia membranes by mercury intrusion: asymmetric zirconia membrane (a) and composite membrane (b).

according to Fig. 6a. On the other hand, longer milling time resulted in pores with smaller average size. Therefore, the milling time of the sucrose may interfere in the average size of the pores of the alumina membranes, influencing both selectivity and permeability membranes [17]. The manufacture method utilized produced zirconia and alumina membranes with the same average size of pores (1.8 μm), but with different distributions of pores, according to Fig. 6. Thus, the membrane's material also influences its porous structure.

Fig. 7 presents the size distribution of pores for the supported membranes (asymmetric zirconia membrane and supported zirconia–alumina composite membrane) sintered at 1500 °C.

Pores with average sizes of 0.015 and 0.03 μm are found in the zirconia active layer of the asymmetric zirconia membrane (Fig. 7a) and supported zirconia–alumina composite membrane (Fig. 7b), respectively. The pores with larger average size than 1 μm are present in the support of these membranes, while the pores of 0.1 μm are intrinsic pores from the manufacture process, that is, they are not originated due to the porogenic agent. Porosimetry analysis shows that the manufacture method produced supported zirconia membranes with different structures (different distributions of pores), since different materials (alumina and zirconia) are used as support. Besides, the method could also produce ultrafiltration supported membranes (zirconia active layer) with average pore sizes of 0.01 and 0.03 μm (Fig. 7).

Immersion tests in water were conducted for the ceramic membranes. The results obtained for those membranes are described in Table 3.

Table 3 shows that the introduction of 50 vol.% of porogenic agent caused an apparent porosity of 39.05 and 33.91 vol.% in the alumina porous membranes manufactured with 2 h and with 20 min of sucrose's milling, respectively. The reduction in the apparent porosity is directly related to the decrease in the milling time, since the sintering temperature was the same for both membranes.

The data indicate that between the supported membranes, the asymmetric zirconia membrane (ZrO_2–ZrO_2) obtained lower apparent porosity, but the porous zirconia membrane obtained the least apparent porosity. Therefore, the membranes that present only zirconia in their structures obtained fewer open pores and higher density, due to the high retraction of the zirconia during the sintering. In the final stage of the sintering, i.e., at 1500 °C, the grains' growth is predominant, which leads to a decrease in the volume of the open pores in the membrane's structure and an increase in the material's density.

Although the membranes have also presented an expressive quantity of closed pores, the total porosity of the membranes (except the porous zirconia membrane) is higher than 50%, which is recommended by the literature [18].

The morphology of the porous and supported membranes was analyzed through SEM images, as shown in the figures that

Table 3
Results obtained from immersion tests for the porous (or non-supported) and supported membranes.

Intrinsic properties of the membranes	Porous and supported membranes				
	Zirconia supported on zirconia support (ZrO_2–ZrO_2)	Zirconia supported on alumina support (ZrO_2–Al_2O_3)	Porous alumina membrane (2 h of milling)	Porous alumina membrane (20 min of milling)	Porous zirconia membrane (20 min of milling)
Total porosity (%)	50.97	60.78	65.6	63.2	47.75
Apparent porosity (%)	21.42	30.77	39.05	33.91	17.21
Apparent density (g/cm^3)	3.93	2.26	2.25	2.22	3.98
Closed pores (%)	29.54	30.01	26.6	29.31	30.54

follow. Images of Fig. 8 correspond to the porous alumina membranes manufactured with different milling times, and the porous zirconia membrane.

In membrane A (2 h of milling), there was a decrease in the large particles of sucrose during the milling, promoting a smaller and more homogeneous distribution of the pores, which can be observed by darker region filled with resin (Fig. 8a). In Fig. 8a is observed that some pores were not filled with resin (white arrows) embedded in vacuum. Fig. 8 also shows that the decrease in the milling time (from A to B) generated an increase in the quantity of large pores situated non-uniformly in the ceramic structure (Fig. 8b).

In agreement with the literature [19], when the volumetric fraction of particles in a structure (considered spherical) is higher than approximately 22%, the percolation ways are interconnected like a net. Thus, in membrane B (with 33.91% of porosity), the porosity relative to the large pores predominates as a permeable medium.

Fig. 8c shows that the pores (darker region) are filled with resin and the dense area of the porous membrane corresponds to the zirconia. It is also evident that there is a higher volume of large pores in the membrane's structure, which is coherent with the porosimetry result presented, as the porous zirconia membrane presented a high frequency of pores with average size of 1.8 μm (Fig. 6b). The morphology of this membrane also indicates that its structure has a large dense area, since this membrane presented the least apparent porosity in comparison to the other membranes.

The SEM images below show the morphology of supported membranes. Fig. 9a and b shows images of the supported zirconia–alumina composite membrane cross-section. The structure of the membrane was filled with epoxide resin and then polished with sand-paper and diamond pastes in order to improve the visualization of the membrane's morphology.

Fig. 9a clearly shows the zirconia film (top layer) on the porous alumina support, testifying the formation of a supported zirconia–alumina composite membrane. Fig. 9b represents the amplified image of the composite membrane that presents an asymmetric structure and top layer of approximately 40 μm thickness.

The SEM image of the asymmetric zirconia membrane cross-section is shown in Fig. 9c. Fig. 9d represents the amplified image of that membrane. The thickness of zirconia active layer on the porous zirconia support is 50 μm, approximately. Fig. 9b and d demonstrates the good adhesion of the zirconia film on the alumina and zirconia porous support, respectively.

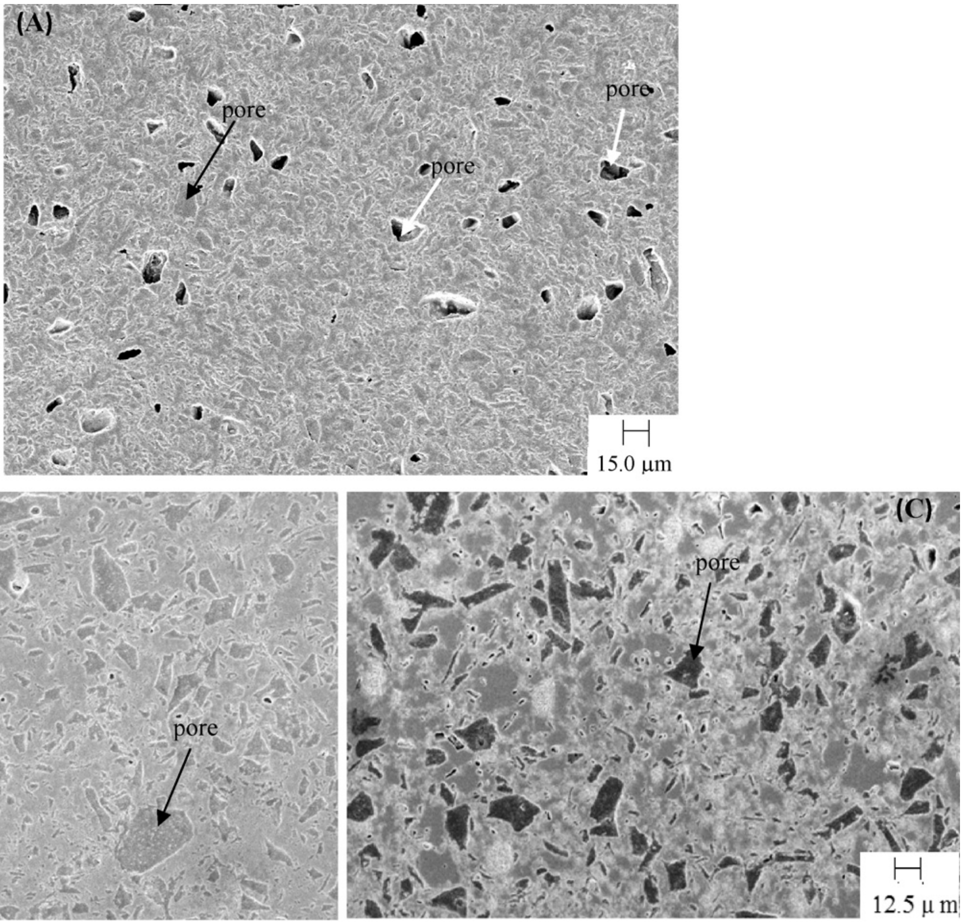

Fig. 8. SEM images of the porous membranes cross-section (with amplification of 500×). Porous alumina membrane manufactured with: 2 h (a) and 20 min (b) of sucrose's milling and porous zirconia membrane (c).

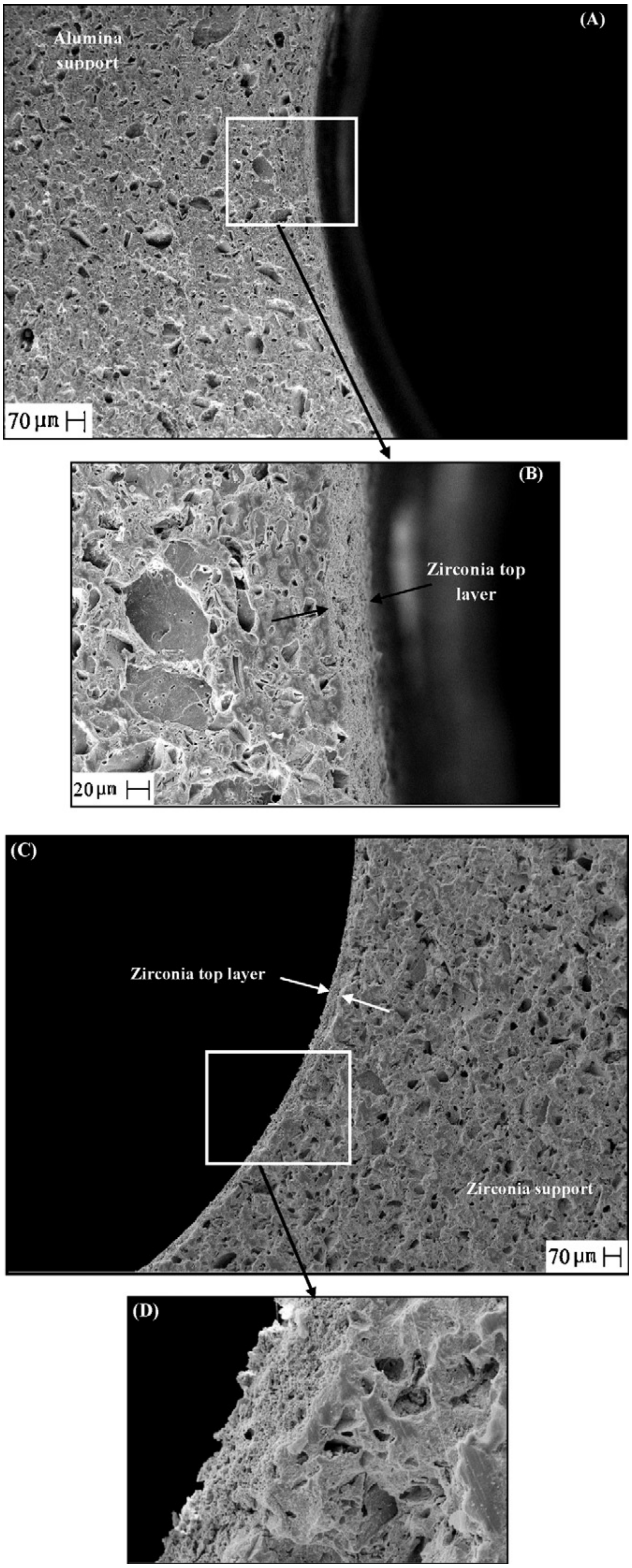

Fig. 9. SEM images of the zirconia membranes. Supported zirconia–alumina composite membrane (a), image increased 500× (b), asymmetric zirconia membrane (c), image increased 500× (d).

4. Conclusions

The manufacturing process is considered novel due to the use of sucrose particles as a porogenic agent, since it could to generate porous ceramic membranes with specific porosity and pores size for applications to micro and ultrafiltration processes. Isostatic pressing was originally employed as a forming method for the adsorption of a zirconia thin film (zirconia top-layer) on the zirconia and alumina support to obtain asymmetric and composite membranes (or supported membranes). In comparison with others methods used to produce supported membranes, the isostatic pressing made possible to obtain together top layer and support by co-pressing.

Acknowledgements

The authors would like to acknowledge FAPESP, CAPES and CNPq for their financial support, Prof. Valdir Schalch, head of the laboratory of sanitation (EESC-USP), for the use of the measurement equipment of TOC, and Prof. Benedito de M. Purquerio for permitting the use of the laboratory of tribology and composites (EESC-USP) to manufacture the ceramic membranes.

References

[1] C. Psoch, B. Wendler, B. Goers, G. Wozny, B. Ruschel, Waste oil conditioning via microfiltration with ceramic membranes in cross flow, Journal of Membrane Science 245 (2004) 113–121.
[2] P. Wang, N. Xu, J. Shi, A pilot study of the treatment of waste rolling emulsion using zirconia microfiltration membranes, Journal of Membrane Science 173 (2000) 159–166.
[3] C. Yang, G. Zhang, N. Xu, J. Shi, Preparation and application in oil–water separation of $ZrO_2/\alpha\text{-}Al_2O_3$ MF membrane, Journal of Membrane Science 142 (1998) 235–243.
[4] Y. Hao, J. Li, X. Yang, X. Wang, L. Lu, Preparation of $ZrO_2–Al_2O_3$ composite membranes by sol–gel process and their characterization, Materials Science & Engineering A 367 (2004) 243–247.
[5] S. Koonaphapdeelert, K. Li, Preparation and characterization of hydrophobic ceramic hollow fibre membrane, Journal of Membrane Science 291 (2007) 70–76.
[6] S. Khemakhem, A. Larbot, R. Ben Amar, New ceramic microfiltration membranes from Tunisian naturals materials: application for the cuttlefish effluents treatment, Ceramics International 35 (2005) 55–61.
[7] S. Masmoudi, A. Larbot, H. El Feki, R. Ben Amar, Elaboration and properties of new ceramic microfiltration membranes from natural and synthesized apatite, Desalination 190 (2006) 89–103.
[8] J. Cui, X. Zhang, H. Liu, S. Liu, K.L. Yeung, Preparation and application of zeolite/ceramic microfiltration membranes for treatment of oil contaminated water, Journal of Membrane Science 325 (2008) 420–426.
[9] Q. Zhang, Y. Fan, N. Xu, Effect of the surface properties on filtration performance of $Al_2O_3–TiO_2$ composite membranes, Separation and Purification Technology 66 (2009) 306–312.
[10] S. Zhou, Y. Fan, Y. He, N. Xu, Preparation of titania microfiltration membranes supported on porous Ti–Al alloys, Journal of Membrane Science 325 (2008) 546–552.
[11] C. Wang, T. Kasuga, M. Nogami, Macroporous calcium phosphate glass-ceramic prepared by two-step pressing technique and using sucrose as a pore former, Journal of Materials Science: Materials in Medicine 16 (2005) 739–744.
[12] V.V. Kharton, A.L. Shaula, F.M.M. Snijkers, J.F.C. Cooymans, J.J. Luyten, I.P. Marozau, A.P. Viskup, F.M.B. Marques, J.R. Frade, Oxygen transport

in ferrite based ceramic membranes: effects of alumina sintering aid, Journal of the European Ceramic Society 26 (2006) 3695–3704.

[13] A.L. Moster, B.S. Mitchell, Mechanical and hydration properties of nafion/ceramic nanocomposite membranes produced by mechanical attrition, Journal of Applied Polymer Science 111 (2009) 1144–1150.

[14] R. Del Colle, C.A. Fortulan, S.R. Fontes, Manufacture of ceramic membranes for application in demulsification process for cross-flow microfiltration, Desalination 245 (2009) 527–532.

[15] M. Cheryan, Ultrafiltration and Microfiltration Handbook, Technomic Publishing Company, Inc., Lancaster, 1998.

[16] American Society for Testing and Materials, C373-88: Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products, West Conshohocken, 1999.

[17] D.S. Rosa, V.R. Salvini, V.C. Pandolfelli, Processing and evaluation of porous ceramics for micro filtration of emulsions, Cerâmica 52 (2006) 167–171.

[18] H.J. Veringa, R.A. Terpsta, A.P. Philipse, in: R.W. Davidge, M.H. Van de Voorde (Eds.), Designing with Structural Ceramics, Elsevier Applied Science, London, 1990, pp. 312–320.

[19] C.A. Fortulan, D.P.F. Souza, Microstructural evolution of the Al_2O_3–ZrO_2 composite its correlation with electrical conductivity, Material Research 2 (1999) 205–210.