

STUDIES ON TiO₂ CERAMIC MEMBRANES PREPARED BY ELECTROLYTIC METHOD

Livia GHEORGHIES¹, Constantin GHEORGHIES¹,
Viorel PĂUNOIU², Mihai BERCEA³

¹ Dunarea de Jos University of Galati, Faculty of Science and Environment

² Dunarea de Jos University of Galati, Faculty of Mechanics

³ Gh. Asachi Technical University of Iasi

Romania

lgheorg@ugal.ro

ABSTRACT

TiO₂ microporous membranes were prepared on graphite support by an electrolytic method using an alcoholic solution of TiCl₄. After electro-deposition, the samples thus obtained were allowed to dry in air atmosphere at room temperature and were subsequently heat treated to 400°C for 4 hours. Optical microscopy (OM), X-ray diffraction, thermal gravimetry, differential thermal analysis and nitrogen adsorption method were used to investigate structure and morphology of TiO₂ membranes. The results show that the membranes thus obtained shows a porosity that decreases increases with temperature, while the average pore size results show that the membranes thus obtained shows a porosity that decreases with temperature, while the average pore size increases.

KEYWORDS: ceramic, membranes, structure

1. INTRODUCTION

Membranous material presents a particular interest due to applications in a various operations of separation such as hyper-filtration, reverse osmosis, high-temperature gas separation, and catalysis. The membranes used for this purpose can be of two types: organic polymeric and inorganic ceramic. The last type membranes have advantage that they have a high mechanical strength, are thermally stable, and have a satisfactory chemical resistance. Membranes may also be porous and non-porous. Porous membranes, depending of their pore diameter, d , are considered to macroporous, when $d > 50$ nm, mesoporous, when $2 \text{ nm} < d < 50$ nm, and microporous, when $d < 2$ nm, according to International Union of Pure and Applied Chemistry (IUPAC) classification [1]. The micropores may be considered ultramicropores, when $d < 0.7$ nm, or supermicropores, when $0.7 < d < 2$ nm.

Materials commonly used to fabricate the membranes are: γ -Al₂O₃, TiO₂, ZrO₂ and SiO₂ or a combination of these. [2].

A ceramic membrane is usually a composite system made from several different layers of ceramic materials. They have a macroporous substrate, maximum two mesoporous intermediate layers and a microporous layer.

As presented schematically in Figure 1, depending on pore size, in porous membranes may be different processes.

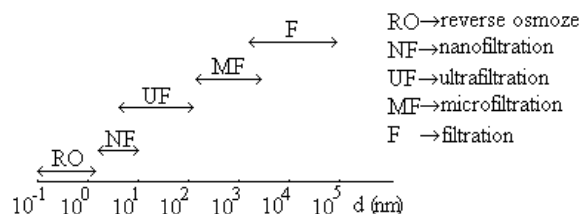


Fig. 1. Relation between membrane process and the pore size

TiO₂ ceramic membranes are given a special attention due to, natural availability, chemical stability, lack of toxicity, photocatalytic and antifouling properties.

In order to obtain TiO₂ layers, besides the established sol-gel, CVD and PVD processes, electrolytic method was tried relatively recently [3].

Electrolytic method is often preferred due to primarily relatively simple technique which takes place at normal temperature and pressure. Also, it can be applied on an industrial scale and is suitable for automation. The electrolytic obtained ceramic

membrane have a high purity and their microstructure can be controlling and managed by monitoring operating parameters such as electrolyte type, its concentration and pH, and other process variables, i.e. voltage, electric current, temperature, speed of reaction. The electro-deposition offers the opportunity to achieve a thin layer of controllable thickness on a substrate with planar or irregular surface.

In the present work, TiO₂ membranes prepared from an alcoholic solution of TiCl₄ were obtained and investigated by optical microscopy, thermal analysis, X-ray diffractometry and N₂ adsorption method.

2. EXPERIMENTAL WORK

The electrolytic depositions of TiO₂ were obtained on porous graphite substrate prepared in the square form of 5×5 mm specimens with current densities of 50 mA/cm² and a deposition time of 60 minutes. For this purpose, a VoltaLab 10 PGZ 100 system was used. During electro-deposition process, the pH and temperature of the solution were monitored. After electro-deposition process, the samples were dried in air at room temperature and then thermal treated in air up to 400°C for 4 hours [4, 5]. The thus obtained deposits had 100 μm in thickness measured using an optic microscope.

Electrodeposition microstructure was monitored with a ZEISS JENA Neophot type 21 microscope.

Using a Zygo NewView 200 Interferometer, were drawn the surface profile and histogram of the microstructural groups that make up the electrodeposition.

Crystallization and phase transition which occurred as a result of thermal treatment of these obtained membranes at various temperatures were monitored using a DRON-3M diffractometer with monochromatic X_{CuKα} radiation.

Thermal gravimetry (TG) and differential thermal analysis (DTA) were conducted on MOM (Paulik, Paulik and Erdey) thermal analysis system. Samples were heated from room temperature to 800°C with a heating rate of 2°C/minute. The reference standard used for DTA measurement was α-Al₂O₃ which was fired at 1000°C for two hours before use.

The porous structure of samples was characterized by nitrogen adsorption using the TriStar II 3020 instrument. Each sample was degassed under high vacuum (10⁻⁵Torr) before a measurement. The porosity was determined from the adsorption maxima. Pore size distribution based on either adsorption or desorption isotherms was calculated using the capillary condensation model assuming cylindrical pores [6]. The mean pore diameter was determined from the peak value taken from the pore size distribution diagram, because the capillary condensation model is not applicable in the microporous region, calculated distribution diagrams were always truncated at a pore diameter about 2 nm. The presence of micropores is indicated by the

corresponding adsorption isotherm which was close to Langmuir type. The percentage of total micropore volume, V_{d<2 nm} %, was calculated by the following equation: $V_{d<2\text{ nm}}\% = [(V_T - V_{d>2\text{ nm}}) / V_T] \cdot 100$, where V_T is the total pore volume calculated from the maximum value of the adsorption isotherm; V_{d>2 nm} is the mesopore volume which can be deduced by integrating the pore size distribution curve measurements and associated calculation showed a value of less than 10%.

3. RESULTS AND DISCUSSIONS

The obtained TiO₂ ceramic layer is affected by the microcracks, as shown in Figure 2, probably caused by the bubbles of hydrogen gas released during electrodeposition.

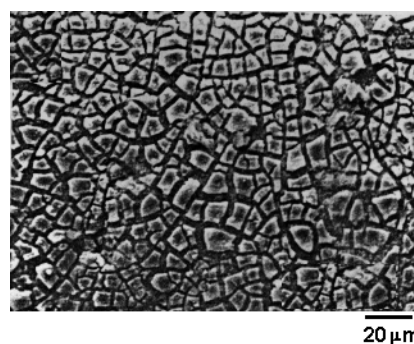


Fig. 2. Microstructure of the electrodeposition dried in air at room temperature

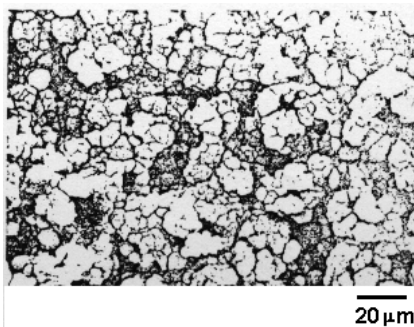


Fig. 3. Microstructure of the electrodeposition after heat treatment

The heat treatment leads to increasing the dimension of the structural groups as result of their coalescence.

Interferometric study of the structural groups forming the layer, under the direction indicated in the figure by a dotted line, permit tracing the 2D profile of the surface and corresponding histogram as shown in Figure 3. Bearing ratio plot t_p (%), plotted by curve type Lorentz, allows an overall assessment of the coverage of the support.

A detail of the same layer, both 2D and 3D representation, obtained by computational processing of the data, is shown in Figure 4 and 5.

X-ray diffraction analysis shows that the crystallization of amorphous TiO₂ takes place around 350°C. The samples subjected to X-ray diffraction analysis were maintained 30 minutes at each thermal treatment temperature

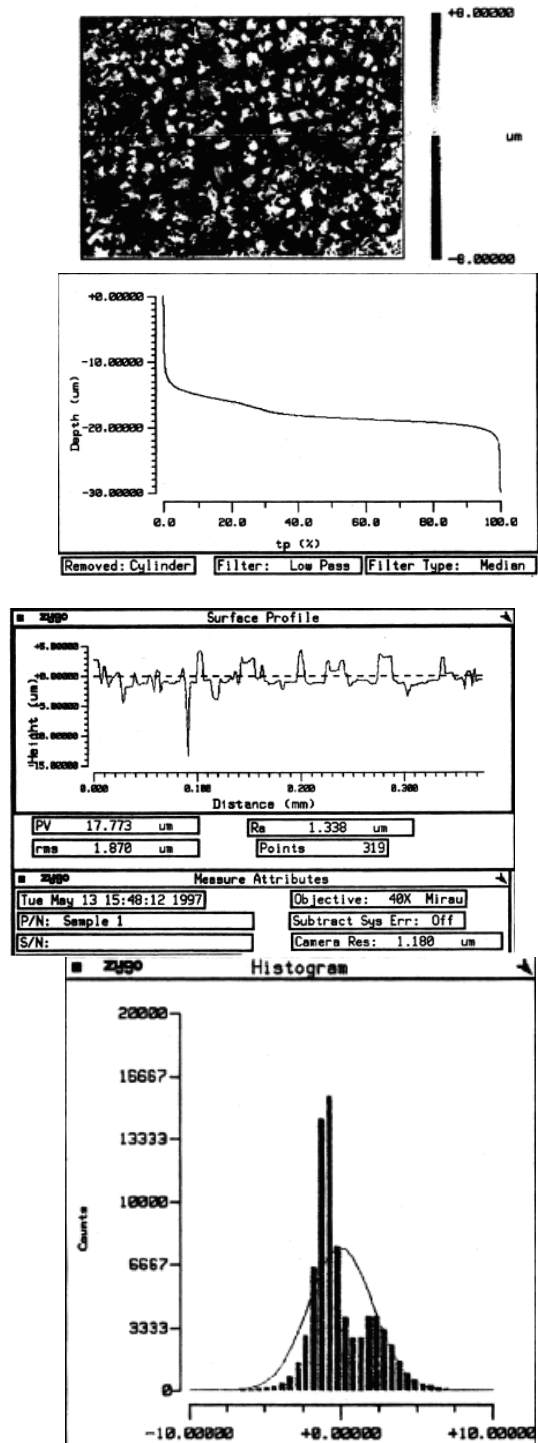


Fig. 4. 2D image of the coating surface, bearing ratio plot curve, 2D surface profile and the roughness histogram

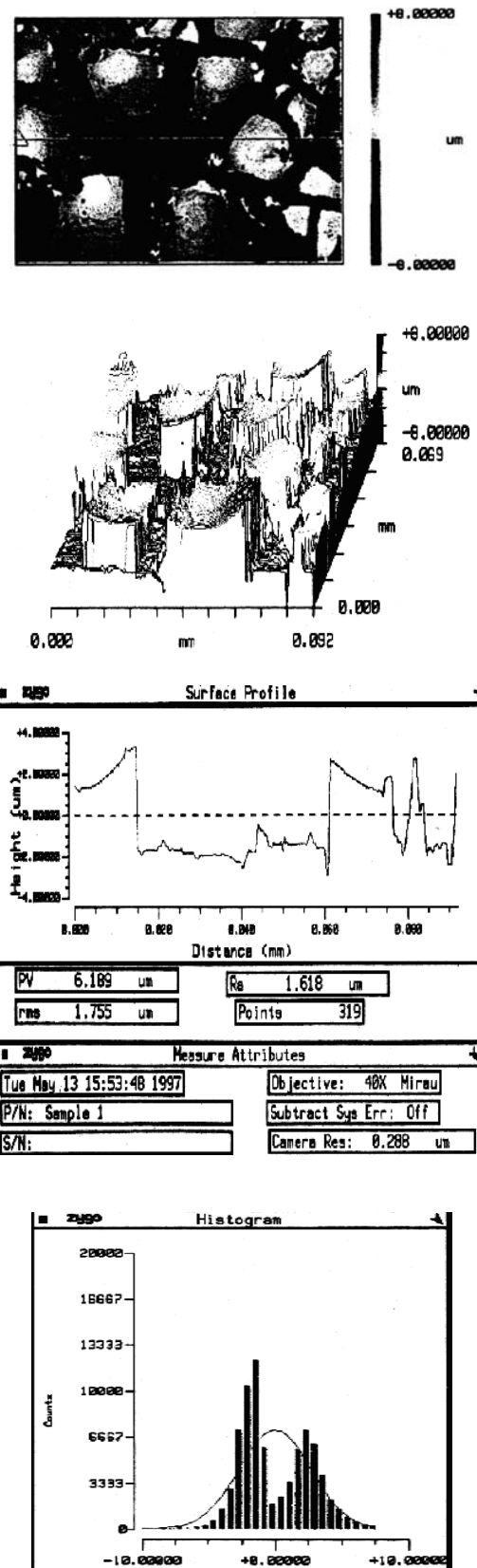


Fig. 5. 2D and 3D images of the coating surface obtaining by computational processing, bearing ratio plot curve, 2D surface profile and the roughness histogram

Figure 6 presents the X-ray diffraction patterns of TiO_2 samples for 2θ between 10° and 60° . The first four diffraction peaks located at around $\theta=12,5^\circ$; 19° ; 24° ; $27,5^\circ$ represent the diffraction lines (101), (004), (200) and (211), respectively, of anatase TiO_2 , in accord with the standard values of Joint Committee on Powder Diffraction Standards (JCPDS no.21-1272).

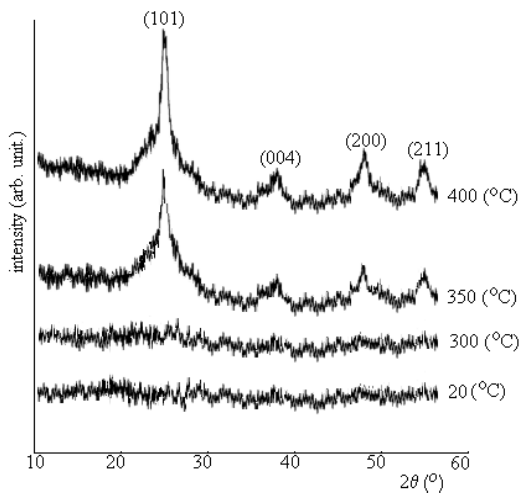


Fig. 6. X-ray diffraction patterns of TiO_2 samples

Figure 7 illustrates the TG and DTA curves of TiO_2 samples. These curves contain information about water elimination and the sharp exothermic peak appeared at approximate 385°C suggests the transition of TiO_2 from an amorphous to a crystalline phase. The reason for the difference between crystallization temperatures determined by XRD and thermal analysis (TG and DTA) is probably the different time maintaining in the two situations.

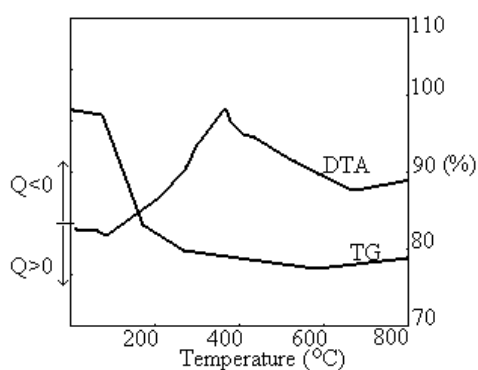


Fig. 7. DTA and TG curves of TiO_2 samples

Porous structure of TiO_2 samples subjected to thermal treatment at various temperatures has been characterized by specific surface area determined by Brenauer-Emmett-Teller (N_2 -BET) adsorption method [7, 8]. Densification and particles growth with temperature can be observed by porosity measurements (%) and determination of the hydraulic

radius of particle, respectively. The hydraulic radius of particle is defined by $2 \times \text{total pore volume} / \text{specific surface area}$. Because the capillary condensation model for calculation pore size is not accurate in the microporous region was used a supplementary method to indicate the degree of microporosity. This method consisted in determination of percentage of the micropore volume ($V_{d<2 \text{ nm}}$) in the total pore volume. Figures 8 and 9 illustrate the change of porosity and mean pore radius (MPR) versus temperature, respectively. Their analysis reveals the following results. The hydraulic radius and porosity show that particle growth and densification process slowly progress during increasing temperature up to 300°C . TiO_2 particle size and sample density drastically change over the thermal treatment temperature range from 300°C to 350°C .

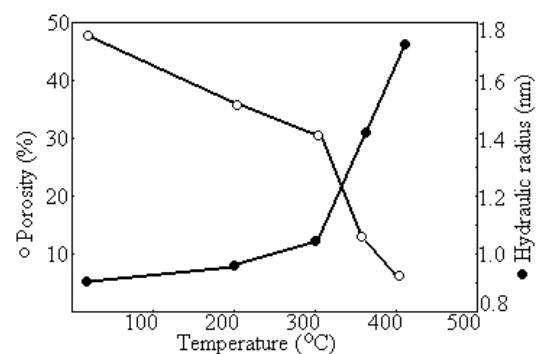


Fig. 8. Dependence of porosity and hydraulic radius on temperature

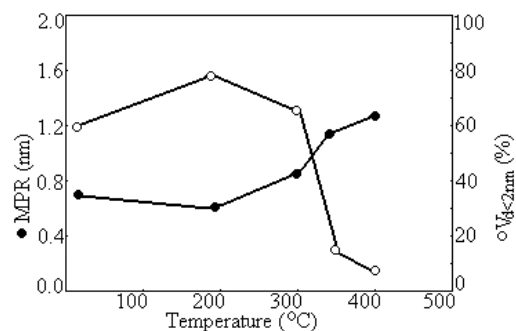


Fig. 9. Dependence of MPR and $V_{d<2 \text{ nm}}$ on temperature

In the same temperature range a rapid change of pores dimension also occurred. The value of MPR remains in the micropores region until the temperature reaches 350°C after which only less than 10% of microporosity remained [9, 10]. According to the thermal analysis and crystallization degree measurements discussed above, the sharp change in the particle size and porosity occurred at 350°C is likely due to the crystallization process of TiO_2 particles. The crystallization becomes a key factor affecting thermal stability of micropores in this type of membranes [11].

4. CONCLUSIONS

TiO₂ microporous membranes can be prepared by an electrolytic method using an alcoholic solution. The mean pore diameter of TiO₂ membranes can be strongly influenced in a well established temperature range. N₂-BET adsorption analysis shows that the TiO₂ particle growth and their densification process slowly progress with temperature up to 300°C. The crystallization process of TiO₂ deposition occurs at 350°C when a dramatically change of microporosity has been found.

REFERENCES

- [1] Akbarnezhad, Sh., Mousavi, S. M., and Sarhaddi, R., *Sol-gel synthesis of alumina-titania ceramic membrane: Preparation and characterization*, Indian Journal of Science and Technology Vol. 3 No. 10 (Oct 2010) ISSN: 0974- 6846
- [2] Van Gestel T., Kruidhof, H., Blank, D.H.A., Bouwmeester, H.J.M., *ZrO₂ and TiO₂ membranes for nanofiltration and pervaporation Part 1. Preparation and characterization of a corrosion-resistant ZrO₂ nanofiltration membrane with a MWCO300*, Journal of Membrane Science 284 (2006) 128–136
- [3] Mazzoni, C., Orlandini F., and Bandini, S.,

Role of electrolyte type on TiO₂ ZrO₂ nanofiltration membranes performances, Desalination 240 (2009) 227-235

- [4] Gheorghies, C., Gheorghies, L., *Study of Zirconia Powder Obtained by Electrodeposition Method*, Tech., Sept. 18-21, 2001, Leganes, Madrid, Spain, p.455-459;
- [5] Gheorghies, C., *The Electrolytic Preparation and Physical Characterization of ZrTiO₄ Films*, J. Cryst. Growth 213, 112-115, 2000
- [6] Azzouz, A., *Physicochimie des tamis moléculaires*, Office des publications universitaires, Ben-Aknoun, Alger, 1994
- [7] Elineema, G., Kim, J.K., Hilonga, A., Shao, G.N., Kim, Y.N., Quang, D.V., Sarawade, P.B., Kim, H.T., *Quantitative recovery of high purity nanoporous silica from waste products of the phosphate fertilizer industry*, Journal of Industrial and Engineering Chemistry 19 (2013) 63–67
- [8] Gheorghies, L., Gheorghies, C., *Advanced Ceramics Materials* (in Romanian), Ed. Evrika, Braila, Romania, 2001.
- [9] Kujawa, J., Kujawski, W., Koter, S., Jarzynka, K., Rozicka, A., Cerneaux, K.B., Pesin, M., Larbot, A., *Membrane distillation properties of TiO₂ ceramic membranes modified by perfluoroalkylsilanes*, Desalination and Water Treatment, Vol. 51, Issue 7-9, 2013.
- [10] Zheng, X., Chen, D., Wang, Z., Lei, Y., Cheng, R., *Nano-TiO₂ membrane adsorption reactor (MAR) for virus removal in drinking water*, Chemical Engineering Journal, Vol. 230, 15 August 2013, pp.180-187.
- [11] Hu, Y., Milne, N.A., Gray, S.R., Morris, G.E., Jin, W., Duke, M. and Zhu, B., *Combined TiO₂ Membrane Filtration and Ozonation for Efficient Water Treatment to Enhance the Reuse of Wastewater*, Desalination and Water Treatment, 34 (1-3). pp. 57-62, 2011.