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# PORE STRUCTURE STABILITY OF ALUMINA BASED MEMBRANES

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**ABSTRACT.** Certain sintering agent decrease the alumina membranes burning temperature and the other maintain the porosity parameters at stable values, even we increase the burning temperature.

The membranes were prepared from industrial alumina powder, $\alpha$-$Al(OH)_3$ (Alor-Oradea). The thermally pre-treated powders and the sintering agents, like $TiO_2$ anatas, $Cr_2O_3$, $La_2O_3$ and ceramic binder (Zettlitz kaolin), were mixed in porcelain ball mill for several hours. Before the final thermal treatment, the ball milling powder was compacted by pressing in disks of 30 mm, at 342 daN/cm$^2$.

The starting materials and the porous ceramics resulted from thermal treatments, were studied by the following methods: X-ray diffraction working with $Cu_{K\alpha}$ radiation, DTA/TG analysis, between 20 and 1000℃, with a rate of 10℃/minute, optical microscopy and Hg porosimetry.

## INTRODUCTION

The alumina membranes were used widely in many filtration processes, due to their excellent properties regards to thermal resistance, which affords utilization in separation processes at high temperatures; mechanical strength, which allows their surface to stand high pressure or pressure gradients; chemical inertness, i.e. no corrosion during utilization in acid, basic, and oxido-reducing media. Moreover, there are many possibilities to prepare them in any configuration, according to the separation processes.[1,2]

The alumina based ceramics, sinter at very high temperatures, generally above 1500$^0$C.[3] In order to reduce the firing temperature, we added to the thermally pre-treated powders the sintering agents mentioned above. The role of these agents was double: first, to reduce the high firing temperature and second, to inhibit the $Al_2O_3$ crystal growth in the porous ceramic, which lead to the stabilization of the entire membrane texture.[4,5]

## EXPERIMENTAL

### Obtaining of alumina membranes

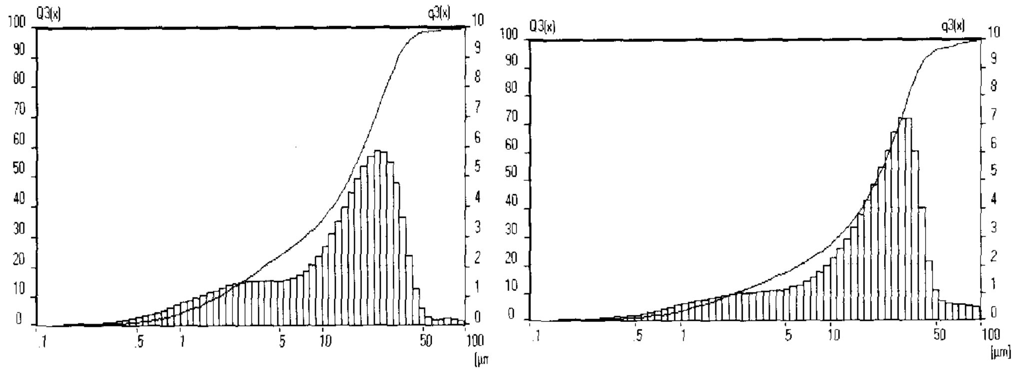
The characteristics of alumina powder and some conditions of obtaining membranes by pressing are listed in Table 1 and 2.[6]

The pressing powders were ball milling for seven hours in porcelain mill, with the ratio of 1:1.5:1 for dry powder, balls and water. Rest on the 0056 sieve established the finesse of the milling powders. After milling, the powders were set to maceration for three days. Before pressing, to powders without ceramic binder, was added organic binder (polyvinyl alcohol) in order to enhance the dry disks mechanical strength. The pressing powders granulometric distributions curves were established by a Fritsch Analysette laser granulometer (fig. 1a, b).

**Table 1**

*Structure of thermally treated alumina powder*

| Powders | | Preliminary thermal treatment | | Final thermal treatment |
|---|---|---|---|---|
| Alumina hydrate | $\alpha$–$Al(OH)_3$ | 450°C/60 min | $\gamma$-AlO(OH) | 1380°C/45 min<br>1590°C/90 min |
| Alumina hydrate | $\alpha$–$Al(OH)_3$ | 600°C/60 min | $\gamma$-$Al_2O_3$ | 1380°C/45 min<br>1590°C/90 min |
| Alumina hydrate | $\alpha$–$Al(OH)_3$ | 1260°C/240 min | $\alpha$-$Al_2O_3$ | 1380°C/45 min<br>1590°C/90 min |




*a). sample A* *b). sample B*

Fig. 1 The granulometric distribution curves of some pressing powders

The $Al_2O_3$ crystals are smaller than the granules. The crystals mean diameter established by optical microscopy were between 2-20 µm, depending on the $Al_2O_3$ powder structure. The granules mean diameter were almost the same, but the porosity parameters of membranes were thoroughly different, depending on the burning temperatures and the sintering agents used.

After drying, the disks were burned at 1260°C, 1380 °C and 1590°C for 4 hours, respectively, 45 and 90 minutes at the final temperatures.

### The textural characteristics of alumina membranes

The pore size distribution and total volume of pores were established by a Carlo Erba porosimeter, between 0.2 and 200 atmospheres. The membranes porosity parameters are listed in Table 3.

**Table 2**

*Certain variants of preparing alumina membranes with different sintering agents*

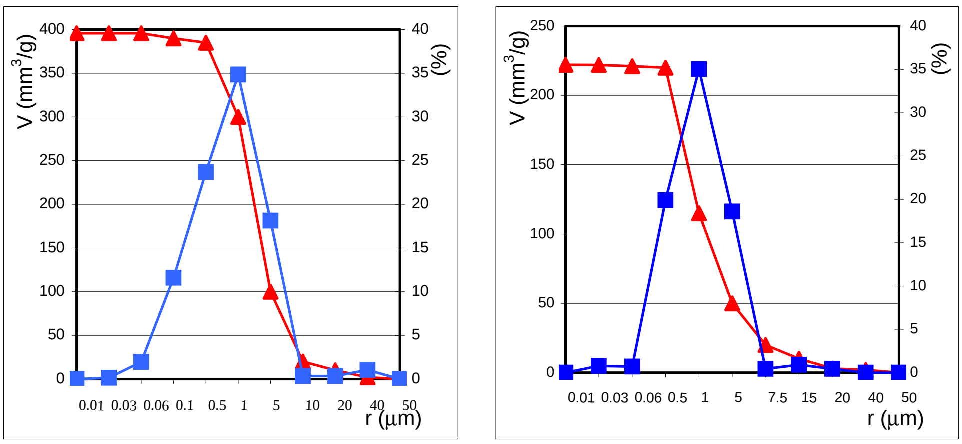
| Pressing powders | Rest on the 0056 sieve (%) | Granules mean diameter (μm) | Binder | Sintering agents | The structure after final thermal treatment | Symbol of sample |
|---|---|---|---|---|---|---|
| γ-AlO(OH) | 0.12 | 22.80 | 20% APV | 0.5% $Cr_2O_3$ | α-$Al_2O_3$ | A |
| γ-AlO(OH) | 0.12 | 23.10 | 20% APV | 2% $TiO_2$ | α-$Al_2O_3$ $Al_2TiO_5$ | B |
| γ-AlO(OH) | 0.10 | 22.80 | 20% APV | 5% $La_2O_3$ | α-$Al_2O_3$ $LaAl_{11}O_{18}$ | C |
| γ-$Al_2O_3$ | 0.10 | 22.80 | 15% kaolin | - | α-$Al_2O_3$ $Al_2SiO_5$ | D |

**Table 3**

*Porosity parameters of the membranes*

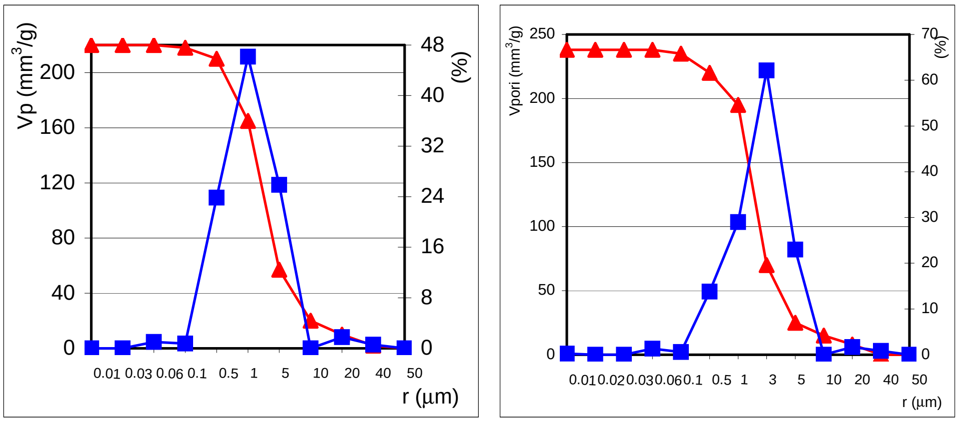
| Symbol | Composition | Firing temperature ($^0$C / min.) | Total volume of pores ($mm^3$ / g) | Porosity (%) | Pore radius average (μm) | Specific surface area ($m^2$ / g) |
|---|---|---|---|---|---|---|
| $A_1$ | -AlO(OH)/$Cr_2O_3$ | 1380/45 | 395.82 | 64.439 | 0.841 | 3.29 |
| $A_2$ | -AlO(OH)/$Cr_2O_3$ | 1590/90 | 222 | 47.16 | 1.189 | 0.92 |
| B | -AlO(OH)/$TiO_2$ | 1380/45 | 237.64 | 27.20 | 3.35 | 0.75 |
| C | -AlO(OH)/$La_2O_3$ | 1590/90 | 210.69 | 47.25 | 0.841 | 0.84 |
| $D_1$ | -$Al_2O_3$/kaolin | 1220/60 | 426.66 | 74.40 | 0.053 | 8 |
| $D_2$ | –$Al_2O_3$/feldspar/kaolin | 1100/120 | 175.30 | 21 | 0.596 | 0.93 |
| $D_3$ | γ–$Al_2O_3$/kaolin | 1590/90 | 330 | 47.85 | 0.299 | 0.71 |

Pore size distribution curves of the samples A, B, C and D, are represented in fig. 2a, b, fig. 3a, b and fig. 4a, b.



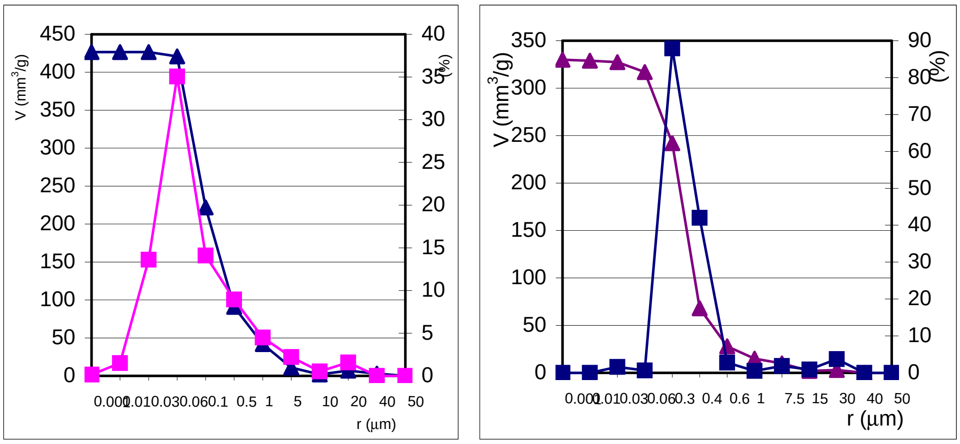

*a). sample $A_1$*  *b). sample $A_2$*

Fig. 2 Alumina membranes with $Cr_2O_3$, burned at different temperatures




*a). sample C* *b). sample B*

Fig. 3 Alumina membranes with different sintering agents, burned at different temperatures.




*a). sample $D_1$* *b). sample $D_3$*

Fig. 4 Alumina membranes with ceramic binder, burned at different temperatures.

## RESULTS AND DISCUSSION

The alumina membranes porosity parameters, depended of the powders composition, the sintering agents used and the burning temperatures.

The sample D burned at 1220℃ with ceramic binder (Zettlitz kaolin), have the greatest pore volume, above 426 $mm^3/g$ and the smallest pore radius average, 0.053 µm, but its mechanical strength is the lowest. For this reason, unfortunately, this membrane could not applied in separation processes. Increasing the temperature until 1590℃, the pore radius average growth to 0.299 μm and the total volume of pores decrease to 330 $mm^3/g$ (fig. 4a, b). At this temperature, alumina reacted with kaolin and result small amounts of $SiO_2$ from mulit.

We have been tried to decrease the alumina membranes high burning temperature with feldspar adding (sample $D_2$). But due to melt forming, the porosity decrease to 21%, not enough for filtration processes.

The pore radius average of alumina membranes with $Cr_2O_3$ (sample A), growing from 0.84 μm to 1.18 μm, as we increasing the burning temperature from 1380℃ to 1590℃ (fig. 2a, b). This means that $Cr_2O_3$ has inhibiting effect on $Al_2O_3$ crystal growth. In other words, $Cr_2O_3$ stabilises the texture and therefore the alumina membrane porosity parameters.

The results obtaining for samples B and C prepared with $TiO_2$ and $La_2O_3$ are the most interesting. Some experiments confirmed that $TiO_2$ anatas decrease the alumina based ceramics burning temperature.[7] We observed that the membranes prepared with $TiO_2$ anatas, sintered until 1380℃. Unfortunately, this sintering agent has a v ery undesirable effect, upon the membrane pore structure. So, the anatas enhance the $Al_2O_3$ crystal growth, followed by the increase of pore size until 3.35 μm and by the decrease of total volume of pores, to 237 $mm^3/g$.

$La_2O_3$ has the opposite effect of $TiO_2$. After burned at 1590℃, the membrane pore radius average is 0.84 μm and the total volume of pores is above 210 $mm^3/g$, which are very nearest to that of alumina membranes prepared with $Cr_2O_3$.

The sintering agents, pore structure stabilising effect, result also from the fig.5 represented below.

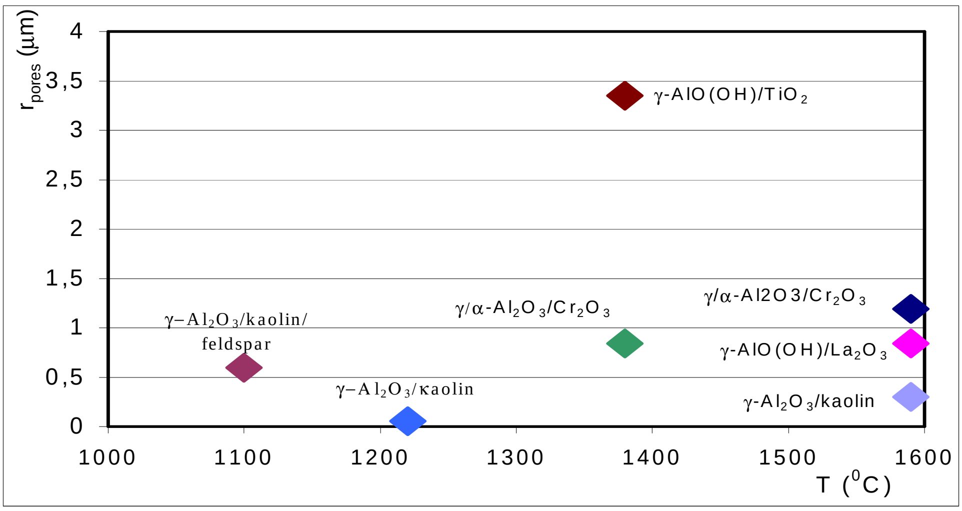



Fig. 5 Pore radius average, depending of temperature and sintering agents.

## CONCLUSIONS

The burning temperatures and the sintering agents used, have been influenced the texture and the porosity parameters of alumina membranes. Certain sintering agents decrease the burning temperature of alumina membranes, but unfortunately the textural characteristics alters in a very undesirable manner. Other, maintain the porosity parameters at stable values, even we increasing the burning temperature.

Unfortunately, the $TiO_2$ sintering agent has a very undesirable effect upon the membrane pore structure. So, at $1380^0C$ the pore radius average reached 3.35 μm, due to $Al_2O_3$ crystal growth, what means that pores growing too.

$La_2O_3$ has the opposite effect of $TiO_2$. After burned at 1590℃, the membranes pore radius average is 0.84 μm and the total volume of pores is above 210 $mm^3/g$.

The effect of $Cr_2O_3$ is near to that of $La_2O_3$. The pore radius average growing lightly from 0.84 μm to 1.18 μm, as we increasing the burning temperature from 1380℃ to 1590℃.

The ceramic binder enhances the percent of small pores in the membrane texture. For this reason, at $1220^0C$, we have been obtained the smallest pore radius average, 0.053 μm and the greatest pore volume, above 426 $mm^3/g$ With increasing the burning temperature to $1590^0C$, the pore radius average growing to 0.299 μm and the total volume of pores decrease to 330 $mm^3/g$.

Utilizing certain sintering agents, like $La_2O_{3,}$ $Cr_2O_3$ or even kaolin, we could obtain alumina-based membranes with stabilised pore structure. These membranes are appropriate for use in microfiltration processes, or as supports, for thin, mezoporous films deposition.

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