EFFECT OF TEMPERATURE IN THE TUBULAR CERAMIC MEMBRANE SINTERING OBTAINED WITH KAOLIN AND BALL CLAY

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Abstract*. Due to the increase in membrane technology in the last years and its applications are also widespread to different areas of science, it become more important the studies of the parameters that affect its properties. In this way, the aim of this work is to evaluate how the increase in sintering temperature changes structural and morphological characteristics of the ceramic membrane obtained from raw materials: kaolin and ball clay. Ceramic membranes were obtained from vacuum extrusion processing and sintering at temperatures of 900ºC, 1000ºC and 1100ºC.The ceramic mass was characterized by thermogravimetric analysis, X-ray diffraction (DRX) and particle size distribution. The membranes were also characterized by DRX and scanning electron microscopy. The results showed a total mass loss of 13.8% due to water loss adsorbed on the surface of the particles, organic materials, hydroxyls from clay and from carbonates decompositions. The value of particle size with 50% of accumulated mass was 3.52µm. The crystalline phases present were kaolinite, quartz and mica. After sintering at 900°C, the crystalline phases present were quartz; at 1000°C and 1100 present quartz and mullite. After sintering the membranes presented the linear shrinking of 1.23%, 3% and 9.18%, to sintering temperature of 900ºC, 1000ºC and 1100ºC, respectively. The images from microscopy showed porous membranes and with the increase of sintering temperature it was observed an increase in the grain size and more homogeneous distribution of them.*

Keywords*: ceramic membrane, sintering, kaolin, Ball clay.*

1. INTRODUCTION

Membrane separation process are considered a clean technology and is each time more applied by the industry in substituting conventional process, due to advantages, such as: make the separation without phase changing, appreciable energy savings, are environmentally benign; the technology is clean and easy to operate; can replace conventional processes like filtration, distillation, and ion exchange; produce high-quality products; and offer greater flexibility in system design (Silva *et al.* 2005, Silva, 2002).

Among materials used to prepare inorganic membranes, ceramics are highlight. It can produce membrane with tangential velocity, with turbulent flow to prevent the formation of fouling and maintain high permeate flow (Delcolle, 2010). Ceramic membrane properties include high temperature resistance, good biological resistance and allow sterilization with vapor and its contamination with bacteria is less probably. This characteristic is very attractive to the food and pharmaceutical industry (Chi-Sheng Wu and Lee, 1999, cited by Alicieo *et al*., 2008).

The first researches about ceramic membrane used α-Al_2O_3 as precursor, followed by γ-Al_2O_3, zirconia, titania and silica were used to membrane preparation. Recently, some researchers start to work with raw materials of low cost, such as: apatite, ash and kaolin, to reduce membrane cost (Jana *et al*. 2010).

Membranes can be classified into two geometrical shapes: plane and cylindrical. This later can be tubular, capillary and hollow fiber. The tubular membrane present good resistance to fouling and are currently used when the feed contain high amount of solids in suspension (Gea Filtration, 2010). Howell et al. (1993) describe a new application of tubular and plane membrane to collect yeast. The research done by Ahn et al. (1998), showed the possibility to use ceramic membrane to effluent treatment generated by the hotels and building and to reuse for secondary purposes.

The field of application of membrane technology has been expanded in the last years and the interest of the researchers is to develop new methods with low cost to be applied in different membrane separation process.

2. MATERIALS AND METHODS

Raw materials used in the ceramic membrane preparation were: ball clay from Alhandra, Paraiba state, kaolin from Junco do Seridó, Paraiba and liquid additives. The raw materials were submitted to sieve ABNT 200 mesh (0.075mm) and mixed in a blender METVISA model. The mixture was homogenized with water and additives to reach a plasticity fit to extrusion. It was used a vacuum extruder Verdés 051 model. The extruded parts in a tubular shape were dried and sintering at 900°C, 1000°C and 1100°C, using an electrical oven JUNG model.

The ceramic mass was characterized by thermogravimetry, using a thermal analyzer, from BP Engenharia, RB-3000-20 model, with heating rate of 12.5oC/min and using nitrogen gas. It was used a platinum crucible and temperature range from room temperature to 1000°C. Particle size analysis was done in diffraction laser particle size analyzer from Cilas, 1064 LD model, with a measurement range from 0.04 to 500 µm. To phase identification it was used a X-ray diffractometer from Shimadzu, XRD-6000 model. Ceramic membranes were characterized also by scanning electron microscopy (SEM) from Shimadzu, SSX-550 model. It was also calculated shrinking of the membranes after sintering with a digital caliper and using the Eq. (1), where R means the shrinking, Da is the length of the membrane before sintering, in mm, and Dq is the length of the membrane after sintering, in mm.

$$R = \left(1 - \frac{D_q}{D_a}\right) x\, 100\% \tag{1}$$

3. RESULTS AND DISCUSSION

Figure 1 shown the thermogravimetric curve of the ceramic mass before sintering. It was observed a first mass loss (1.6%) starting at 25°C until 200°C related with adsorbed water on the surface. Between 200°C and 350°C the curve showed another mass moss of 0.84% due to loss of organic matter. At 365°C it was observed the beginning of third mass loss that finishes at 625°C (10%) and is due to the elimination of hydroxyl groups from clay fraction. Between 630°C and 1000°C there is a small mass loss of 1.32% due to the decomposition of carbonates. The total mass loss was 13.8%.

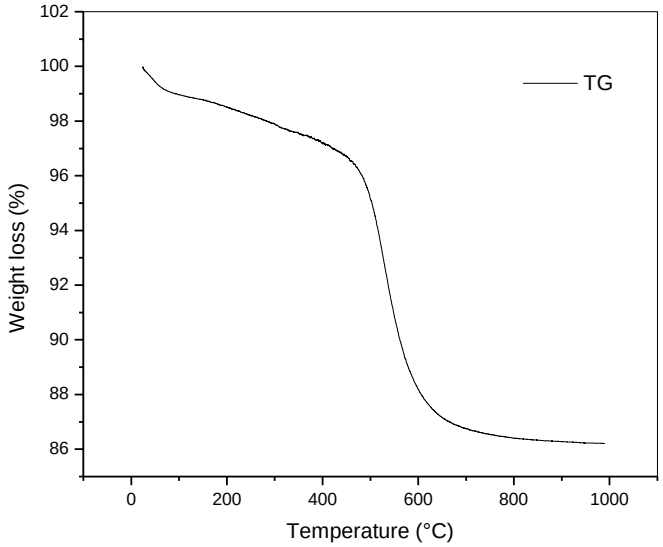

Figure 1. TG and DTG curves of ceramic mass before sintering.

Figure 2 present particle size distribution of the ceramic mass before sintering. The results showed a narrow distribution of the particle with 50% of the accumulate average mass of 3.52µm.

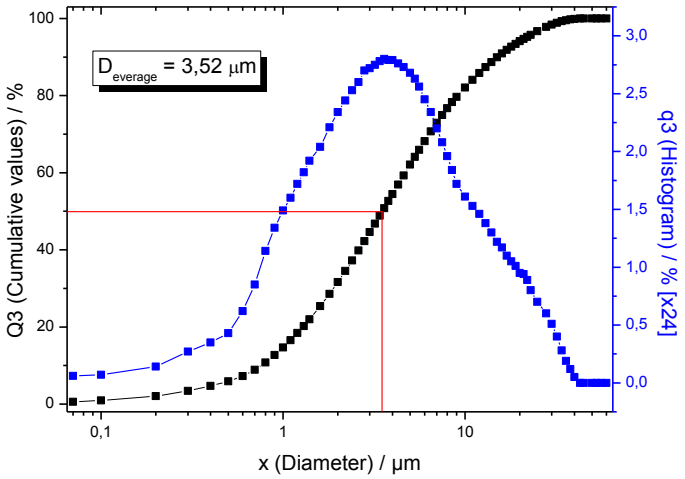

Figure 2. Particle size distribution of ceramic mass before sintering.

Figure 3 present the results from X-ray diffraction of the mass before sintering and after sintering at 900°C, 1000°C and 1100°C. It was observed that the mass before sintering, Fig. 3(a), show the presence of crystalline phases such as kaolinite, quartz and mica. The two main peaks are related to kaolinite.

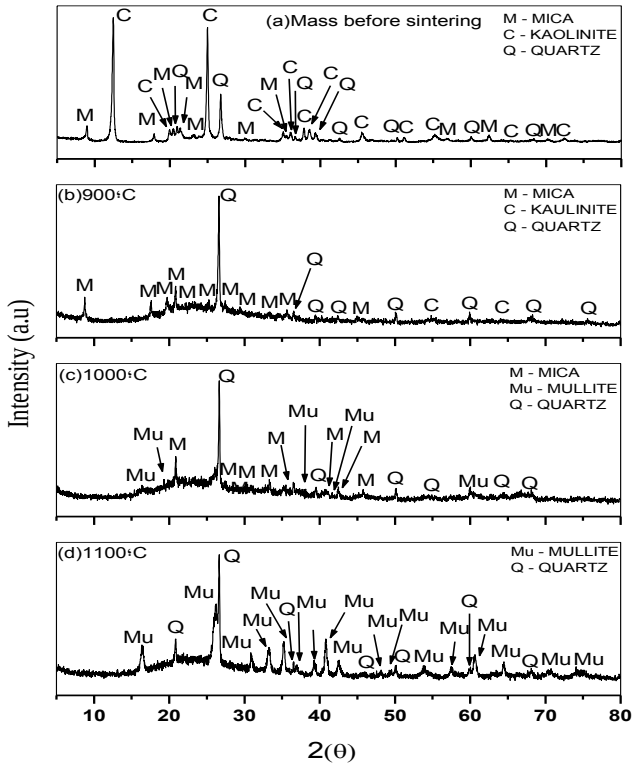

Figure 3. X-ray curves of (a) mass before sintering, (b) sintered at 900ºC, (c) sintered at 1000ºC e (d) sintered at 1100ºC.

After sintering at 900°C it also observed peaks related with quartz and mica and traces of kaolinite. Due to the increase in temperature during the sintering process there is a reaction between silica (SiO_2) and alumina (Al_2O_3) present in the raw materials, to produce mullite ($3Al_2O_32SiO_2$) that appear when the membrane was sintering at 1000°C.

For the sintering temperature of 1100°C, it was presented also two crystalline phases, quartz and mullite, with more intense and defined peaks when compared with the temperature of 1000°C.

Figure 4 present the shrinking of the ceramic membranes before and after sintering at 900ºC, 1000ºC e 1100ºC.

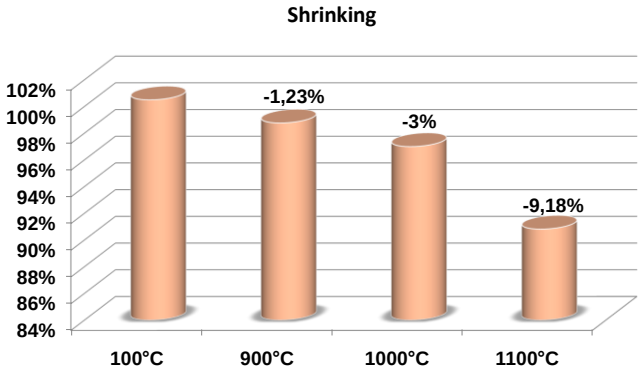

Figure 4. Linear shrinking of the ceramic membrane before and after sintering at 900°C, 1000°C and 1100°C.

After sintering process membranes present a shrinking in relation to the initial length and diameter. The shrinkage increase with the increase of sintering temperature, that is, to the ceramic membrane sintering at 900°C, 1000°C and 1100°C presented shrinkage of 1.23%, 3% and 9.18%, respectively.

In relation to the color, it was observed that the increase in sintering temperature cause a change in color intensity and became more light, probably due to the small amount of iron present in the ceramic mass.

Figure 5 show the SEM images for the membrane sintering at 900°C. It was observed a porous structure, with presence of grains with irregular shape and distribution, also with some agglomerates with different sizes and plate shape. This temperature was not enough to promote a good sintering of the particles. Although a porous structure, from the image it was not possible to estimate with precision the pore size as well as the porosity of the membranes.

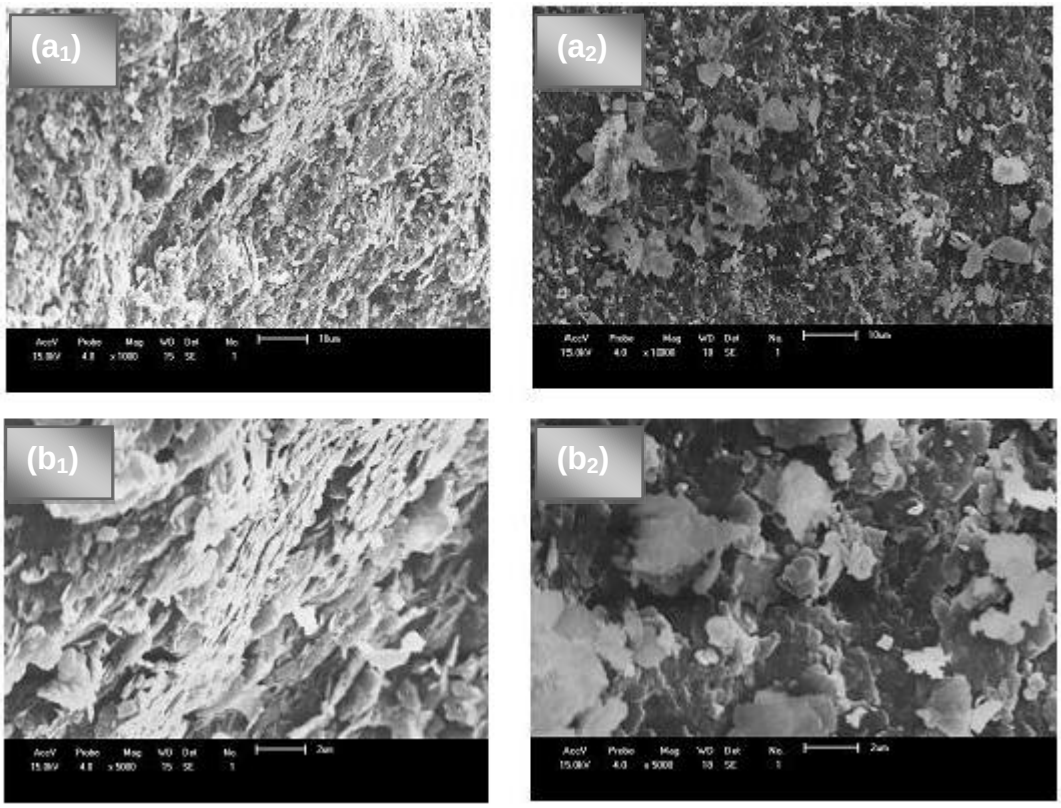

Figure 5. SEM images for the tubular ceramic membrane sintering at 900°C. (a_1 and b_1) transversal section of the membrane and (a_2 and b_2) longitudinal section of the membrane. Magnification of (a)1000 times and (b) 5000 times, respectively.

Figure 6 presents images for membrane sintering at 1000°C. It can be observed that an increase in sintering temperature of 100°C produced an increase in grain size. Also it was observed the presence of agglomerates with different geometries and improperly distributed on the membrane surface. In the image a_1 it was observed a porous structure of the membrane and in b_1 it was observed an increase in particle sintering. As also mentioned to Figure 5, from Figure 6 images it was not possible to estimate the pore size of the membranes.

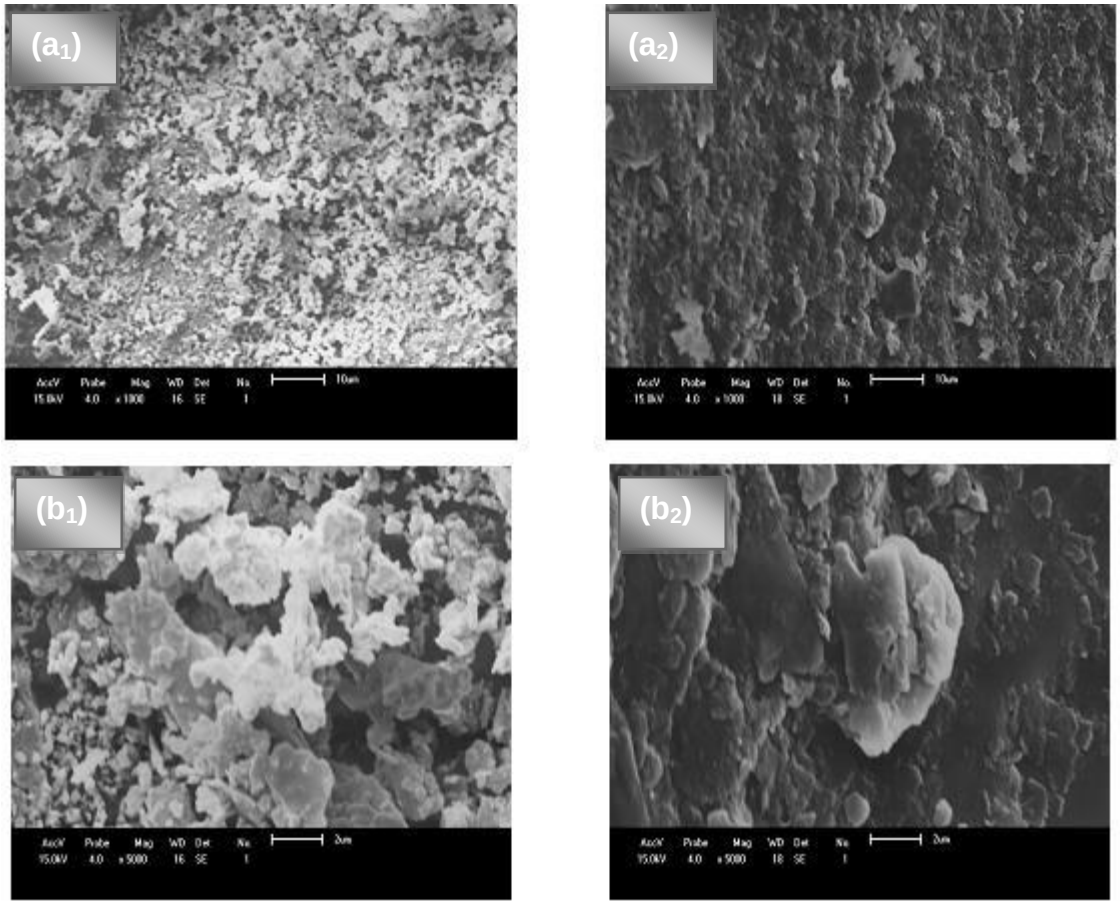

Figura 6. SEM images for the tubular ceramic membrane sintering at 1000°C. (a_1 and b_1) transversal section of the membrane and (a_2 and b_2) longitudinal section of the membrane. Magnification of (a)1000 times and (b) 5000 times, respectively.

Figure 7 showed the SEM images from ceramic membrane sintering at 1100^{o}C. From these images it can be observed an changin the the surface aspect of the membrane when compared with Figure 5 and 6. In spite of the presence of sintering grains, still possible to see a more distributed and homogeneous particles on the membrane surface. Also with these images it was not possible to estimate the pore size.

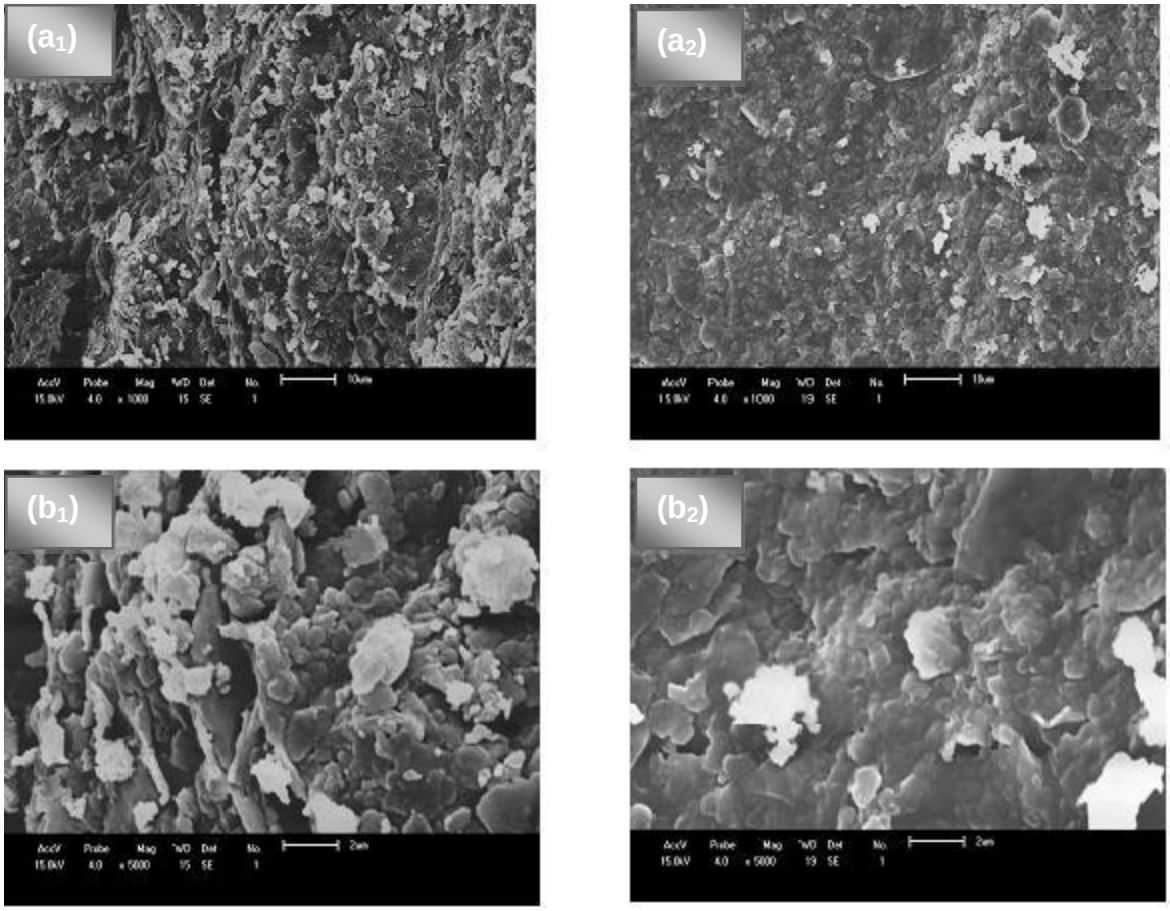

Figura 7. SEM images for the tubular ceramic membrane sintering at 1100°C. (a_1 and b_1) transversal section of the membrane and (a_2 and b_2) longitudinal section of the membrane. Magnification of (a)1000 times and (b) 5000 times, respectively.

4. CONCLUSIONS

After this study it can be concluded that:

Tubular ceramic membranes were produced with success. The ceramic mass used to produce membrane presented a total mass loss of 13.8%. The particle size distribution presented 50% of the mass with size of 3.52µm. After sintering at 1000^{o}C it was observed the presence of quartz and mica and trace of kaolinite and at 1100^{o}C it was observed the presence of mullite and quartz. The membranes presented shrinkage from 1.23% (900^{o}C) to 9.18% (1100^{o}C) and presented a porous structure with changing in aspect when sintering at different temperature.

5. ACKNOWLEDGEMENTS

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