Ceramic Material Porous Structure Prepared Using Pore-Forming Additives

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A B S T R A C T

Porous ceramic materials exhibit high permeability, specific surface, and thermal shock resistance, and therefore they may be used successfully in the production of filters, membranes, and as a substrate for catalytic reactions, etc. One method for preparing high material porosity is addition of a pore-forming substance. Porosity (open and closed), pore size distribution, their size and shape, depend on the nature, amount, and morphology of pore-forming substance. In this article, the effect is elucidated of three different types of carbon additives on porosity of ceramic prepared from clay and chemical binder precursor. Carbon materials are studied in an x-ray diffractometer. Ceramic material properties are studied using a mercury porosimeter, the Archimedes method, scanning electron and optical microscopes, and microcomputer tomography.

Keywords: ceramic materials; porous structure; pore-forming additive; carbon.

1. Introduction

The porous ceramics are widely used in high temperature processes due to the ceramic properties and because of its low thermal conductivity, high permeability, low density, high specific surface, etc. Some applications include molten metal filters, filtration of exhaust gas in engines, membranes, catalytic support, thermal insulation, etc. [1, 2].

There are several methods for the formation of porous structures using different materials and processes [3-5]. Among them the most used are the addition of pore forming agents such as starch, graphite and other organic substances that decomposes leaving holes in the matrix during thermal treatment. The percentage of porosity (open or closed), distribution, size, and shape of the pore is related to the nature, size and morphology of the forming agent.

This work analyzed how three different types of coal (charcoal, lampblack and residual petroleum coal) influence on the porous texture of ceramics obtained from mixtures of clay and a chemical binder precursor.

2. Experimental

2.1 *Obtention of porous ceramic materials*

Porous materials were made from Tincar super clay, chemical binder precursor and three different carbon sources: charcoal, lampblack and residual petroleum coal. Carbon sources were ground until a particle size between 76-106 µm, except lampblack that is formulated as a fine material agglomerate.

Prismatic bars were made by uniaxial pressing at 40 MPa. A mixture of clay, 25% of different coals and 10% of the chemical binder precursor (percentages are based on the amount of clay), were pressed and thermally treated in an electric furnace in air atmosphere at a heating rate of 5 ºc/min up to 1550 ° C. At that temperature they were hold during 2 hours.

2.2 *Analysis of the carbonaceous raw materials and the clay*

The characterization of the different coals were performed by X-rays diffraction (DRX) using a Philips PW-3710 with Cu-Kα radiation (λ = 0, 154 nm) at 40 kV and 20 mA. The tests were carried out with samples previously dried at 110ºC for 24 hours.

The XRD diagrams are shown in **Figure 1**, in which crystalline structures are identified associated with graphite. The presence of broad-peaks are because of the low crystallinity of the coals. In the case of charcoal are also distinguished phases corresponding to calcium and magnesium carbonate. The most cristalline arrangement are showed in residual petroleum coal.

The loss on ignition (LOI) at 1000°C of residual petroleum coal and lampblack were 100.00%; while in the case of charcoal loss was 98.56%. In this case the ashes were analysed by x-ray diffraction distinguishing calcium and magnesium oxide, corresponding this with the observation of the overall sample.

The clay was characterized by chemical analysis as it is shown in table 1, and by X-ray diffraction shown in **figure 2**. As a result of this analysis, the Tincar super clay evidence that is a caolinitic clay with important amount of quartz. This kind of clay when is calcined at temperatures higher than 1400°C convert to mullite and cristobalite as a main crystalline phases.

2.3 *Characterization techniques of the obtained porous ceramics*

The calcined samples evaluated by mean of different techniques.

The apparent density and the open porosity of the ceramic materials obtained were determined by the Archimedes method, using liquid water (under guidelines of standard IRAM 12510).

It was also determined the real density of the ceramic obtained with Tincar super clay and the chemical binder precursor without any source of coal through two trials: 1) Pycnometer, using kerosene as immersion fluid (under guidelines of standard IRAM 12517), and 2) Mixture of phases, determining the percentage of each of them by the Rietveld method. This method is a tool that quantifies the crystalline and non-crystalline phases in a sample from a X-ray diagram.

In order to determine the real density of the material, samples were grounded in Herzog mill up to a size of less than 44µm particle.

The estimated real densities were used to calculate the closed porosity of the material by considering the open porosity obtained with the method of Archimedes to reach a value of total porosity which was compared to the total porosity provided by x-ray microtomography. The microtomograph used was a Bruker Skyscan 1173 with a resolution of 3 µm.

The open pore size distribution was studied by mercury intrusion with a Porosimeter Pascal - Thermo Fisher 440 and 140.

The microstructures were observed with an scanning electron microscopy (SEM) with a JEOL CM-600 Neo Scope, X-ray microtomography (Bruker Skyscan 1173) and an optical microscopy (Olympus BX 60). The flexural strength at three points was determined with a universal testing machine JJK. Lemes T22K.

3. Results and discussion.

The XRD diagrams of the ceramic materials obtained are shown in **Figure 3**, in which crystalline structures shows mullite and cristobalite as main crystalline phases.

The apparent densities and apparent densities in water (densities of the solid including closed pores) obtained for the ceramics made from the clay mixture, chemical precursor and coals are shown in **Table 2**. No significant differences were observed in density values when using different carbon sources.

The phases present in a ceramic material without any carbon source were determined by Rietveld: 35% of cristobalite, 24% of mullite and 41% of amorphous phase. From these values and the theoretical densities of each phase (taken from bibliography **[6-8])** the theoretical density was

calculated ($\delta_{theoretical}$) as 2.46 g/cm^3. The real density without carbon determined by pycnometer (δ_{pic}) was 2.40g/cm^3.

Through these densities closed porosity were calculated when the pore-forming agents were added with the equation 1, where P_i= closed porosity, δ_{th}= theoretical density, $\delta_{Apparent\ H20}$= apparent density in water.

$$\%P_i = \frac{(\delta_{th} - \delta_{ApparentH20})}{\delta_{th}} * 100\% \qquad \textbf{Equation 1}$$

Table 3 shows the percentage of open porosity determined by Archimedes method, closed porosities calculated with the real densities described previously and the total porosity obtained by x-ray microtomography, also the flexural strength at three points. The total porosity when lampblack is used was high compared to the other sources of carbon arising more difference in the open porosity of the material.

There are differences between the closed porosity estimated according to the pycnometer measurement and the theoretical density in a range of 8,00 - 20,59 %, these differences may be due to errors in the trial of pycnometer if the sample was not completely pulverized there could be closed pores within the particles or in estimating the percentage of amorphous had similar density of a silica glass.

The size distribution of open pores of the materials obtained less than 3000 nm and until 7nm (mesopores) are shown in **figures 4a**. The distribution using lampblack is narrow in the range of 500-1100 nm with a pore volume (100 mm^3/g) much greater than when the other carbon sources were added.

The charcoal has a continuous pore distribution in a range of 40-400 nm being the pore volume less than 1 mm^3/g. In contrast, residual petroleum coal shows a wider distribution than in the previous cases but in a range of 10-2000 nm with a cumulative pore volume of $7mm^3/g$.

The size distribution of macropores (> 10000 nm) for materials analyzed is shown in the **figure 4b**. As in the case of the mesopores exist greater volume of pores when lampblack is used compared with other carbon sources and a dual-mode distribution is observed. The pore distribution with charcoal and residual petroleum coal present a wide distribution, while charcoal has the lower pore volume ($2,3\ mm^3/g$) among the three samples.

The mechanical resistance shown in **table 3** correlates with the total porosity and also with pore size distribution obtained in **figure 4**. As the mechanical resistance increase the total porosity decrease, while exists a difference between lampblack and the other two coals due to the large amount and size of pores of the first one.

The total pore size distribution of the materials obtained by microtomography is shown in the **Figure 5**. The pore volume values when lampblack is added were in the order to those obtained by mercury porosimetry in the range of macropores, indicating that most of the pores were open. In contrast, the other two materials obtained with charcoal and residual petroleum coal presents higher values than the ones of the mercury porosimetry (macropores), being the difference due to the closed pores. This agrees with the results obtained in **table 3**.

The microstructure observed by x-ray microtomography, scanning electron microscopy and optical microscopy are shown in the **figures 6, 7 and 8** respectively. These techniques allow us to analyze the distribution of macropores.

The lampblack addition as a forming agent of pores generates large pores with varied forms, in contrast with the other two types of coal were a smaller and homogenous pores as observed. This

may be due to the particle size of lampblack (< 50 nm.) which contributes to the generation of agglomerations which does not allow a homogeneous distribution of the carbon in the mixture.

The evaluated techniques correlate and allow to interpret the porous texture of the ceramic materials obtained.

There is consistency between the results obtained with the different microscopies, microtomography and the size distribution of macropores obtained with the porosimetry. The distribution of mesopores and macropores shows consistent results with the densities and porosities evaluated by the Archimedes method.

4. Conclusions.

- The addition of pore-forming agents allowed to obtain ceramic materials with a varied porosity and a density value under or equal to 2 g/cm^3.
- The use of charcoal and residual petroleum coal do not present significant differences on the percentage of total porosity in the obtains ceramic.
- The open porosity of the materials made with charcoal and residual petroleum coal present lower values than the one obtained with lampblack.
- Lampblack as a pore forming agent generates large volume of mesopores compared with other sources of carbon due to the difficulty in the carbon nanoparticles dispersion.

5. References.

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	Arcilla Tincar Súper (Atincar)
SiO_2	65.70
Al_2O_3	21.10
Na_2O	0.07
K_2O	0.68
CaO	0.26
Fe_2O_3	0.85
MgO	0.22
TiO_2	0.43
Others	2.92
LOI	7.77

Table 1 *Chemical Analysis of Tincar super clay.*

Type of coal	Apparent density (g/cm^3)	Apparent density in water (g/cm^3)
Charcoal	**2.00**	**2.08**
Lampblack	**1.93**	**2.18**
residual petroleum coal	**1.97**	**1.99**

Table 2 *Archimedes method, values of apparent density and apparent density in water for the ceramic materials obtained at 1550°C during 2hs.*

Type of coal	Open porosity	Closed porosity (δ_{pic})	Closed porosity ($\delta_{theoretical}$)	Total porosity (microtomography)	Flexural strengh (Mpa)
Charcoal	**0.76**	**13.33**	**15.45**	**16.42**	**23.24**
Lampblack	**13.41**	**9.17**	**11.38**	**20.45**	**15.98**
Residual petroleum coal	**0.56**	**17.08**	**19.10**	**15.78**	**22.36**

Table 3. *Open and closed porosity of the ceramics obtained by different techniques and Flexural Strength.*

Fig. 1 *Diagrams of x-ray of carbonaceous raw materials. (a) Charcoal. (b) Lamblack. (c) Residual petroleum coal.*

Fig. 2 *Diagram of x-ray of Tincar super clay. Crystalline phases: quartz (Q) and kaolinite (K).*

Fig. 3 *Diagrams of x-ray of the ceramic material obtained at 1550°C during 2hs. (a) Charcoal. (b) Lamblack. (c) Residual petroleum coal. Crystalline phases: mullite (M) and cristobalite (C).*

Fig. 4 *Mercury Porosimetry using carbons as pore forming agent (a)mesopores (b) macropores.*

Fig. 5 *Microtomography using coals as a pore forming agent.*

Fig. 6 *X-ray microtomography ceramic using (a) Charcoal. (b) Lampblack and (c) Residual petroleum coal.*

Fig. 7 *SEM photographs (27 x) of the ceramic obtained using (a) Charcoal, (b) Lampblack and (c) Residual petroleum coal.*

Fig. 8 *Optical microscope pictures(40 x) for the obtained ceramics (a) Charcoal, (b) Lampblack and (c) Residual petroleum coal.*

Fig. 1 :

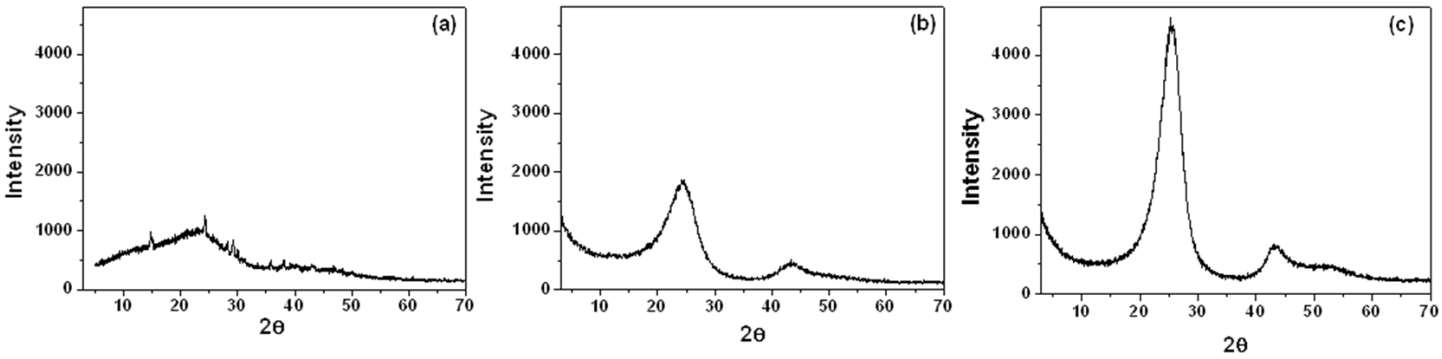


Fig. 2 :

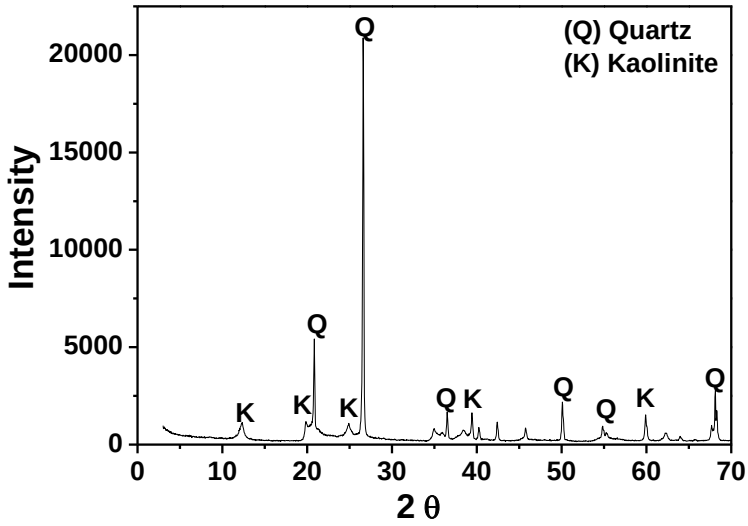
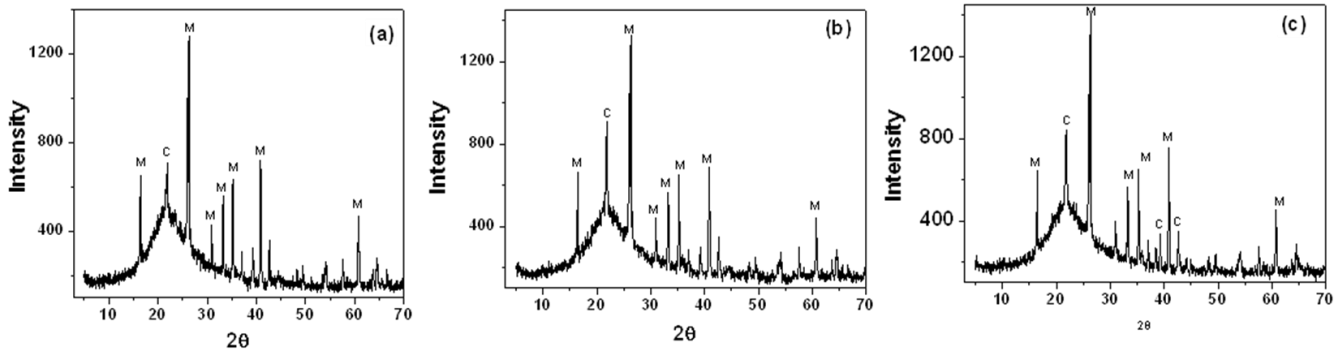


Fig. 3:



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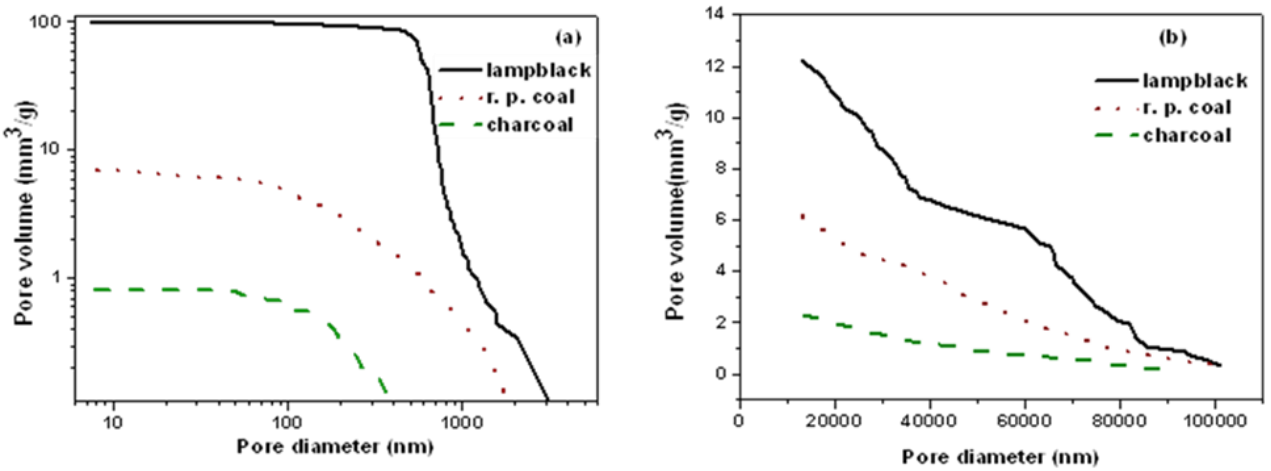
(a)
lampblack
r. p. coal
charcoal
Pore volume (mm3/g)
Pore diameter (nm)
100
10
1
10
100
1000
(b)
lampblack
r. p. coal
charcoal
Pore volume(mm3/g)
Pore diameter (nm)
14
12
10
8
6
4
2
0
0
20000
40000
60000
80000
100000

Fig. 5:

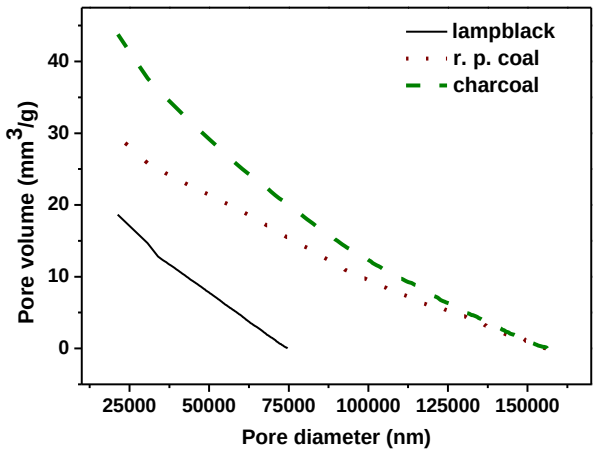
lampblack
r. p. coal
charcoal
Pore volume (mm3/g)
Pore diameter (nm)
40
30
20
10
0
25000
50000
75000
100000
125000
150000

Fig. 6:

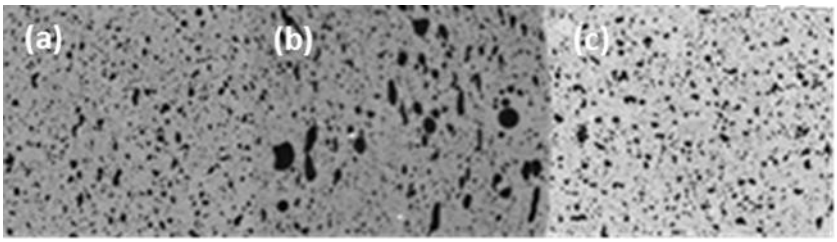

Fig. 7:

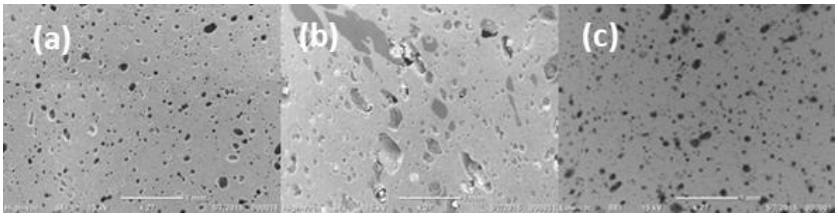
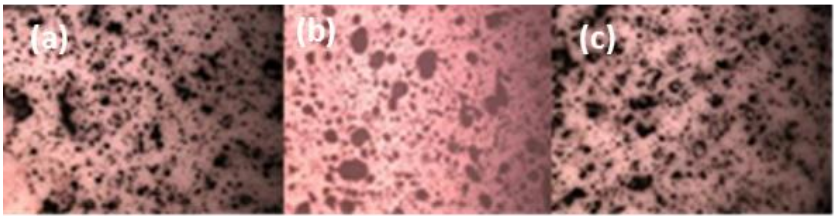
Fig. 8: