MANUFACTURE OF MACROPOROUS CERAMICS BY SPARK PLASMA SINTERING

Guillaume Jean[1], Valérie Sciamanna[1], Maurice Gonon[1], Maryse Demuynck[2], Francis Cambier[2]

[1]UMONS, Faculté Polytechnique, Service de Science des Matériaux, 56, rue de l'Epargne, 7000 Mons (Belgium)

[2] Belgian Ceramic Research Centre, 4, avenue du gouverneur Cornez, 7000 Mons (Belgium)

The aim of this research is to develop a new route for manufacturing macroporous ceramics characterized by a porosity level higher than 30% and highly interconnected pores, with sizes between 30 µm and 80 µm. Such porous materials could find applications in the fields of fluid transfer/mixing, catalysis or filtration. Porous materials made by this new method have a structure which differs from that obtained with the conventional techniques (replica technique, sacrificial template method, direct foaming) and a better ability to fluid mixing is expected. The process must be sufficiently versatile in order to tailor: i)- the porosity fraction within a large range (typically 30 to 80 %); ii)- the pore size distribution (single or multimode). The originality of this work is to "bridge" packing of basic ceramic "units" by sintering. The sintering must promote diffusion at interfaces between units with a limited densification to keep high porosity. Initially, the study was performed on alumina granules obtained by spray-drying. The consolidation of the material is carried out by conventional sintering techniques (free sintering, Hot Pressing) and by Spark Plasma Sintering.

INTRODUCTION

Because of their excellent properties (high temperature stability, high corrosion and wear resistance, possibility to functionalize surface, …), porous ceramics are used in many applications : molten metal and hot gas filtration (Acosta et al. [1], Li et al. [2]), fluid transfer or mixing, catalysis (Richardson et al. [3]), bone substitute materials (Burg et al. [4]), …

There are three main methods to produce macroporous ceramics (pore sizes larger than 50 nm): the replica technique, the sacrificial template method and the direct foaming method. The microstructure of the final material (porosity level, pore size, interconnectivity) is closely linked to the selected process (Studart et al. [5]).

The replica technique involves the impregnation of a porous polymeric sponge (usually polyurethane) or natural cellular structure with a ceramic suspension in order to produce a macroporous ceramic with the same morphology as the template. After drying, the template is removed by pyrolysis and the ceramic is finally densified by sintering. This technique leads to highly porous ceramics (porosity level between 40% and 95%), exhibiting open and interconnected pores with sizes from 200 µm to 3 mm [5].

The sacrificial template method is based on the incorporation of a sacrificial phase (pore former) in a ceramic suspension. The pore former can be natural or synthetic organics

(extracted by pyrolysis), volatile oils, … After removal of the sacrificial material, the ceramic is sintered. Porous ceramics made by this method exhibit better mechanical strength than that obtained with replica, but pore interconnectivity is lower. The final material presents porosity level between 20% and 90%, and pore sizes within the range of 1 µm to 700 µm [5].

In the case of direct foaming method, a gaseous phase is incorporated into a ceramic suspension through mechanical frothing or gas released by chemical reaction. The critical step is the stabilization of the air bubbles in the suspension. Foams can be stabilized with surfactants or surface modified particles. With this method, the ceramic just undergoes setting and drying before sintering. Highly porous materials, with porosity level between 45% and 95% and average pore sizes between 10 µm and 300 µm are obtained [5].

In this paper, we propose an innovative method to produce macroporous ceramics with highly interconnected pores, for applications in the fields of liquid transfer/mixing. The open porosity level should be higher than 30% and pore size between 30 µm and 80 µm. The criteria in terms of pore size distribution will depend on the operating conditions (pressure drop, fluid viscosity, …).

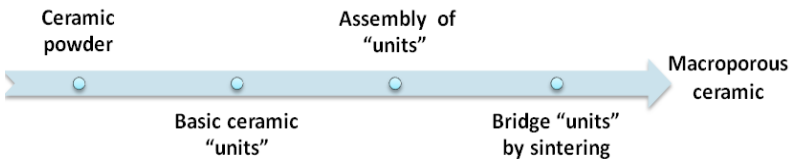
EXPERIMENTAL

Materials and methods

The method consists to "bridge" packing of basic ceramic "units" by sintering (Figure 1). The sintering must promote diffusion at interfaces between units with a limited densification to keep high porosity. The porosity results from the void spaces between granules. The ceramic "units" must have a fine-grained structure and the bridges between the units will develop at the level of powder grains.

The sinterability will be strongly linked to powder grain size which constitutes surface structure of ceramic "units". If the powder size becomes too coarse, it will not be possible to obtain a material with good mechanical properties by sintering. The maximum grain size that can be used to produce porous ceramics depends on sintering conditions (temperature, pressure, time) and the type of device used. For example, Nanko et al. [6] showed that SPS process, contrary to conventional sintering, allows the production of macroporous materials from alumina balls of very high diameter (about 2.8 mm) without any sintering additives.

FIGURE 1: Principle scheme of the method



Alumina granules, obtained by spray-drying of Alcan P172LSB alumina powder (d_{50} = 0.41 µm), are used as ceramic units. The assembly consists of granules packing into a uniaxial die pressing. The consolidation of the material is carried out by conventional sintering techniques (free sintering, Hot Pressing) and by Spark Plasma Sintering (SPS). SPS allows the manufacture of porous alumina ceramics at lower heating temperature, high heating

and cooling rates and short holding time than conventional techniques (Jayaseelan et al. [7], Wang et al. [8]).

The sintering parameters (cycles of temperature and pressure versus time) were studied to determine their influence on the microstructure and mechanical properties of the material.

The porous structure that may result of this process is the negative image than that resulting of sacrificial methods using organic beads.

Sintering techniques

Hot Pressing was carried out in an electrical furnace (Pyrox) under air. This equipment allows applying a uniaxial load from 0 kg to 42 kg. Granules (~ 9 g) were introduced in a die having a diameter of 21 mm.

The Spark Plasma Sintering equipment is the HPD10 model from FCT systeme GmbH (Max. pressing force = 100 kN). Granules (40 g) were introduced in a carbon die (diameter = 40 mm).

Characterizations

Granulometric and morphometric analysis were performed with a "QICPI" equipment from SYMPATEC society.

Compaction curves of the granules were obtained thanks to two INSTRON universal testing machines (Max load 10000 N and 500000 N) with a load rate of 0.5 mm/min.

Pore size distribution of the sintered materials was evaluated by mercury intrusion porosimetry (Micromeritics Autopore III 9410).

The microstructure of porous materials was observed by SEM analysis with a "JEOL JSM-5900 LV" equipment.

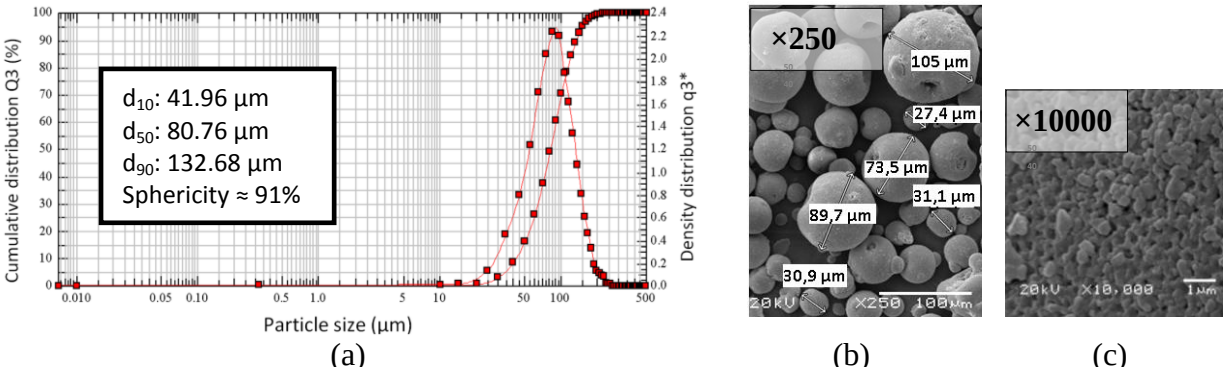
A "Belsorp-Max" instrument was used for specific surface measurement (BET).

RESULTS AND DISCUSSION

Characterization of the alumina granules

The grain size distribution is presented in figure 2a. A nearly single mode distribution (d_{50} = 80.76 µm) is obtained. The SEM picture (SEI mode) of these granules is shown in Figure 2b and agrees with these results. The fine-grained structure of the granules is highlighted on figure 2c. The granules present intragranular porosity (~ 50%) due to spray-drying process. The high specific surface area of 6.88 m^2/g corroborates this observation.

FIGURE 2: (a) Granulometric distribution and (b-c) SEM pictures (SEI mode) of the granules.



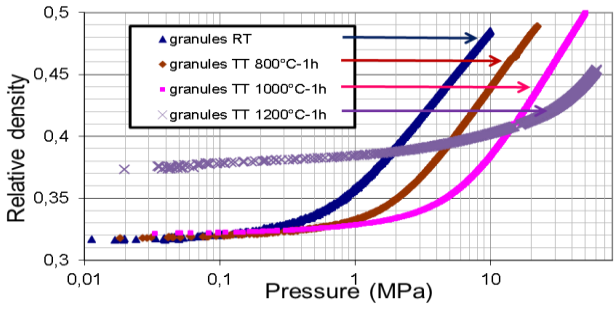
(a) (b) (c)

Manufacture of porous materials

Alumina granules were introduced in a uniaxial die pressing and sintering was performed at 1600°C, during 1h, without pressure (< 0.01 MPa). The final material is very friable and brittle. A pressure is required during sintering in order to activate diffusion through the contact points of the granules.

Compaction tests were performed on alumina granules. 20 g of granules were introduced in a 28.58 mm diameter stainless steel die. Figure 3 shows that above 0.2 MPa, the deformation of granules occurs and leads to porosity elimination. In order to improve their mechanical properties, granules were heat treated at 800°C, 1000°C and 1200°C for 1 hour. As a result, the applied pressure can be increased (figure 3).

FIGURE 3: Compaction curves of granules (room temperature and heat treated)



Two sintering treatments were initially applied: one at high temperature under low pressure (Hot Pressing), and another at lower temperature under higher pressure (Spark Plasma Sintering).

According to figure 3, the first test was performed under 1.3 MPa and the second one under 10 MPa, with the aim to limit the plastic deformation of the granules and thus to preserve the void spaces between the granules (intergranular porosity). Figures 4 and 5 show sintering cycles.

FIGURE 4: sintering cycles used with HP temperature and pressure applied versus time

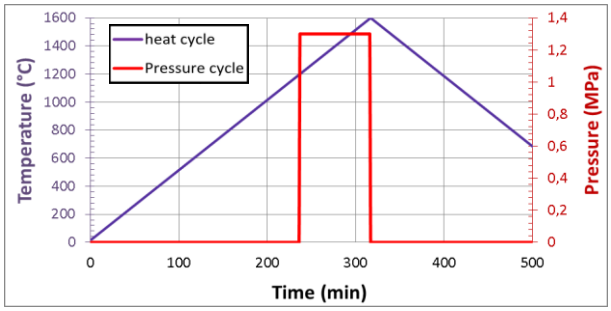
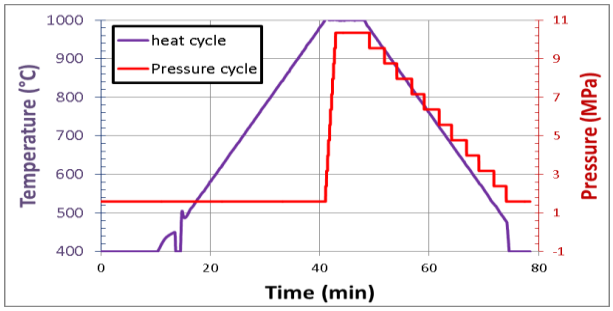


FIGURE 5: sintering cycles used with SPS temperature and pressure applied versus time



Consolidated compacts obtained by Hot Pressing and SPS are presented in figure 6 (a-d). The open porosity level of Hot Pressing sample is about 30% and the specific surface area is 0.37 m^2/g. The sample obtained by SPS has an open porosity level of 51.2%.

Pore size distribution of HP sample shows a monomodal distribution centered on 10 µm while SPS sample has a bimodal distribution (figure 7). The first mode is centered on 0.2 µm and the second one is centered on 7 µm. The pores with sizes around 7 and 10 µm correspond to the intergranular porosity. The second mode (0.2 µm) corresponds to intragranular porosity. According to figure 7, the sintering temperature needs to be limited in order to keep intragranular porosity. Moreover, lowering applied pressure promotes the rate and the size of the intergranular porosity.

FIGURE 6: SEM pictures of HP (a,c) and SPS (b,d) samples

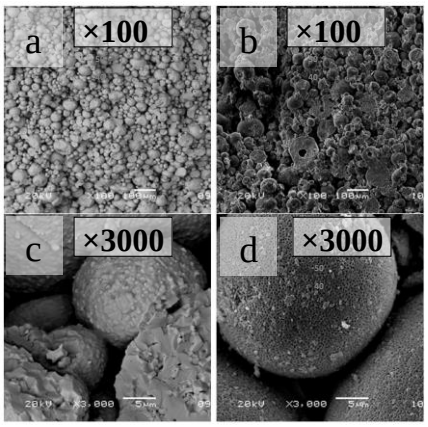
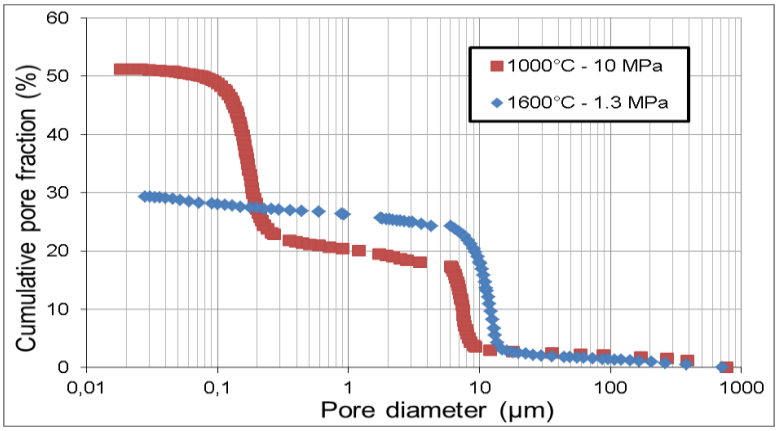


FIGURE 7: Pore size distribution of samples obtained by mercury intrusion porosimetry



By changing the sintering conditions (temperature, pressure …), it is possible to modulate the proportion of intergranular and intragranular porosities, or to keep only the intergranular porosity.

The application of a pressure substantially reduces the sintering temperature but has a negative effect on the intergranular porosity. Compared with Hot Pressing, SPS process allows to reduce significantly the temperature without increasing too much the pressure applied.

CONCLUSIONS AND OUTLOOKS

This paper presents a new technique for the manufacture of macroporous ceramics. The process involves consolidation of spray-dried ceramic granules by sintering. The investigation of the feasibility was performed with an alumina spray-dried powder. The consolidation was carried out by Hot Pressing or SPS. Macroporous ceramics with an open porosity of about 30% (Hot Pressing) and about 55% (SPS) were obtained. By changing the sintering parameters (temperature, pressure, …), a wide range of porosity can be obtained. With SPS, porous materials can be made at lower temperature. As a result, pore size distribution is bimodal with a contribution of intragranular and intergranular porosities.

The next step of this work will be to change granules characteristics: increasing the size of granules will rise the size of intergranular porosity (pore diameter between 30 and 70 μm). We will also examine different possibilities to increase the porosity level (adding sacrificial template within the granules or between them).

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