MANUFACTURE OF MACROPOROUS CERAMICS BY SPARK PLASMA SINTERING

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Summary

The aim of this work is to develop a new route for manufacturing macroporous ceramics characterized by a high porosity rate (over 30%) and highly interconnected open pores. In addition, this new route must lead to a good control of the pore size and also to a possible hierarchical distribution. These features open the door to several application fields as: mixing and fluid transfer, hot gas and molten metal filtration, bone substitutes, catalyst supports, etc.

The innovative aspect of the method consists in the "bridging" of controlled ceramic powder agglomerates by partial sintering. In the present work, alumina powder granules obtained by spray-drying are used as agglomerates. Sintering is performed by Hot Pressing (HP) or Spark Plasma Sintering (SPS). Influence of the sintering parameters (temperature, pressure, time) on the characteristics of the porous fraction and on the mechanical properties is investigated.

According to the sintering conditions, the macroporous ceramic obtained can contain two categories of pores: inter-granule pores (voids existing between the granules packing) and intra-granule pores (pores related to the internal structure of the granule).

HP performed at high temperature (1600°C) leads to materials exhibiting good mechanical performances but characterized by low porosity rates due to the almost full resorption of the intra granule porosity. On the contrary, applying low temperature sintering cycles is favorable to a high intra-granule porosity rate. However, in this later case, high sintering pressures are required in order to obtain a "good bridging" and then sufficient mechanical performances. Consequently, inter–granule porosity rate is poor. In any case, samples obtained by HP show limitations in terms of quality factor porosity rate x mechanical strength.

In comparison, SPS provides better quality factors than HP by allowing a lowering in the pressure and temperature required for a same consolidation state. Moreover, the short thermal treatment times enable to keep the initial fine-structure of the granules and then small intra-granule pores.

Introduction

Because of their excellent properties (high temperature stability, high corrosion and wear resistance, possibility of functionalized surfaces, …), porous ceramics are used in many applications: filtration [1, 2], fluid transfer or mixing, catalysis [3], bone substitute materials [4], … There are four main methods to produce macroporous ceramics (pore sizes larger than 50 nm): the partial sintering of powder compact, the replica technique, the sacrificial template method and the direct foaming method [5, 6]. The microstructure of the final material (porosity level, pore size, pore shape, interconnectivity) is closely linked to the selected process. However, these conventional techniques show limitations in terms of control of pore size and interconnections. Therefore the aim of this research is to develop a new route for manufacturing macroporous ceramics characterized by a porosity rate higher than 30% and highly interconnected pores.

The innovative aspect of this method consists in the “bridging” of controlled ceramic powder agglomerates packing by partial sintering. The success of the method lies on the mastering of the sintering parameters in order to achieve consolidation at the contact points of the granules packing while limiting the densification of the granules structure. The material resulting of this new method can exhibit a hierarchical interconnected porous network composed of up to three different levels of porosities: i) - the large voids between the agglomerates, ii) - the medium pores related to the internal structure of the agglomerates, iii) – the possible internal porosity of the powder grains (intragranular porosity).

In this work, alumina granules obtained by powder spray-drying have been used (Figure 1). Granules packing have been sintered by Hot Pressing (HP) but also Spark Plasma Sintering (SPS) in order to investigate if the usual advantages of this specific sintering process (lowering of the sintering temperatures and time [7, 8]) are of interest in the present case. 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.

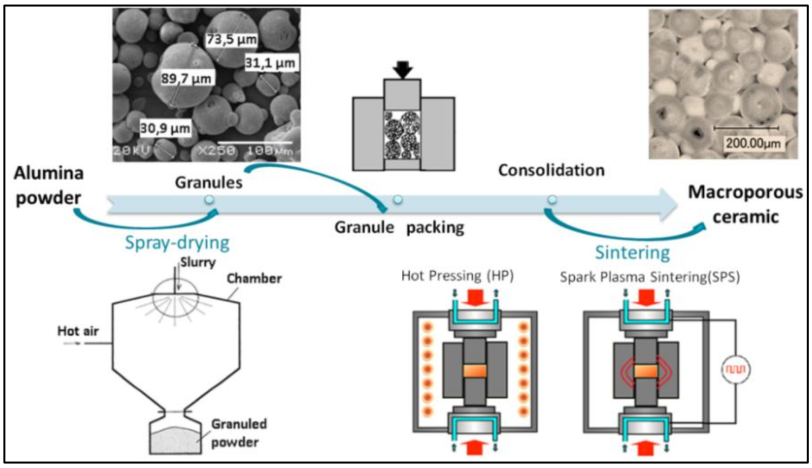

Figure 1: Principe pattern of the method

Experimental

Granulometric and morphometric analysis were performed with a “QICPI” equipment from SYMPATEC society.
A “Belsorp-Max” instrument was used for specific surface measurement (BET).
Compressive strength of the sintered materials was 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 and by a digital microscope (Keyence VHX Series).
Hot Pressing was carried out in an electrical furnace (Pyrox) under air with a die of 21 mm diameter.
The Spark Plasma Sintering equipment is the HPD10 model from FCT systeme GmbH with a die of 40 mm diameter.

Results and discussion

Powder agglomerates

Alumina granules obtained by spray-drying of Alcan P172LSB powder (d_{50} = 0.41 µm), are used as ceramic powder agglomerates. The size distribution of the granules is shown in Figure 2a. SEM pictures are in agreement with a d_{50} of about 80 µm for the granules (Figure 2b) and of about 0.4 µm for the alumina grains (Figure 2c). The high specific surface area is 6.88 m^2/g.

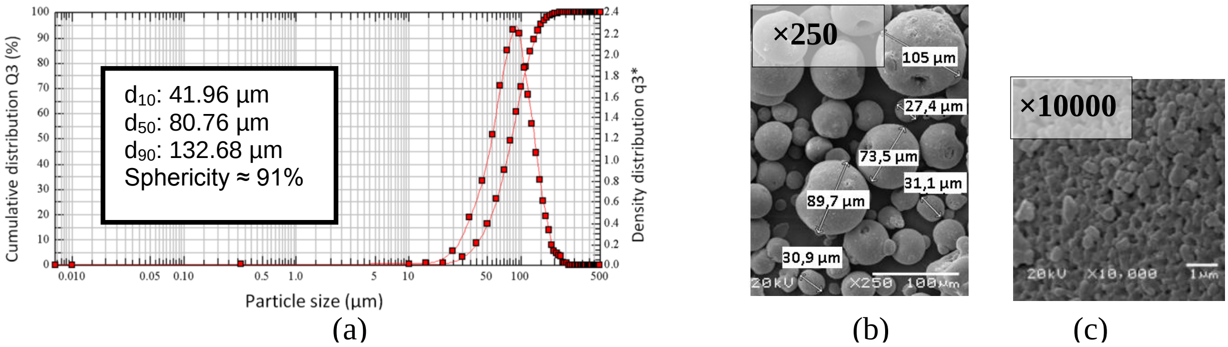

Figure 2: (a) Granulometric distribution and (b-c) SEM pictures (SEI mode) of the granules

Sintered materials

Figure 3 shows an example of porous structure obtained after SPS sintering at 1100°C under 10 MPa. The initial shape of the granules seems well preserved. At low magnification, the voids between the granules can be clearly observed but the sintering necks (between granules) are not visible.

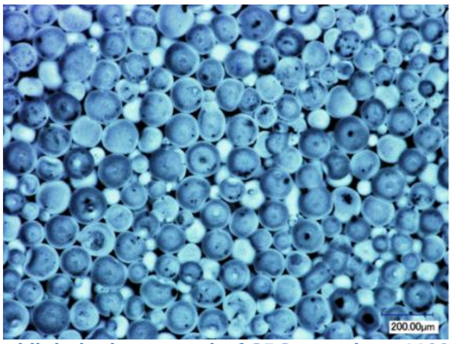
Figure 3: Picture (digital microscope) of SPS sample at 1100°C under 10MPa

Sintering at lower temperatures allows a better conservation of intra-granule porosity while sintering under lower pressure allows a better conservation of inter-granule porosity level and an increase of inter-granule pore size. Thus, by changing the sintering conditions (temperature, pressure,…), it is possible to modify the rate of inter-granule and intra-granule porosities, or to keep only the inter-granule porosity (Figures 4 and 5).

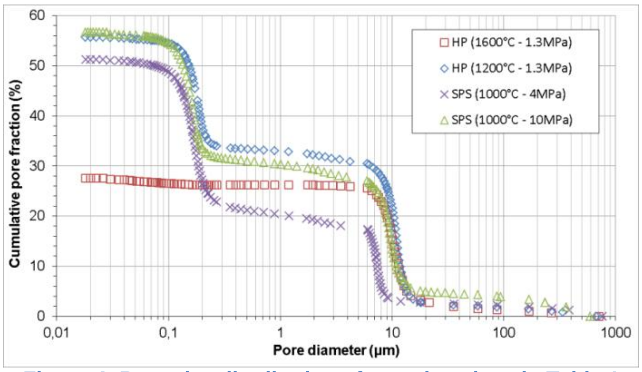

Figure 4: Pore size distribution of samples given in Table 1

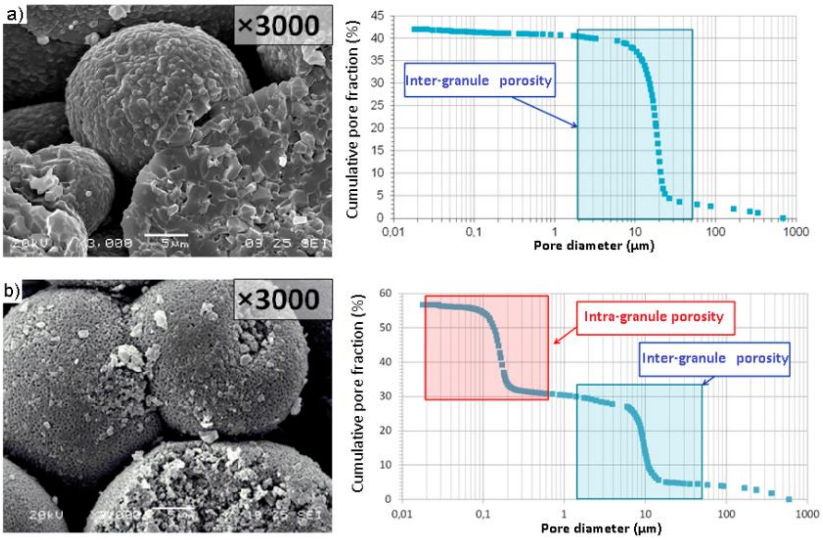

Figure 5: SEM picture and pore size distribution of a) HP sample at 1600°C under 0.2MP a) and b) SPS sample at 1000°C under 4 MPa)

SPS enables the manufacture of porous alumina ceramics at lower heating temperature and shorter sintering cycle time than HP for a same consolidation state (Table 1). Consequently, it provides a better quality factor porosity rate x mechanical strength than HP (Table 1). Moreover, the short treatment time resulting of the use of the SPS allows to keep the initial fine-structure of granules (Figure 5.b) and so intra-granule pores of smaller size.

Table 1: Porosity rate and compressive strength of samples obtained with different sintering conditions

	HP samples		SPS samples		
Temperature (°C)	1600	1200	1000		
Pressure (MPa)	1.3	1.3	4	8	10
Heating rate (°C/min.)	5		100		
Dwell temperature (min.)	120		7		
Porosity rate (%)	29	55.7	56.7	52.7	52
Compressive strength (MPa)	110	7	10	25	30

Conclusion

This paper presents a new processing route to manufacture macroporous ceramics. The method consists in the “bridging” ceramic powder agglomerates (of controlled geometry) by partial sintering.

At this stage of the work, alumina granules obtained by spray-drying are used as “ceramic agglomerates”. Macroporous ceramics with single- or bimodal pore size distribution were obtained. It was shown that by changing the sintering conditions (temperature, pressure,…), it is possible to modify the rate of inter-granule and intra-granule porosities, or to keep only the inter-granule porosity

SPS allows the manufacture of porous alumina ceramics at lower heating temperature and pressure than HP for a same consolidation state. This allows to a better versatility in the control of the pore size distribution. Moreover, SPS enables high heating and cooling rates and short holding time. The speed of the process allows to keep the initial fine-structure of granules and so pores of smaller size (intra-granule porosity in this case).

References

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