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A Structural Investigation of Sintering Conditions for Freeze-Cast Alumina Tubular Membranes

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Abstract

Different forming techniques can be used in the industrial production of tubular-shaped ceramics; these techniques include extrusion, slip casting and uniaxial pressing. Each of these methods has its own merits and drawbacks, but all of them result in final products with random porosity [1]. Freeze-casting, also called ice-templating, is an emerging technology to produce hierarchically porous ceramics with aligned and directional pores. Furthermore, the freeze-cast samples can exhibit a wide range of porosity (30 – 99 %), which can be controlled based on the suspension concentration and processing parameters [2].

Owing to the versatility of the process, the porous materials obtained with the freeze-casting technique have wide application potential in different technologies, such as supports for membranes in the petrochemical industry (oil/water separation [3] as well as in natural gas purification [4], solid oxide fuel cells (SOFC) and catalysts [5].

After the ceramic forming process, to transform the “green body” ceramic to a resistant solid structure, a heat treatment at high temperatures should occur [6]. A conventional way of sintering under ambient pressure is to heat the sample to an elevated temperature, holding this temperature for some time and then cooling it to room temperature. However, many authors have reported that heating ceramic specimens using slow heating rates and long dwell times can induce the phenomenon of exaggerated particle growth. In general, the mechanical strength of ceramic materials decreases significantly with increasing average particle size [7].

Special sintering step control processes are reported as strategies capable of refining the microstructure and improving the mechanical properties of the final product, compared to conventional sintering. Examples of variation in the ambient pressure sintering process are rate-controlled sintering, two-step sintering and the rapid-rate sintering method [8].

Rapid-rate sintering, also called fast-firing, consists in faster heating to the desired temperature, followed by subsequent cooling to room temperature without isothermal dwell [9]. In the two-stage sintering method, the first stage consists of heating the samples to a high temperature, when the material reaches an intermediate porosity, and the second stage consists of a rapid cooling to a lower temperature with an isothermal dwell at that lower temperature for a specified time. Fast cooling to a lower temperature suppresses particles growth and allows densification to occur at a lower temperature.

Although many studies reporting the use of sintering control in the heat treatment of ceramics have been published, this control has not yet been discussed for porous alumina obtained by freeze-casting. In this context, the use of the technique deserves analysis, mainly for comparison with the use of conventional sintering at ambient pressure.

The aim of this study is to investigate the influence of sintering control on the microstructure and mechanical properties of alumina samples obtained by freeze-casting. Two different heat treatment routes (rapid-rate sintering and two-stage sintering) were applied to the specimens and the results were compared with the alumina samples obtained by the conventional sintering technique.

Different sintering routes were used in this study, namely SR 1 (conventional sintering), SR 2 (conventional sintering), SR 3 (two-stage sintering) and, SR 4 (fast sintering). In the conventional sintering routes SR 1 and SR 2, the alumina samples were heated to 1500 °C and 1600 °C at a heating rate of 2 ºC/min, respectively, and kept constant at this temperature for 1 hour. For the two-stage sintering SR 3, the green samples were heated to 1600 °C at a heating rate of 2 ºC/min, then cooled down to the temperature of 1500 °C and held at this temperature for 1 hour. In the fast sintering route SR 4 the specimens were heated up to the maximum temperature of 1600 °C and then immediately, without isothermal dwell, cooled down to room temperature. The cooling rate for all samples was 5 ºC/min.

An analysis on the variation of the average particle diameter and average pore size of the outer surface of the green body and sintered samples showed that the conventional sintering routes exhibited the smallest average pore

size (0,66 µm and 0,33 µm for SR1 and SR2, respectively) and the largest average particle diameter among the analyzed samples (1,15 µm for SR1 and 1,26 µm for SR2). The final stage of conventional sintering of a solid solution is usually accompanied by rapid particle growth, as the driving forces for sintering and particles growth are comparable in order of magnitude. This phenomenon was more pronounced for samples sintered by the SR 2 route, since a higher temperature (1600 °C) was used compared to the SR 1 route (1500 °C). The use of higher temperatures in conventional sintering route SR 2 enhanced the diffusion of aluminum ion and thus the sample densification, leading to the formation of ceramics with smaller average pore size [10].

Among the sintering routes studied, the two-stage route was the one that resulted in samples with the smallest particle size (0,8 µm), suggesting the occurrence of a “kinetic window” in the second stage of the heat treatment. The "kinetic window" corresponds to the interval between the temperatures required for sintering and particles growth [11]. This phenomenon can be assessed by exploring the difference between the activation energy for sintering and the activation energy for particles growth. In the first stage of sintering (1600 °C) the temperature is high enough to reach the activation energy required for particle boundary mobility, allowing the alumina particles to form particles boundary network throughout the bulk. Subsequently, the samples are cooled to a lower temperature (1500 °C) where the activation energy is sufficient for particle boundary movement, resulting in samples densification. Thus, the samples cooling from 1600 ºC to 1500 ºC suppresses the particles growth by “freezing” the microstructure, at the same time, the retention step in 1500 ºC allows the sample densification.

The results of the samples flexural strength indicates that alumina samples heat treated using the conventional route SR 1 exhibited the lowest flexural strength (3,6 MPa) compared to the other samples (14,8 MPa for SR2, 6,1 MPa for SR3 and 6,2 MPa for SR4). This behavior can be associated with the large number of pores present in this sample and also with its larger average alumina particle size. Similarly, the alumina samples sintered with the conventional route SR 2 had a considerable improvement in mechanical properties, which can be associated with their significant reduction in open porosity.

For samples sintered by the SR3 route, the improvement in flexural strength can be associated with the reduction in open porosity and also with the microstructural refinement caused by the two-stage sintering. The SR 3 heating led to a microstructure with smaller particles, improving the mechanical strength of alumina samples.

The results of this work showed that the microstructure (average pore size, and average particle diameter) of alumina samples obtained by freeze-casting can be tailored by altering the sintering route. Depending on the application, the control of the pore network of a ceramic material is crucial for its performance. The structural parameters and mechanical properties of alumina samples obtained in this work suggest the potential of application of these supports in the manufacture of membranes for liquids and gases separations.

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