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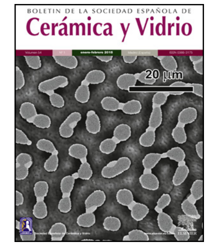

Review

Freeze-casting: Fabrication of highly porous and hierarchical ceramic supports for energy applications

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A B S T R A C T

The manufacture of structured ceramic porous support knows an important boom since more than a decade with the development of new shaping techniques. Among the most promising ones, the *freeze-casting* also called *Ice-Templating* allows the fabrication of ceramic parts exhibiting high porosity (>50%) and vertically aligned and hierarchically organized pores. Such structures were firstly conceived for biomedical applications like bone substitute and tissue engineering, but the distinctive features of freeze-cast structures have attracted the attention of diverse scientific fields, especially in high temperature ceramic-based energy production systems. Indeed, technologies like (a) Solid Oxide Fuel Cell (SOFC) and Electrolyser Cell (SOEC), (b) gas separation (O_2, H_2) by asymmetric supported membranes based on mixed ionic and electronic conductors (MIEC) or hydrogen-permeable metals, and (c) Catalytic Membrane Reactor (CMR) systems present a porous component in their physical structure. This latest, presenting a tortuous pathway for gas access and as a consequence, a high transport limitation, is known to be a limiting component for the operation at high flow streams that would enable to reach industrial target.

The aim of this paper is to give an overview of the freeze-casting ceramic shaping method and to show how its implementation could be useful for several energy applications where key components comprise a porous scaffold. A detailed presentation of the freeze-casting process and of the characteristics of the resulting porous parts is firstly given. The characteristic of freeze-cast parts and the drawbacks of conventional porous scaffolds existing in energy applications are drawn in order to highlight the expected beneficial effect of this new shaping technique as possible substitute to the conventional ones. Finally, a review of the state of the art freeze-cast based energy applications developed up to now and expected to be promising is given to illustrate the large perspectives opened by the implementation of the freeze-casting of ceramics for energy fields. Here we suggest discussing about the feasibility of incorporate freeze-cast porous support in high temperature ceramic-based energy applications.

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Artículo de revisión. Freeze-casting: Fabricación de soportes cerámicos con porosidad elevada y altamente estructurada para aplicaciones energéticas

Palabras clave:
Freeze-casting
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Porosidad jerárquica
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RESUMEN

La fabricación de soportes cerámicos porosos a través de nuevas técnicas de conformado es clave en el desarrollo de nuevos dispositivos en el sector energético y de la ingeniería química. La técnica de *freeze-casting* (colado por congelación) permite obtener componentes cerámicos muy bien sinterizados, con muy alta porosidad y poros con formas concretas. Los poros se orientan de manera que las propiedades de transporte de fluidos a su través son óptimos con respecto a otros tipos de estructuras porosas más irregulares. Concretamente, en el sector de la energía los soportes porosos se utilizan en aplicaciones tales como pilas de combustibles de óxidos sólidos o electrolizadores, membranas para la separación de gases, típicamente O_2 o H_2, y reactores catalíticos de membrana. En este artículo se revisan de manera exhaustiva los desarrollos en estos campos utilizando *freeze-casting* para el conformado de cuerpos porosos cerámicos.

Introduction

Freeze-casting process

Since more than a decade, the growing interest for the development of ceramic parts with hierarchical porosity exhibiting high mechanical properties led the scientific community to focus on alternative shaping technique to substitute the conventional foaming technique [1,2] and the use of pore former precursors. Indeed, they are quite simple to implement but the organization of the resulting porosity remains random in most of the cases. Even if new mathematical models for the representation of the tortuosity have been recently given [3], it remains very difficult to model such random microstructures. Among the emerging techniques, freeze-casting also known as ice-templating, is an attractive shaping method for the fabrication of highly porous and hierarchically organized ceramic structures. It consists of freezing generally by the bottom a ceramic slurry followed by the sublimation of the solvent by freeze-drying at both low pressure and temperature. The freezing of the ceramic slurry induces, in a repetitive pattern, the growing of vertical solvent crystals along the freezing direction and the associated rejection of ceramic particles between these crystals (Fig. 1). Finally, the as-obtained green body after solvent removal by freeze-drying is sintered for consolidation and the final freeze-cast sample exhibits hierarchically and vertically aligned porosity which is the replica of the original solvent crystals.

Slurry formulation and porosity control

A basic ceramic slurry formulation for the freeze-casting comprises at least 3 components and its fine tuning enables to tailor pore size and shape, and overall porosity [4–8]:

1. The first component is the ceramic powder. Its loading is usually in the range 10–50 vol% of the whole slurry [9]. A lower value would be problematic for the mechanical integrity of the final structure with very thin ceramic walls while a higher value would not be favourable for the growing of solvent crystals and the subsequent formation of connected porosity due to the low solvent content in the slurry. Several physico-chemical characteristics of the powder will influence the slurry stability like the grain size, the acidity or the basicity, the distribution size or the specific surface area. Nevertheless, since the first pioneering shaping experiments using freeze-casting, it has been shown that almost all ceramic materials but also some metals can be used and shaped: alumina [10], yttria-stabilized zirconia YSZ (Y_2O_3 doped ZrO_2) [11], titanium oxide [12,13], glasses [14–16], but also composite materials like NiO-YSZ [17], LSCF ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$)–CGO ($Gd_2O_3$ doped CeO_2) [18] and metals [19].
2. The second component of the slurry is the solvent. Up to now, literature details the use of three main solvents which are water [7,20], camphene [21–24] and tert-butyl alcohol [25–27], each one resulting in a different porosity shape. Water is the most common in the freeze-casting process due to the absence of chemical toxicity all along the process. The resulting porosity associated to the use of

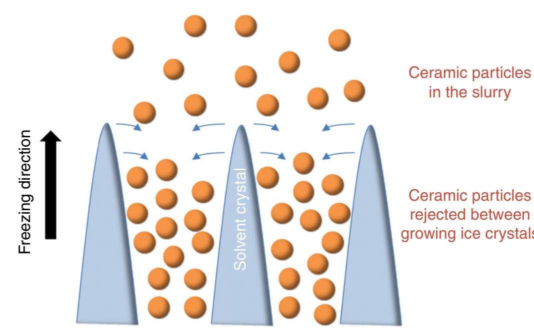

Fig. 1 – Sketch of the growing of ice crystals during the freezing step and the associated distribution of ceramic particles rejected between the ice crystals.