Available online at www.sciencedirect.com
SciVerse ScienceDirect
Acta Materialia 60 (2012) 4594–4603
Acta MATERIALIA
www.elsevier.com/locate/actamat

Particle redistribution and structural defect development during ice templating

Audrey Lasalle [a], Christian Guizard [a], Eric Maire [b], Jérôme Adrien [b], Sylvain Deville [a,*]

[a] *Laboratoire de Synthèse et Fonctionnalisations des Céramiques, UMR 3080 CNRS/Saint-Gobain, 84306 Cavaillon, France*
[b] *Université de Lyon, INSA-Lyon, MATEIS CNRS UMR5510, F-69621 Villeurbanne, France*

Received 21 November 2011; received in revised form 13 February 2012; accepted 14 February 2012
Available online 20 March 2012

Abstract

The freezing of colloidal suspensions is encountered in many natural and engineering processes. It can be harnessed, through a process known as ice templating, to produce porous materials and composites exhibiting unique functional properties. The phenomenon by itself appears simple: a solidification interface propagates through a colloidal suspension. We are nevertheless still far from a complete understanding and control of the phenomenon. Such lack of control is reflected in the very large scattering of mechanical properties reported for ice-templated ceramics, largely due to the formation of structural defects. Through systematic in situ investigations, we demonstrate here the role of suspension composition and the role of particle–particle electrostatic interactions on defect formation during ice templating. Flocculation can occur in the intercrystal space, leading to a destabilization of the solid–liquid interface and triggering the growth of crystals perpendicular to the main ice growth direction. This mechanism contributes significantly to the formation of structural defects and largely explains the scattering of compressive strength values reported in the literature.

Keywords: Freeze-casting; Ceramic material; Cellular solids; Mechanical properties; Defects

1. Introduction

The solidification or freezing of colloidal suspensions is commonly encountered in a variety of natural processes such as the freezing of soil and the growth of sea ice. It is also seen in everyday life and engineering situations such as food engineering, cryobiology, filtration and water purification. In materials science, the solidification of colloidal suspensions is finding applications in various processes such as the processing of particle-reinforced alloys and composites, and the processing of porous materials, usually referred to as ice templating or freeze-casting. This simple process, where a colloidal suspension is simply frozen under controlled conditions and then sublimated before sintering, provides materials with a unique porous architecture, where the porosity is almost a direct replica of the frozen solvent crystals. When a colloidal suspension is frozen unidirectionally, an initial transient regime is observed, corresponding to the initial nucleation and growth of the ice crystals. After this transient regime, a steady-state regime is established, where lamellar ice crystals grow steadily along the direction imposed by the temperature gradient.

Applications of ice templating have been demonstrated for bone substitutes [1], drug delivery [2], acoustic insulation [3], solid oxide fuel cells [4,5] piezoelectric materials [6] and ultrasensitive sensors [7]. The great interest in this versatile technique comes from the ease of implementation and the large range of porosity in terms of size (0.2–100 μm), volume fraction (30–90%) and morphologies [8]. It was also shown that the composition of the ice-templated suspensions influences the final microstructures through the nature of additives [8] or the quantity of dispersant [9]. For any application, a proper control of the structure is of critical importance. However, little is understood

* Corresponding author.
E-mail address: sylvain.deville@saint-gobain.com (S. Deville).

1359-6454/$36.00 © 2012 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2012.02.023

about the dynamics of structure formation mechanisms during freezing. The characteristics of the colloidal suspension are often critical to the behaviour of the system during freezing, both in technological and natural occurrences of colloid freezing, but have rarely been analysed or understood.

A wide range of compressive strength values is reported for ice-templated materials (Fig. 1) when tested along their freezing direction. The compressive strength is, of course, dependent on composition and is greater for porous titanium or zirconia than for calcium phosphate, but the data show substantial variation even within identical systems. Because of the unusual spread in the literature data, we performed a careful review of the methods and microstructures in the literature. Microstructural observations revealed that many of the weakest samples in the literature had structural defects oriented perpendicular to the ice growth direction, as shown, for example, in Figs. 2b or 8 of Ref. [10]. This orientation is the worst-case scenario for compressive strength measurements, and we believe that these defects are the root cause of many anomalously low-strength ice-templated materials found in the

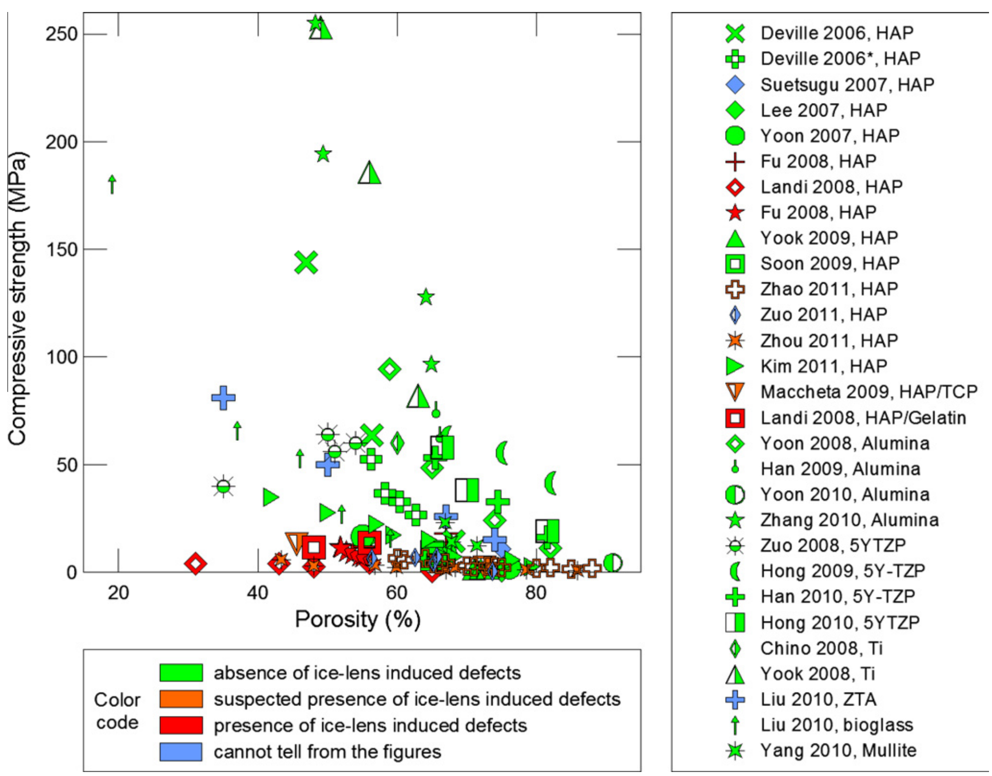

Fig. 1. Compressive strength vs. total porosity, data from Refs. [1,20–46]. The colour code indicates the presence or absence of crack-like defects perpendicular to the main ice growth direction, as identified from the corresponding published figures. Such defects result from the ice-lense formation during freezing. The presence of ice-lense-induced defects is systematically correlated to a low compressive strength. A low strength can also result from an excessively large pore size. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

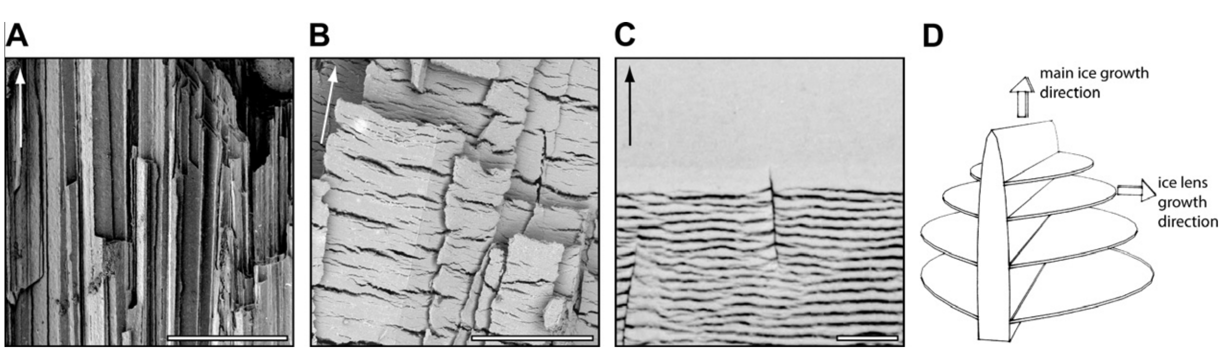

Fig. 2. Occurrence of ice lenses and corresponding microstructures. Typical microstructure (A) without and (B) with ice-lense-induced defects; (C) ice lens in 60 wt.% kaolinite clay suspension, frozen unidirectionally. The concentrated kaolinite is in white; the ice lenses are the dark horizontal stripes. Arrows indicate the main ice growth direction. Ice lenses grew approximately perpendicular to the main ice growth direction. (D) Schematic representation of the typical lamellar ice crystal growing along the temperature gradient and ice lenses growing perpendicularly. Scale bars: (a and b) 500 μm; (c) 2 mm.