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Feature article

Mechanical properties of hybrid composites prepared by ice-templating of alumina

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ABSTRACT

Ceramic-polymer hybrid composites are often designed for its high strength and low density. Ice-templating (freeze casting) is a promising method for preparation of such composites. However, the most of the reported mechanical properties were gained from a small volume of material. In this work 70 cm^3 of the lamellar composite with lamella length, up to 70 mm was prepared by ice-templating followed by polymer infiltration. The volume of ceramic (alumina) in starting suspensions was varied from 25 to 45 vol.% and the same manufacturing process was applied. The fracture toughness and flexural strength were determined on prepared beams from plates by loading in bending. The fractographic analysis conducted on the fracture surfaces and obtained mechanical properties demonstrated that an optimal strength/density ratio lies between 51 and 55% of alumina volume fraction. The density ranking from 2.6 to 2.8 cm^{-3} of these composites results in values of Weibull strength above 110 MPa.

1. Introduction

During the last decades, advanced ceramics materials have many new technological applications due to it low density and high strength. Unfortunately, ceramics are in general brittle, so consequently, there has been a strong emphasis on understanding the mechanical properties of ceramics and improving their strength, toughness and contact damage resistance [1]. Even though the fracture toughness of advanced ceramics has been improved, the pure ceramic materials are still brittle and cannot be deformed plastically [2]. Ceramic-polymer composites can combine high strength, toughness; mechanical properties are based on internal microstructure. High ceramic contents generally increase flexural strength but also the total density is rising. Toughening mechanisms such as crack bridging [3] are often implemented to improve toughness, but the common drawback is the strength reduction. Layered ceramics is one design of structural ceramics for enhanced fracture toughness, reliability, and mechanical strength [4]. One example is multilayer alumina–zirconia system with either internal or external compressive residual stresses [5–7]. The layered ceramics can change of the crack direction when a crack propagates through alternating layers under different angels were described, and the internal compressive stresses proved to be advantageous in terms of both strength and toughness. Natural composites are a source of inspiration because many natural materials like bone, wood, and nacre have highly sophisticated structures with complex designs whose properties far exceed expectation from a simple mixture of their components [8].

One approach to creating bio-inspired composite materials is to create the internal lamellar structure by ice-templating [9]. Ice-templating, also known as freeze-casting, is a complex process, where many parameters can affect the results: formulation of the suspension (nature of solvent, particle distribution of starting powder, solid loading, binder, surfactant, nature of the materials, pH, viscosity, etc.), and freezing conditions (setup temperature, cooling rates, etc.) [10]. Despite its complexity is ice-templating technically relatively simple, inexpensive, and very versatile method to fabricate bulk bio-inspired porous scaffolds. The basic idea of ice-templating is to obtain porosity replicating of ice crystals, by freezing suspension and subsequently removing the ice crystals by sublimation of the solvent (commonly water). The solid phase in the suspension can be any kind of particles from ceramic, metal, or polymer materials, but ceramic particles are the most used. Porous ceramic scaffolds can be obtained by controlled freezing of ceramic suspensions, which is followed by sublimation of water and sintering (densification). During ice-templating particles in ceramic suspension are ejected from the moving solidification front and pile up between growing ice crystals creating multilayer porous

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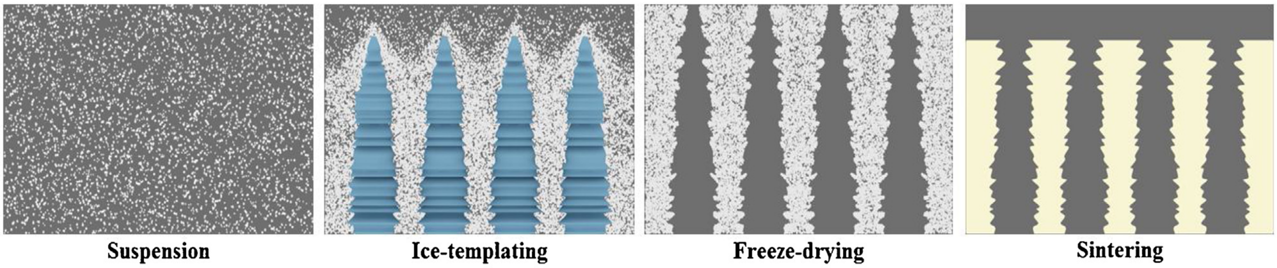

Fig. 1. Typical processing steps of the ice-templating process.

ceramic structures with well-defined architecture. The process is based on the very low solubility of the second phase in the solvent, which ensures its segregation during solidification [10].

Although there is growing interest in ice-templating method over the last decade, the first observation of the formation of cellular structures upon freezing goes back to over a century ago. The idea of using segregation to obtain specific architectures was firstly pursued by Mahler et al. [11] to obtain fibres from froze silica gels. Processing of macroporous ceramic structures was firstly reported in 2001 by Fukasawa et al. [12]. Over the past 15 years, ice-templating has been widely applied to various classes of materials, in particular ceramics to produce macroporous samples. Typical processing steps of ice-templating are shown in Fig. 1, and the process shows the ability to use a wide variety of nano- to macro-scaled powders and various dispersion liquids (solvents). The composition of suspensions and process parameters, often inter-reliant, affect the final scaffold because it is hard to understand relationships of various parameters. Only a few of these complex relationships have been investigated and published until now [10,13]. Furthermore, different additives (to aqueous ceramic suspension) can change the structure of ice-templated scaffolds from lamellar to cellular; roughness and density of inter-lamellar bridges can be adjusted. Addition of 10 wt.% of sucrose in citric water with pH = 2.5 resulted in a cellular structure with very smooth ceramic walls; 4 wt.% of ethanol addition resulted in a lamellar structure with smooth roughness; 4 wt.% of sodium chloride addition resulted in a sharp-faceted lamellae surface; and 4 wt.% sucrose addition promoted a lamellar structure with microscopic roughness [14].

The aim of this work is to find the impact of ceramic loading on mechanical properties in alumina-epoxy composites prepared by ice-templating. Relatively large-scale samples were prepared, with lamellae length up to 70 mm, to demonstrate the applicability of ice-templating for the preparation of bulk low-density composites. The volume of alumina powder loading in suspension was 25, 30, 35, 40, and 45, vol.%, and ice-templating conditions/parameters remained constant. Therefore, the materials under investigation reflect also defects introduced by ice-templating of up-scaled samples compare with the literature [9]. Hybrid composite materials target the application where low weight to strength ratio is expected. An important factor for an application is the reliability of the final product and investigated mechanical properties reflect the behaviour of hybrid ceramic composites with various alumina content, prepared at same ice-templating conditions.

2. Materials and methods

2.1. Suspension composition

Water-based suspensions for ice-templating were prepared from alumina powder AES-11C (Sumitomo, Japan) with average particle size $D_{50} = 390$ nm. Suspensioní s solid loading was varied from 25 to 45 vol.% of Al_2O_3. Typical composition of suspension with 45 vol.% of alumina is shown in Table 1.

For improving mechanical properties of ice-templated scaffolds and controlling the micro roughness of lamellae surface several additives were added to basic suspensions (sugar, dextrin, maltodextrin and starch). The 3 wt.% sugar appears to be the best additive, in terms of formed microstructure of ice-templated green samples with sufficient mechanical properties necessary for manipulation.

2.2. Ice-templated alumina body

Alumina wafers with controlled lamellar structure and dimensions of $70 \times 80 \times 15\,mm^3$ were prepared by ice-templating. The optimal initial temperature of the cooling plate, for our ice-templating vessels design, was set up at −5 °C. This starting temperature was used during all ice-templating experiments. The cooling rate (for this stage of experiments) was chosen so that the temperature of the cooling plate was decreased by 5 °C every 20 min down to −35 °C. This cooling rate enables lamellae formation in the whole volume of wafers for all suspensions with various solid loadings. Samples were kept at −35 °C for 1 h to ensure complete freezing and to balance the temperature throughout the wafers. The freezing step was followed by sublimation of ice crystals in a vacuum chamber with a pressure of approximately 10 Pa for 24 h with a gradual temperature increase up to 40 °C, this procedure avoids damage of the lamellar structure of ceramic bodies by ice melting or achieving sugar glass transition temperature. Therefore, it was necessary to moderate the heat transfer during the freeze-drying period, the implementation of freeze-drying in the whole process of the hybrid composite preparation is shown in Fig. 2.

2.3. Sintering

Heat treatment (annealing) was carried out at 800 °C for 1 h in an air atmosphere with heating rate 5 °C/min to achieve complete burn off the organic compounds and separators used for ice-templating. Sintering was performed at 1550 °C for 1 h in an air atmosphere. The heating rate was set to 5 °C/min and cooling rate from the sintering temperature was set to 10 °C/min to avoid thermal shock and cracking.

2.4. Hybrid ceramic composites

Sintered alumina wafers with lamellar structure were placed in a silicone mould and embedded in the polymer resin. The whole assembly was put into the vacuum chamber and evacuated for 20 min to ensure penetration of the epoxy resin into all free spaces of ceramic wafers. After evacuation step, infiltrated ceramic wafers were left at room temperature for 24 h to let the resin harden. The final hybrid composites Al_2O_3–epoxy resin were removed from the mould and neatened. A basic criterion for successful preparation of hybrid ceramic composites is the complete filling of empty space in the ceramic scaffolds. Therefore, the viscosity of the polymer is a crucial factor for the preparation of bubble free composite.

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