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SUPPLEMENTARY INFORMATION

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Strong, Tough and Stiff Bioinspired Ceramics from Brittle Constituents

Florian Bouville [1,2], Eric Maire [2], Sylvain Meille[2], Bertrand Van de Moortèle [3], Adam J. Stevenson [1], Sylvain Deville [1*]

[1] Laboratoire de Synthèse et Fonctionnalisation des Céramiques, UMR3080 CNRS/Saint-Gobain, Cavaillon, France

[2] Université de Lyon, INSA-Lyon, MATEIS CNRS UMR5510, Villeurbanne, France

[3] Laboratoire de Géologie de Lyon, Ecole Normale Supérieure de Lyon, Lyon, France

* *Corresponding author. E-mail: sylvain.deville@saint-gobain.com*

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Methods

Suspensions preparation

All the constituents where added in distilled water and then ball-milled for 24 hours, except the alumina platelets that have been added 3 hours before the end of the cycle to avoid any excessive breakage by the milling media. A rheology modifier (Carbopol ETD 2691) was added to form a soft gel (yield stress suspension) in order to avoid any settling of the large particles during the freezing and thus ensuring the homogeneity of the sample throughout the specimen.

Freezing under flow

To obtain dense structures by pressing the porous sample obtained after ice templating, further control of the crystal growth is needed to obtain parallel crystals over large dimension. Indeed, the crystals are vertically aligned in the direction of the temperature gradient, but because nucleation occurs at different spots, different domains of lateral orientation are present[1]. To induce long range order of the crystals, different strategies have been developed[2]. Here we use a method in which we let the slurry flow on the cooling plate where freezing occurs, leading to a second perpendicular temperature gradient during the freezing. The crystals thus guided in two directions are all parallel, and we repeatedly obtain sample of relatively large dimensions (a few centimeters) with aligned crystals. A 1°C/min cooling rate is used for all suspensions.

Field Assisted Sintering (FAST)

The equipment used for sintering is a HPD25 device from FCT System GmbH. The sample is compressed between two graphite punches inside a cylindrical graphite die (20 mm diameter). The heating of the sample is obtained by injecting electrical current through the

punches. This leads to a very high heating rate and the presence of the electrical current accelerates the sintering. The FAST device is known to allow sintering ceramics and metals at lower temperature than conventional sintering resulting in finer microstructures due to the applied pressure. As described, a system composed of alumina platelets (7 µm diameter, 500 nm thickness), alumina nanoparticles (diameter around 100 nm), and a silica-calcia liquid phase (diameter around 20 nm) have been used. The molar composition of 75:25 (SiO_2:CaO) have been chosen because of its high wettability of alumina surface and a relatively high melting point[3–5], between 1300°C and 1500°C. The densification behavior of different compositions is described in figure 1B. The linear shrinkage rates were obtained from the movement of the die during the sintering. All the relative density of the sample prepared here are above 98% after sintering at 1500°C with 100°C/min heating rate and a constant applied pressure of 100 MPa.

Microstructural characterization

SEM pictures were taken on uncoated samples by a Supra 55 microscope (Zeiss) and a ZEISS NVision40. The pictures were taken at low acceleration voltage (typically 1 kV) to avoid any charging effects.

Preparation of SENB and bending samples

Disk shaped samples with 20 mm diameter were obtained after sintering. Beam shaped specimens with dimensions around 14x2x2 mm^3 where then cut from the sintered disks. The beams for bend testing where mirror polished and beveled to avoid any crack departure from the sides. SENB test specimen were first notched with a diamond saw of 200 µm thickness and then the bottom of each notch was sharpened by repeatedly passing a razor blade with diamond paste (1µm). Using this method, the final notch radiuses were always below 40 µm. At least 5 specimens were tested for each composition and setup. Mechanical testing were

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carried out on an INSTRON machine. Values were determined by monotonically loading the specimens to failure at a constant displacement rate of 1 μm.s^{-1}. The beams deflections were measured by a linear variable differential transformer (LVDT).

Determination of crack length

The indirect method usually used to determine crack length is based on complaisance evolution during cyclic loading. However in our case this method has proven to be unusable here because the repeated cycles applied induce small crack propagation, even at low stress. We instead used a simple equivalence between complaisance and crack length on an SENB test. The complaisance were calculated thanks to the relation $C=u/f$, where u and f are the displacement and force at each point after departure of a crack, respectively. Then the crack length was recursively calculated with (1).

$$a_n = a_{n-1} + \frac{W-a_{n-1}}{2}\frac{C_n-C_{n-1}}{C_n} \qquad (1)$$

where W is the thickness of the specimen, a and C respectively the crack length and complaisance calculated at the n and n-1 step.

Details on J-integral calculation

To assess the different mechanisms that occurred during the stable crack propagation (crack length< 400 μm), a J-integral versus crack extension has been calculated as the sum of elastic and plastic contribution, a method already used to measure the properties of bone[6,7] and similar structures[8,9]. The elastic contribution J_{el} is based on linear-elastic fracture mechanics ($J_{el}=K_{IC}^2/E'$),

The plastic component J_{pl} is calculated with the relation (2):

$$J_{pl} = \frac{1.9A_{pl}}{Bb} \qquad (2)$$

where A_{pl} represents the plastic area under the load-displacement curve, B the specimen lateral dimension and b the uncracked ligament.

A geometric mean of the local stress intensity factor leads to an equivalent stress intensity factor (3).

$$K_{JC} = \sqrt{\left(J_{el} + J_{pl}\right) E} \quad (3)$$

with K_{JC} the back calculated stress intensity factor, J_{el} and J_{pl} elastic and plastic contribution of the J-integral and E the young modulus of alumina.

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