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# Nacre-like alumina composites based on heteroaggregation

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## Abstract

High strength and high toughness are usually mutually exclusive in materials. Among all material classes, ceramics exhibit a high stiffness and strength, but they present a limited plastic deformation, which results in a moderate toughness. However, tough ceramics have been obtained using anisotropic particles organized in a 'brick and mortar' microstructure, inspired by the structure of the natural nacre. Here, we propose to build nacre-like ceramic composites from colloidal suspensions using heteroaggregation of particles. Two different shaping processes are used: direct settling of suspensions or freeze-granulation. After sintering, in both cases, the platelets alignment is very good, close to that of platelets in natural nacre, with a slightly better one noted for direct settling. Despite a better platelet alignment, the toughness is lower than in previous studies showing that further improvement of the interfacial phases present in the material must now be considered to reinforce its mechanical behavior.

*Keywords:* Nacre-like composite; Heteroaggregation; Platelet alignment; Settling; Freeze-granulation

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## 1. Introduction

Nacre, found in several species of seashells, is a natural material composed of 95vol.% of aragonite (CaCO<sub>3</sub>) and 5vol.% of organic materials (proteins), that exhibits a toughness at least three orders of magnitude higher than those of calcium carbonate [1, 2, 3]. The high

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5 toughness of nacre is conferred by its 'brick and mortar' hierarchical architecture composed  
6 of layers of inorganic and organic materials [2]. The alignment of inorganic bricks in nacre  
7 is remarkable, and has been shown to induce several toughening mechanisms [4]. In the last  
8 two decades, natural materials like nacre have been replicated to obtain brick and mortar  
9 composites with mechanical properties greater than those of their elementary constituents  
10 [1, 5, 6, 7].

11 To build brick and mortar materials, the control of platelet-shape particles alignment is  
12 critical [8]. To control this alignment, different techniques have been proposed [9] such as  
13 magnetic fields [10, 11], gravitational settling [12] or ice-templating [7, 13]. Most of these  
14 processes use colloidal suspensions which have to be well-dispersed. For that purpose, the  
15 use of organic binders or dispersants is common, which often imposes a debinding phase  
16 before sintering. An alternative, that avoids the introduction of organic compounds in the  
17 microstructure, is to take advantage of surface charges present at the surface of particles in  
18 aqueous suspensions. Previous studies have shown that the heteroaggregation of particles  
19 under the action of the electrostatic forces represents a promising method to control the  
20 arrangement of particles [14, 15, 16].

21 Here, a nacre-like ceramic composite is elaborated without adding dispersant or carbonated  
22 additives unlike in the previous studies. Its mechanical properties are compared with the  
23 properties reported by Bouville *et al.* [7]. A similar composition is used: crystalline alumina  
24 platelets are used as bricks, and silica nanoparticles are incorporated to form a viscous phase  
25 during sintering acting as the mortar phase. Alumina nanoparticles are also added to create  
26 mechanical anchorage between platelets and reinforce the materials. After consolidation by  
27 sintering the desired structure of the composite is thus composed of layers of micron-size  
28 platelets separated by a silica vitreous phase and alumina bridges. In order to avoid carbon  
29 in the composition to better control the composite color, the vitreous phase formed in this  
30 study does not contain calcium carbonate and thus is different from that reported in [7].

31 Here, we show that such nacre-like ceramic composites can be obtained without addition of  
32 organic additives using simple shaping methods. Brownian dynamics simulations and exper-  
33 iments have indeed shown that using the heteroaggregation between the alumina platelets  
34 and the silica nanoparticles in aqueous suspensions yields at the same time a compact ar-  
35 rangement of the platelets and a good spatial distribution of the silica in between them [16].

36 To shape the composites, two simple methods are used. The first one consists in the natural  
37 settling of suspensions and the second in freeze-granulation and lyophilisation. A thermal  
38 treatment is then applied to consolidate green samples obtained from both shaping methods.  
39 Observations of sintered microstructures and measurements of platelets alignment are per-  
40 formed. Finally, mechanical properties of elaborated composites are determined to establish  
41 a relationship between the microstructure and the mechanical performance.

## 42 **2. Methodology**

43 The alumina platelets ( $\text{Al}_2\text{O}_3$ ) used in this study are supplied by Merck, Germany (sap-  
44 phire alumina RonaFlair® White Sapphire,  $d_{50} \sim 7 \mu\text{m}$ , purity  $\geq 99\%$ ). Silica nanoparticles  
45 ( $\text{SiO}_2$ ) with a mean particle diameter of 25 nm are obtained from a commercial aqueous sus-  
46 pension of Ludox® TM50 supplied by Grace Davidson, United States. High purity  $\alpha$ -alumina  
47 nanoparticles of about 100 nm ( $\alpha\text{Al}_2\text{O}_3$ ), used as reinforcement, are from Taimei Chemical  
48 Company, Japan (TM-DAR, Taimicron, purity  $>99.99\%$ ).

49 The zeta potential of particles as a function of pH is measured using Acoustosizer IIs from  
50 Colloidal Dynamics. For the measurements, aqueous suspensions are prepared with a solid  
51 loading of 1wt.% in osmosed water and pH is adjusted using HCl and NaOH.

52 The mixed suspensions, used for shaping the nacre-like ceramic composites, are prepared by  
53 adding the various constituents in osmosed water and are deagglomerated by an ultrasonic  
54 treatment (300 W, 30 s, pulse on 3 s, pulse off 1 s). The volume ratio between the various  
55 components  $\text{Al}_2\text{O}_3/\alpha\text{Al}_2\text{O}_3/\text{SiO}_2$  is fixed at 94.6%/3.6%/1.8%.

56 Sedimentation tests are performed for suspensions prepared with a solid loading of 3vol.%.  
57 For that, suspensions are prepared and introduced in closed tubes, and allowed to settle.  
58 When all suspensions are settled, the sediment heights are measured. The suspensions are  
59 also characterized by environmental scanning electron microscopy (SEM) on a Quanta FEG  
60 450 from FEI. Droplets of suspensions are deposited directly on the specimen holder. Drying  
61 is performed in real time during the observations in the microscope.

62 In this study, two methods are applied to shape the composites:

63 - The first method consists in obtaining an alumina-based green part in the shape of a pellet  
64 (diameter 25 mm with a thickness comprised between 5 and 13 mm) by settling the suspen-  
65 sions directly in a rubber silicone mold. The water excess is eliminated after 24 hours of

66 settling and, before demolding, samples are left for natural drying during 24 hours.

67 - The second method consists in obtaining powders from the elaborated suspensions, using  
68 freeze granulation and freeze-drying. Freeze granulation is performed with a freeze granulator  
69 LS-2 from PowderPro AB. Air is used as the atomization gas. The atomization conditions are:  
70 air relative pressure of 0.3 bar and suspension flow rate of 33.5 mL/min. The rotation speed  
71 of the magnetic stirrer in the liquid nitrogen is set to 370 rpm. After granulation, the frozen  
72 ganules are freeze-dried in a Christ Beta-1-8-LDplus under a final vacuum of  $10^{-3}$  mbar.

73 For both shaping methods, the same thermal treatment stage is used. Pellets or powders  
74 are sintered using Field Assisted Sintering (FAST, Dr. Sinter Model 825, SUGA, Japan),  
75 deriving benefit of the high heating and cooling rates provided (heating rate:  $100^{\circ}\text{C}/\text{min}$  and  
76 cooling rate:  $50^{\circ}\text{C}/\text{min}$ ). Graphite dies are used for all temperature profiles and a maximum  
77 temperature of  $1400^{\circ}\text{C}$  and a pressure of 100 MPa are reached. A dwell of 5 min in these  
78 conditions is performed before cooling.

79 For both upstream shaping methods, dried samples are characterized by SEM (LEO 1530 vp)  
80 before and after thermal treatment to observe the distribution of particles and the alignment  
81 alumina platelets in the material.

82 The alignment of platelets in the sintered samples is characterized by X-ray diffraction (XRD),  
83 using a Bruker D8 "Discover" diffractometer equipped with a copper target ( $\text{Cu } K_{\alpha 1}$  radia-  
84 tion). A parabolic mirror coupled with a two-reflection Ge (220) monochromator provides a  
85 monochromatic and quasi-parallel X-ray beam. Diffracted X-ray are collected with a linear  
86 position sensitive detector covering a  $2^{\circ}$  angular range with  $0.01^{\circ}$  resolution. The sintered  
87 samples are positioned on a 3-circle goniometer allowing to precisely align the sample surface  
88 with respect to the incident beam. XRD pole figures are recorded from the (0012) planes  
89 of the corundum structure of  $\text{Al}_2\text{O}_3$ . A pole figure displays the intensity diffracted from a  
90 selected set of planes in the hemisphere above the sample and is commonly represented in a  
91 polar plot (stereographic projection) where the angle along the circumference correspond to  
92 the rotation about the surface normal ( $\Phi$  angle), and the radius is the inclination angle of  
93 the crystallographic planes ( $\Psi$  angle). In the present case  $\Phi$  are scanned from  $-180^{\circ}$  to  $180^{\circ}$   
94 with  $5^{\circ}$  steps, whereas  $\Psi$  has been scanned from to 0 to  $80^{\circ}$  with  $1^{\circ}$  steps.

95 Finally, to measure the mechanical properties of the obtained materials, Single Edge Notched  
96 Beam (SENB) and bending tests are carried out. Rectangular beams of dimensions  $B=2\text{ mm}$

97 (thickness),  $W=2.5$  mm (width) and  $L=20$  mm (length) are cut from the sintered pellets.  
 98 The material is solicited perpendicularly to the platelets direction  $ie$  along  $W$ . Three points  
 99 bending (3PB) configurations are used following the ASTM E1820-E01 standard [17] to  
 100 evaluate both the flexural strength of the material and its fracture toughness in terms of  
 101 crack-resistance curve (R-curve). All tests are carried out using a Shimadzu AGS-X ma-  
 102 chine equipped with a 10 kN load cell and using a Linear Variable Differential Transformer  
 103 (LVDT) with a precision of  $1\ \mu\text{m}$  to measure the beam deflection. For each set-up, 4 samples  
 104 are tested.

105 The flexural strength of the material is determined from un-notched and chamfered speci-  
 106 mens. In another hand, SENB specimens are first notched using a  $300\ \mu\text{m}$  diamond blade.  
 107 The bottom of the pre-notch is sharpened using a razor blade with  $1\ \mu\text{m}$  diamond paste. Final  
 108 notches with radius of curvature between  $15$  and  $20\ \mu\text{m}$  are obtained to favour stable crack  
 109 propagation for the R-curves measurements. In both configurations, the specimen are loaded  
 110 monotonically at a constant displacement rate of  $1\ \mu\text{m}\cdot\text{s}^{-1}$  with a support span ( $S$ ) of  $16$  mm.  
 111 The compliance method ( $C = \frac{d}{F}$ ) is used to determine the beginning of the crack propagation  
 112 and to determine the projected crack length during SENB tests using the following recursive  
 113 equation :

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

114 with  $a$  and  $C$  the crack length and the compliance respectively, calculated at the  $n$  and  
 115 the  $n - 1$  steps. Non-linear elastic fracture mechanisms analysis is used to determine the  
 116 crack-resistance curves of the material ( $R$ -curves).  $R$ -curves are measured in terms of the  
 117  $J$ -integral as a function of the crack extension in order to capture both intrinsic and extrinsic  
 118 mechanisms acting as crack-arresters. The  $J$ -integral is computed taking into account an  
 119 elastic ( $J_{el}$ ) and a plastic ( $J_{pl}$ ) contribution :  $J = J_{el} + J_{pl}$ . The elastic contribution  $J_{el}$  is  
 120 calculated using classic linear-elastic fracture mechanics relations :  $J_{el} = \frac{K^2}{E'}$  where  $E' = E$   
 121 (Young's modulus) in plane stress and  $E' = \frac{E}{1-\nu}$  in plane strain ( $\nu$  is the Poisson's ratio).  
 122 The plastic component  $J_{pl}$  is defined as  $J_{pl} = \frac{1.9A_{pl}}{Bb}$  where  $A_{pl}$  is the plastic area under the  
 123  $F - d$  curve and  $b$  the uncracked ligament size. The standard mode I  $J - K$  equivalence  
 124 (eq. 2) permits to back-calculate, from the geometric mean of the local stress intensity factor  
 125  $J$ , an equivalent stress intensity factor  $K_J$  :

$$K_J = (JE')^{1/2} \quad (2)$$

126 Toughness parameters such as crack initiation toughness ( $K_{I0}$ ) and fracture toughness ( $K_{IC}$ )  
127 are directly determined from the R-curves. According to the ASTM criterion, the maximum  
128 crack extension capacity for a specimen is given by  $\Delta a_{max} = 0.25b_0$  where  $b_0 = W - a_0$  is  
129 the initial uncracked ligament. For  $R$ -curves calculation, the considered values for Young  
130 Modulus and Poisson ratio are respectively  $E=368$  GPa and  $\nu=0.24$  since we work with a  
131 system quasi-fully composed of alumina.

### 132 **3. Results**

#### 133 *3.1. Heteroaggregation*

134 The first step in this study is to characterize the particles surface charges in aqueous  
135 suspensions. For each type of particle, zeta potential measurements as a function of pH are  
136 performed (Fig. 1a).

137 The natural pH of both alumina platelets and nanoparticles suspensions is around 6.5.  
138 An isoelectric point around 9 is found for both suspensions: for pH less than 9, both  $Al_2O_3$   
139 platelets and nanoparticles are mainly positively charged and for pH greater than 9, they are  
140 negatively charged. For silica particles, the natural pH is around 9, which can be explained  
141 by the alkaline medium used to stabilize the commercial Ludox TM50 suspension. The zeta  
142 potential of silica is negative on the 2-10 pH range. The goal of this study is to take advan-  
143 tage from the heteroaggregation between the silica nanoparticles and the alumina platelets  
144 as proposed in Ref. [16]. The natural pH of the three-component suspensions being around  
145 7.6, a pH adjustment is not needed. At pH 7.6 (Fig. 1a), both alumina platelets and silica  
146 nanoparticles are oppositely charged, and therefore prone to heteroaggregation.

147 It has been shown [16], that the heteroaggregation of silica nanoparticles and alumina  
148 platelets can help disaggregating the suspension. In this study, a third component is used,  
149 the  $\alpha Al_2O_3$  nanoparticles. To observe the effect of this third component on the suspension  
150 behavior, settling tests are performed. Figure 1b shows the results obtained after 5 days with  
151 a suspension composed of alumina platelets only, with a suspension containing the alumina  
152 platelets and the  $\alpha$ -alumina nanoparticles and with a suspension containing the three com-  
153 ponents. It is observed that even with the addition of  $\alpha Al_2O_3$  nanoparticles, the suspension  
154 remains stable. The sediment height of the three-component suspension is indeed lower than  
155 the two others.

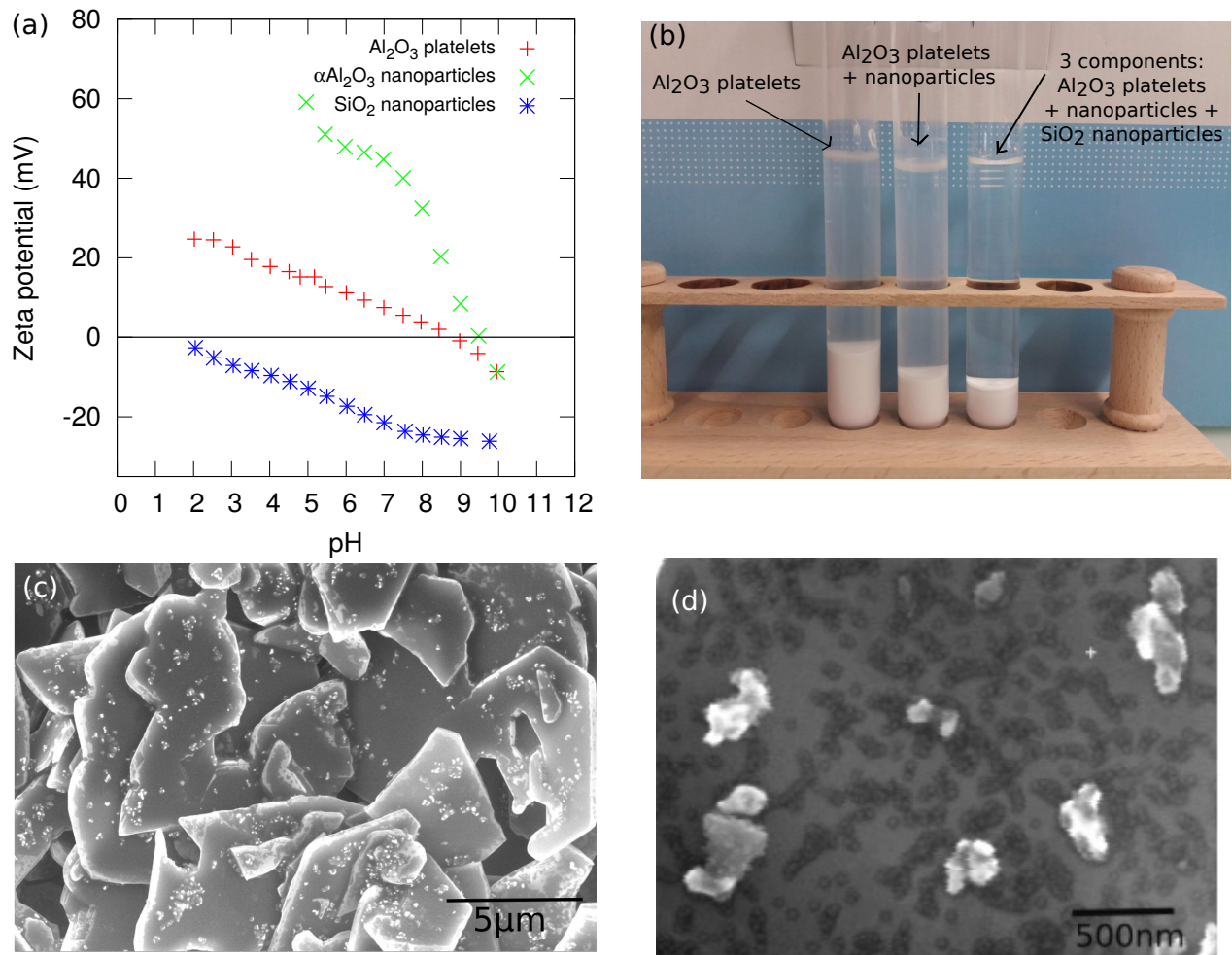


Figure 1: (a) Evolution of the zeta potential as a function of pH for the different components used in the nacre-like composite. Results of alumina platelets and silica nanoparticles are extracted from reference [16]. (b) Pictures of the closed tubes used in the sedimentation tests after 5 days. From left to right: a suspension of Al<sub>2</sub>O<sub>3</sub> only, a binary suspension composed of Al<sub>2</sub>O<sub>3</sub> and αAl<sub>2</sub>O<sub>3</sub> and a suspension with the three components (Al<sub>2</sub>O<sub>3</sub>, αAl<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>). (c) and (d) environmental SEM pictures of the three-component suspension (Pressure 670 Pa, HV 10kV, Humidity: 94.5%). ©2020 M. Cerbelaud et al. (10.6084/m9.figshare.12018501) CC BY 4.0 license <https://creativecommons.org/licenses/by/4.0/>.



156 The three-component suspension is observed by environmental SEM. Figures 1d shows sil-  
157 ica nanoparticles on the alumina platelet faces. Moreover, aggregates composed of alumina  
158 and silica nanoparticles are also present on the platelets. These observations are consistent  
159 with the aforementioned charges of particles. Silica is negatively charged, therefore it is  
160 absorbed onto  $\text{Al}_2\text{O}_3$  platelets and  $\alpha\text{Al}_2\text{O}_3$  nanoparticles surfaces which are themselves pos-  
161 itively charged. This observed arrangement at this early stage of the process is promising  
162 to obtain the desired microstructure in the composites. Silica nanoparticles and  $\alpha\text{Al}_2\text{O}_3$   
163 nanoparticles are both well spread onto the alumina platelet surfaces.

164 The three-component suspensions are then used to shape nacre-like ceramic composites.  
165 First, we use sedimentation to shape pellets. After drying, some pellets are broken in half  
166 and the rupture surface is observed by SEM. Figure 2a shows that in the foreground some  
167 of the platelets are disorganized due to the fracture of the material, however in the back-  
168 ground a preferential orientation of alumina platelets in the pellets is observed. At this  
169 stage, a sedimentation by gravity yields a good alignment of platelets, which form layers in  
170 the samples. In between those layers,  $\alpha\text{Al}_2\text{O}_3$  nanoparticles are dispersed forming potential  
171 anchorage after consolidation by sintering. The dispersion of silica nanoparticles on platelets  
172 faces (Fig. 2b), already observed in the suspensions (Figure 1d), is maintained in the green  
173 sample.

174 Composites are also made by the freeze-granulation method. Because of the low solid load-  
175 ing of the suspensions used for granulation, the granules are not self-supporting and only  
176 aggregated powder is obtained at the end. Figures 2c and 2d show the SEM pictures of the  
177 powder obtained after the freeze-granulation. An homogeneous dispersion of the different  
178 components is observed. Both  $\alpha\text{Al}_2\text{O}_3$  and silica nanoparticles are well-dispersed on the  
179 platelets surface.

### 180 *3.2. Microstructural characterization of the sintered samples*

181 The green samples are then sintered by FAST. After the thermal treatment, an important  
182 linear shrinkage ( $\sim 70\%$ ) is observed in the sedimentation direction for the pellets obtained  
183 by sedimentation. Archimede's Law of Buoyancy gives an apparent density of  $3.93\text{ g.cm}^{-3}$   
184 and an open porosity of  $0.36\%$  for the sample obtained by the sedimentation route and an  
185 apparent density of  $3.85\text{ g.cm}^{-3}$  and an open porosity of  $0.48\%$  for the sample obtained by a  
186 freeze-granulation route. After fracture, a cross section of both samples is mirror polished and

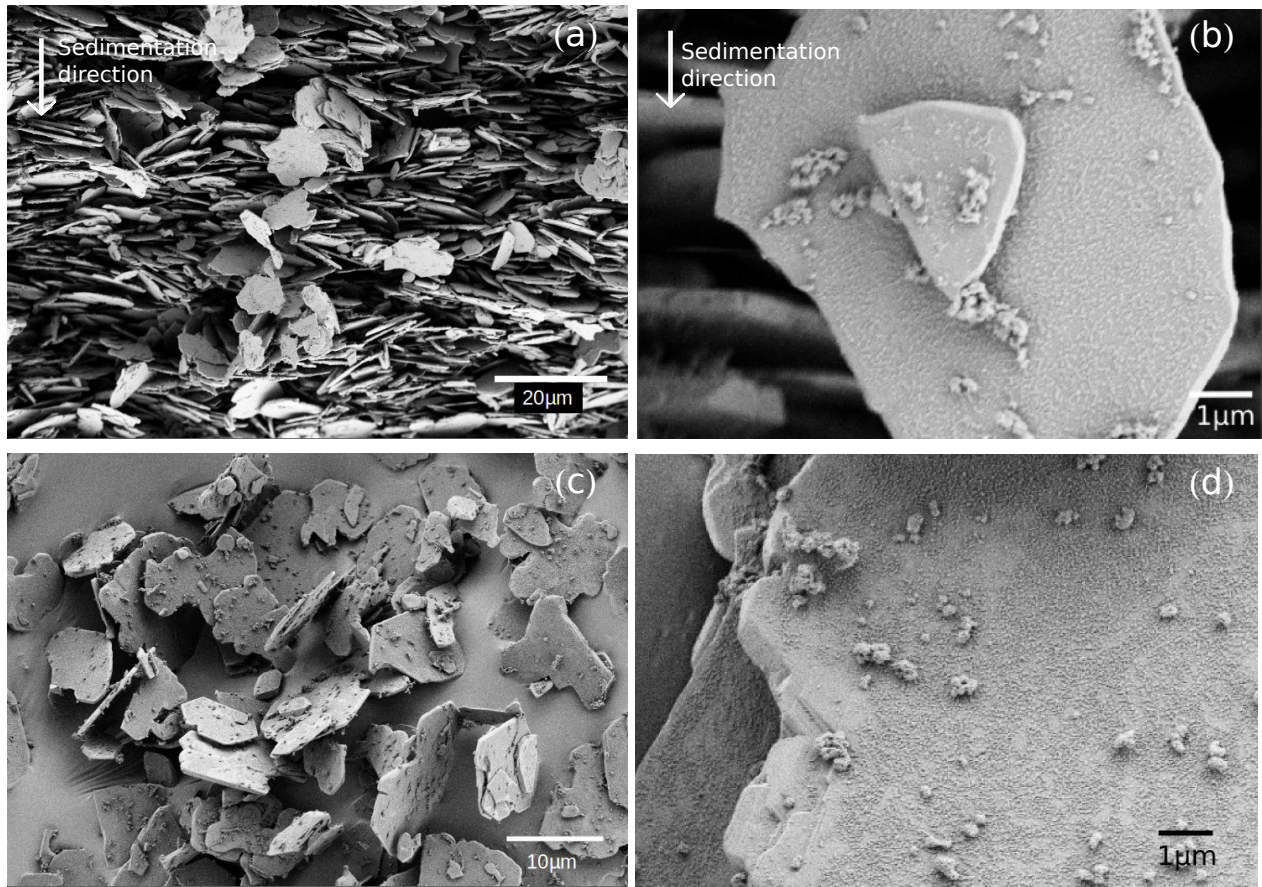


Figure 2: (a) and (b) SEM pictures of a fracture surface of a dried pellet obtained by sedimentation. (c) and (d) SEM pictures of the powder obtained by freeze-granulation. ©2020 M. Cerbelaud et al. (10.6084/m9.figshare.12018501) CC BY 4.0 license <https://creativecommons.org/licenses/by/4.0/>.

	Average strength (MPa)	Standard deviation (MPa)
Sedimentation	454	20
Freeze granulation and freeze-drying	338	46

Table 1: Averaged flexural strength of samples from both shaping methods and post sintered by FAST (averaged over 4 samples).

187 observed by SEM (Fig. 3a and 3b). Alumina platelets are easily recognized on the pictures  
188 because of the contrast difference. A good alignment of platelets is observed in both cases,  
189 with a slightly higher disorder in the freeze-granulated samples. The (0012) XRD pole figures  
190 of both types of samples are shown in Figures 3c and 3d. An estimation of average platelet  
191 disorientation can be obtained by computing the root-mean-squared disorientation obtained  
192 from a Gaussian fit of each  $\Psi$  scan building up the pole figure. With this approach we find an  
193 average disorientation of platelets of  $7.5 \pm 0.4^\circ$  for the sample obtained by sedimentation and  
194  $8.2 \pm 0.2^\circ$  for the samples obtained by freeze-granulation. The disorientation of the platelets  
195 is very low, and comparable to that of the natural nacre which is about  $5^\circ$ [4]. The platelet  
196 alignment is better than that obtained by ice templating and reported by Bouville *et al.* [7]  
197 ( $15^\circ$ ).

### 198 3.3. Mechanical properties

199 The strength of the samples is measured by three points bending. Table 1 shows the  
200 average strength of composites obtained from both methods.

201 The flexural strength values obtained are equivalent to those reported for crystalline  
202 alumina [18, 19] and comparable to the results of Bouville *et al.* (470 MPa) [7].

203 The flexural strength values are a slightly higher for samples shaped by sedimentation.  
204 Because the composition and the tests conditions are the same for both approaches, this  
205 result might be related to the lower porosity and the better alignment of platelets obtained  
206 by sedimentation. To measure the toughness of the elaborated composites, SENB tests are  
207 carried out, and results are compared to those obtained by Bouville *et al.* [7]. The stress-  
208 strain curves are treated to obtain the fracture toughness of composites. Four specimens for  
209 each approach are tested to assess reproducibility. The initiation fracture toughness ( $K_{1c}$ )  
210 obtained for the composite elaborated from the sedimentation route is  $3.8 \text{ MPa}\cdot\text{m}^{1/2}$ , and

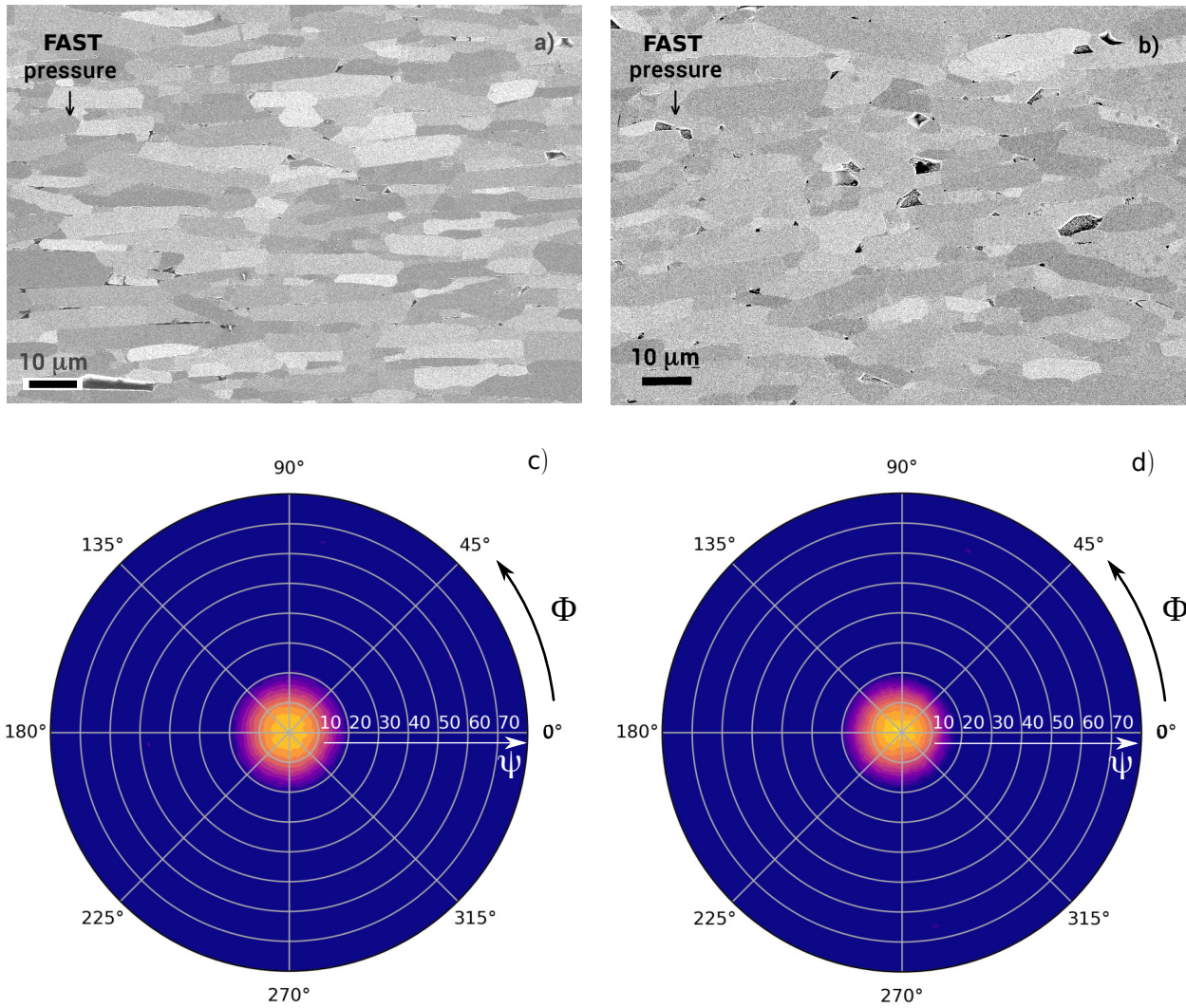


Figure 3: SEM pictures of polished sections of sintered samples and corresponding XRD pole figures used to determine the platelets disorientation: (a) and (c) samples obtained by sedimentation; (b) and (d) samples obtained by freeze granulation. ©2020 M. Cerbelaud et al. (10.6084/m9.figshare.12018501) CC BY 4.0 license <https://creativecommons.org/licenses/by/4.0/>.

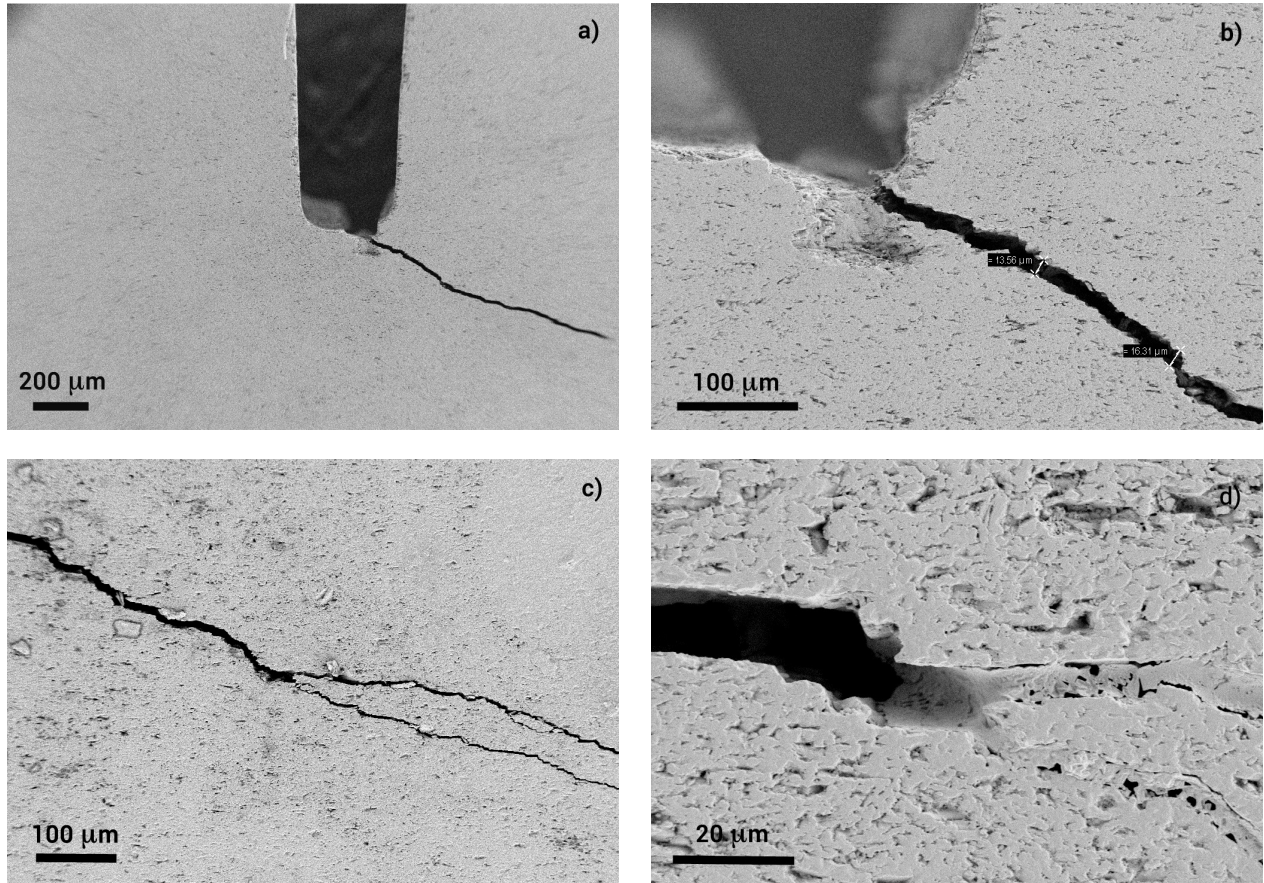


Figure 4: SEM pictures of cracks propagation observed on the samples used for the SENB tests. (a) and (b): Area where crack is initiated: deflection; (c) and (d) crack after propagation: multiple cracks and crack bridging. ©2020 M. Cerbelaud et al. (10.6084/m9.figshare.12018501) CC BY 4.0 license <https://creativecommons.org/licenses/by/4.0/>.

211 that of the composite obtained from freeze-granulation is  $3.6 \text{ MPa}\cdot\text{m}^{1/2}$ . These values are  
 212 equivalent to the reference values of fracture toughness for alumina ( $3.5 \text{ MPa}\cdot\text{m}^{1/2}$ ) but are  
 213 lower than the result for the nacre-like composite from Bouville et al. ( $6.1 \text{ MPa}\cdot\text{m}^{1/2}$ ) [7]. For  
 214 both composites crack propagation shows strong deviation at the interface between platelets,  
 215 multiple cracks are observed as well as some crack bridging (Fig. 4). These toughening  
 216 mechanisms, crack deflection and crack bridging, are similar to those observed in natural  
 217 materials such nacre or bonds, presenting a high toughness [20, 21, 22, 23]. They lead to  
 218 the increase of fracture resistance with the propagation of cracks (i.e. R-curves). The R-  
 219 curves for both composites are plotted in Figure 5. The measurement is done according  
 220 to ASTM E-1820 [17] and is considered as valid until a maximum crack length determined  
 221 by  $\Delta a_{max} = 0.25b_0$ , where  $b$  is the thickness of the specimen ligament. In our case, this

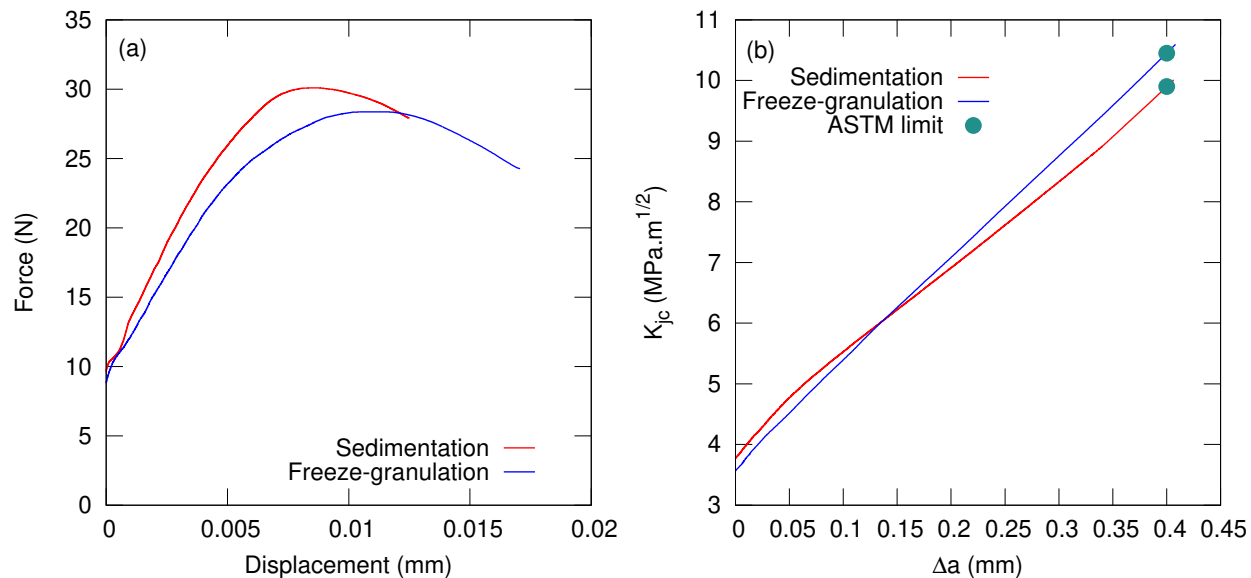


Figure 5: (a) Evolution of the force as a function of the displacement for the three points bending tests on samples with pre-notches obtained by sedimentation and by freeze-granulation routes and (b) corresponding R-curves : Evolution of the fracture toughness  $K_{Jc}$  calculated from the J-integral as a function of crack extension  $\Delta a$ . ©2020 M. Cerbelaud et al. (10.6084/m9.figshare.12018501) CC BY 4.0 license <https://creativecommons.org/licenses/by/4.0/>.

222 maximum crack length is 0.4 mm. The maximum toughness obtained is 10.1 MPa.m<sup>1/2</sup> and  
 223 10.6 MPa.m<sup>1/2</sup> for composites from the sedimentation route and the freeze-granulation route,  
 224 respectively. These values are lower than the 17 MPa.m<sup>1/2</sup>, obtained for the nacre-like alumina  
 225 composite of Bouville *et al.* [7]. According to the observations, cracks propagate in the  
 226 vitreous phase, however it can be noticed that the composition of the vitreous phase in these  
 227 composites is slightly different from the one of the composites of Bouville *et al.* [7] which is  
 228 obtained from a mixture of silica and calcium carbonate. This difference of composition could  
 229 be at the origin of the lower mechanical performances reported here. Moreover, a greater  
 230 grain growth is obtained in our samples probably due to the chemical composition of the  
 231 intergranular phase, which can also be detrimental to the mechanical properties.

#### 232 4. Conclusion

233 Nacre-like ceramic composites are obtained from heteroaggregated suspensions of alumina  
 234 and silica particles by two methods: sedimentation and freeze-granulation. For both methods,

235 a good distribution of the components is obtained, as well as a very good alignment of alumina  
236 platelets in the sintered samples (disorientation of  $7.5^\circ$  and of  $8.2^\circ$  for the sedimentation and  
237 freeze-granulation routes, respectively). The study of mechanical properties of the ceramic  
238 composites shows typical toughening mechanisms of brick and mortar composite materials,  
239 with crack deflection, multiple cracks, and crack bridging. The heteroaggregation between  
240 the silica nanoparticles and the alumina platelets is therefore a good alternative to obtain  
241 nacre-like ceramic composites without polymeric dispersant. In comparison, the composite  
242 obtained by the sedimentation route have slightly better flexural strength, which is attributed  
243 to a better platelet alignment.  
244 Despite a better alignment of platelets, the mechanical properties are however lower than  
245 those obtained previously by freeze-casting [7]. This could be attributed to the difference of  
246 the vitreous phase composition, which appears to be a key point to improve the mechanical  
247 properties of nacre-like ceramic composites.

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