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Journal Article as: peer-reviewed accepted version (Postprint)

DOI of this document*(secondary publication): https://doi.org/10.26092/elib/2629

Publication date of this document: 04/12/2023

* for better findability or for reliable citation

Recommended Citation (primary publication/Version of Record) incl. DOI:

Almeida, RSM, Pereira, TFS, Tushtev, K, Rezwan, K. Obtaining complex-shaped oxide ceramic composites via ionotropic gelation. J Am Ceram Soc. 2019; 102: 53–57. https://doi.org/10.1111/jace.15990

Obtaining complex-shaped oxide ceramic composites via ionotropic gelation

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Abstract

In this communication, we present a new processing method for obtaining oxide ceramic composites based on the ionotropic gelation technique. Nextel 610 fiber fabrics were infiltrated by an alumina-zirconia suspension with a total solid content of 50 vol% and alginate as the binder. Subsequently, the suspension was slowly cross-linked by adding Al^{3+} cations and transferred to a gel state. The gelled fabric layers could be easily cut, stacked and shaped, as well as joined to other ceramic materials and composites. Furthermore, the fiber content could be adjusted by pressing the layers together. In summary, the composites produced with this technique presented a very good fiber bundle infiltration, matrix with fine porosity and excellent mechanical properties. Nextel 610/alumina-zirconia composites sintered at 1200°C for 1 hour showed bending strength of 306 MPa, interlaminar shear strength of 9.8 MPa and nominal fracture toughness of 13.6 MPa $m^{0.5}$.

1 | INTRODUCTION

Ceramics have become essential for applications that require high thermo-mechanical strength and reliability since the development of ceramic matrix composites (CMCs). When oxidation resistance is also required, CMCs based on oxide materials (Ox-CMCs) are of great interest due to their intrinsic oxidation resistance. For such composites, damage tolerance is normally achieved by producing a weak matrix with a finely distributed porosity.[1] Nowadays, Ox-CMCs have reached enough maturity to be applied in different industrial fields like: gas turbine engines, thermal protection systems and hot gas filters.[2] However, an even broader range of applications is still restricted by their current processing methods and the thermal stability of the available oxide fibers.

Even though there are several processing routes for ceramics, the processing of Ox-CMCs is rather complicated due to the presence of the fiber reinforcements. Hence, several processing methods of ceramics are not suitable for the production of CMCs, which in turn, limits the production of complex-shaped CMC components. The production of Ox-CMCs normally involves the infiltration of fiber fabrics by a pre-ceramic fluid, followed by the densification of the matrix at high temperatures. For the infiltration step, the most common approaches seen in the literature are based on the use of aqueous slurries or sols.[2] In order to properly infiltrate fiber bundles/fabrics and fill all the spaces between the fiber filaments, a suspension with low viscosity is generally desired. This poses a challenge to current processing methods, since low viscosity usually implies the use of slurries with a low particle content. Consequently, high matrix shrinkage is observed during the sintering step, which can lead to matrix cracking or formation of residual stresses. This is even more critical if one considers the fact that the presence of the fibers constrains the densification/shrinkage of the matrix. In the literature, there are different approaches to improve the infiltration process, which rely on the use of pressure,[3] vacuum[4] or vibration.[5] All these methods are still limited to suspensions with particle contents of about 30 vol%. Another possibility is to perform several re-infiltration cycles.[6,7] The disadvantage here is

that re-infiltration is not suitable to fill closed pores and cracks, as well as being time consuming and expensive. It should be noted that there are other processing methods applicable to Ox-CMCs such as: electrophoretic deposition, polymer infiltration and reaction bonding. Nevertheless, these processes are either limited in regard to matrix chemical composition, are time consuming or lead to composites with lower mechanical properties than composites produced by slurry infiltration or colloidal route.[2]

In this communication, we present a processing method for Ox-CMCs using ionotropic gelation for the consolidation of the matrix to overcome the problems mentioned above. Ionotropic gelation is based on the ability of metallic cations to crosslink polysaccharide chains.[8] Hence, a ceramic suspension containing such polysaccharide chains can be slowly gelled with this cross-link reaction and, in the meantime, the green body can be easily shaped. This processing route has been used for the green-body formation of several types of ceramics using different shaping techniques.[9] For the production of CMCs, ionotropic gelation presents several advantages over classical slurry infiltration methods: (a) a high ceramic particle content of the slurry, (b) a good control of suspension viscosity over time due to gelling reaction, (c) a low binder content and (d) a flexible shaping method.

Here, composites with an alumina-zirconia (80-20 wt%) matrix reinforced with 0/90° Nextel 610 fiber fabric DF-11 (3M, Maplewood, MN, USA) were produced. Before the production of the composites, the fiber fabrics were thermally desized at 700°C for 2 hours. Figure 1 shows a detailed scheme of the method used for the consolidation of the matrix. Using an overhead stirrer RW20DZN.n (IKA®-Werke GmbH KG, Staufen, Germany), the nontoxic polysaccharide alginate was dissolved in double-deonized water with pH adjusted to 9 by the addition of NH_4OH. A mixture of two different alginates was used (0.6 g each): Protanal LFR5/60 (FMC Corporation, Philadelphia, PA, USA) and Alginic acid sodium salt from brown algae medium viscosity (Sigma-Aldrich Chemie GmbH, Steinheim, Germany). Afterward, ceramic powders were added to obtain a suspension with a solid content of 50 vol% and stirred for 2 hours at 1000 rpm over a water-ice bath. The following ceramic powders were used: alumina CT 1200 (d_{50} = 1200 nm; Almatis GmbH, Ludwigshafen, Germany), alumina TM-Dar (d_{50} = 200 nm; Taimei Chemicals, Tokyo, Japan) and zirconia TZ-3YS-E (d_{50} = 40 nm; Tosoh Corporation, Tokyo, Japan). To avoid agglomeration, 1 g of 5-sulfosalicylic acid dihydrate ReagentPlus® (Sigma-Aldrich Chemie GmbH) was used as dispersant. Aluminum acetate basic (Honeywell Specialty Chemicals Seelze GmbH, Seelze, Germany) was then added to the suspension to start the cross-link reaction. Aluminum acetate dissolves in water and slowly releases Al^{3+} ions that crosslink the alginate chains. The amount of aluminum acetate used was equivalent to 0.3 wt% of the suspension. With the addition of the cross-linker, the fiber fabrics were infiltrated with the ceramic slurry and individually rolled between two metallic rolls to help the infiltration and to achieve a uniform thickness of all layers. The infiltrated fabric layers were gelled for 40 minutes at 50°C and at 80% of air humidity. The gelled layers were then stacked together to achieve the desired composite thickness. It should be highlighted that the gelled layers are very flexible and can be easily shaped. Optionally, the layers can also be pressed together to obtain a more uniform thickness and to increase the fiber volume fraction in the composite. Afterwards, the composites were dried for at least 2 days at room temperature before undergoing the sintering step. Matrix sintering was performed at 1200°C for 1 hour in a high-temperature chamber furnace LHT 04/17 (Nabertherm GmbH, Lilienthal, Germany). It should be noted that the materials used (fiber and matrix composition), as well as sintering parameters, are based on values found in the literature and on preliminary tests.

2 | RESULTS AND DISCUSSION

For the characterization of the composites, CMC plates-containing six fabric layers each were produced. Two types of samples were manufactured. The first set of samples was produced by manually stacking the gelled layers and sintering the plate. Another set of samples was prepared by stacking the gelled layers and pressing them at room temperature with 0.4 MPa using a hydraulic press. The stacked plates had a thickness of 2.33 mm with some variations along the samples, whereas the pressed plates had a more uniform thickness of 1.49 mm. The microstructure of both sample types can be seen in Figure 2. In general, the stacked plates showed higher amounts of matrix between the fiber fabric layers. During pressing, it was observed that the extra slurry between the fabric layers was squeezed out. In addition, a few pores were seen in the matrix of stacked samples, which are presumably due to trapped air between the infiltrated fabrics. For the pressed samples, the layers were distributed more uniformly and no big pores were seen in the matrix. Still, small longitudinal matrix cracks were occasionally seen for both samples. By analyzing the micrographs at higher magnification, it can be seen that the matrix is well dispersed between the fiber filaments for both samples. This confirms that a very good degree of fiber infiltration can be obtained with only one infiltration step, even without the application of pressure.

Characterization of the composite plates included measurements of porosity by Archimedes' principle (standard DIN EN 623-2), the bending strength by four-point

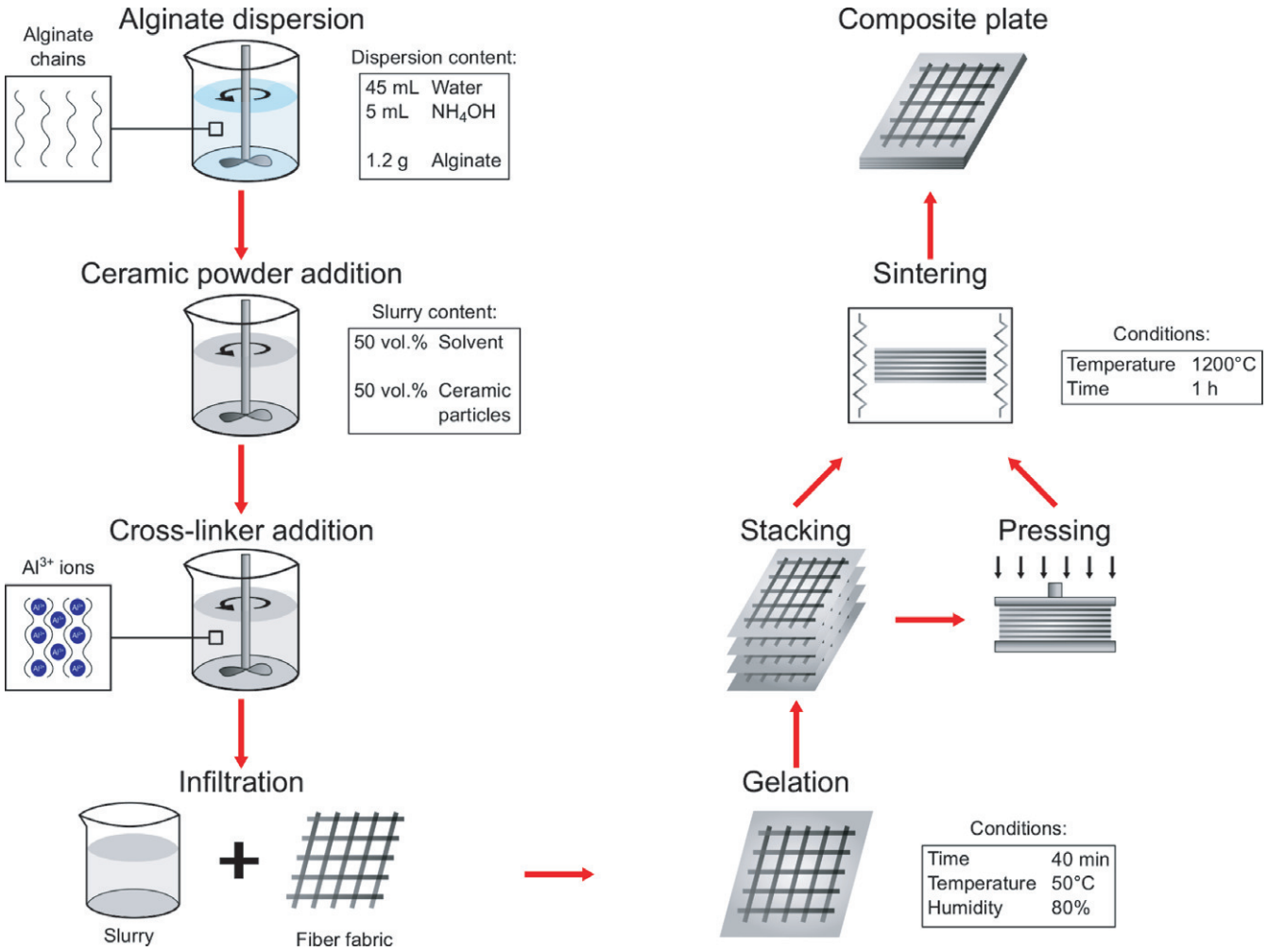

FIGURE 1 Processing route of composites via ionotropic gelation [Color figure can be viewed at wileyonlinelibrary.com]

bending test (standard DIN EN 658-3) and the interlaminar shear strength by short-beam bending test (standard DIN EN 658-5). In addition, the fracture toughness in terms of critical stress intensity factor (K_{IC}) was measured by single-edge notch bending test (SENB) on 70 × 10 mm specimens with a 3 mm notch. For the calculation of K_{IC}, the maximum load and the length of the artificial notch were taken into account. Therefore, the calculated values should be regarded as a nominal fracture toughness. Further details of the procedure for the SENB test were published elsewhere.[10]

The measured properties of both composite plates are summarized in Table 1. As it can be seen in the table, the fiber content of stacked samples was lower than the pressed ones, while the porosity was higher. These differences are because of the higher amount of interfabric matrix seen for the stacked samples (Figure 2), which also influences the mechanical properties of the composites. The pressed plates showed higher bending strength and nominal K_{IC} when compared to the stacked plates, which can be related to the higher fiber content of the pressed samples. The interlaminar shear strength of both composites depends on the properties of the matrix. Hence, the occasional presence of big pores in the stacked plates resulted in lower shear strength. It should be highlighted that the mechanical properties of the obtained composites lie within the range of commercially available composite plates: nominal K_{IC} of 8.9-12 MPa $m^{0.5}$ and bending strengths of 160-340 MPa.[2] Nevertheless, the developed composites show lower fiber contents, ie, 24 vol% for stacked samples and 37 vol% for samples pressed with 0.4 MPa. The fiber content can be raised by increasing the applied pressure, which in turn, can increase the mechanical properties of the composites.

Furthermore, ionotropic gelation is highly suitable for obtaining complex-shaped materials. Figure 3 illustrates the high potential of this method with various forms that can be produced: a nose cone, the letter "A" and a plate. The plate shown in the figure is similar to the ones used for the characterization of the composites. For the production of

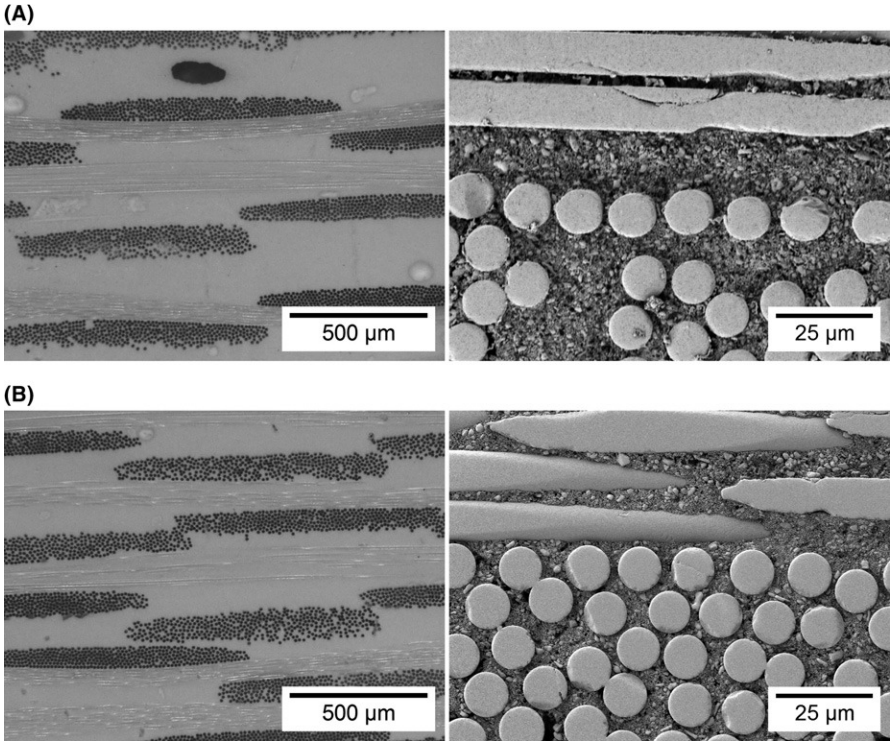

FIGURE 2 Microstructure of the produced composites: composite plate produced by stacking (A) and composite plate produced by stacking and pressing (B)

TABLE 1 Properties of the obtained composite plates. Averages and standard deviations were calculated from five specimens of the same plate

Composite	Fiber content (%)	Porosity (%)	Bending strength (MPa)	Interlaminar shear strength (MPa)	K_{IC} (MPa $m^{0.5}$)
Stacking	24	34.9 ± 0.8	194 ± 19	8.4 ± 0.6	11.4 ± 0.8
Pressing	37	32.6 ± 0.3	306 ± 21	9.8 ± 0.8	13.6 ± 0.6

the nose cone, the flexible gelled layers were stacked above a polymer positive mold. After drying, the green composite could be detached from the mold and sintered. The production of the "A" was done manually. For that, the gelled layers were cut in the desired length, stacked together, and bent to acquire the outer shape of the "A". The "-" in the middle of the "A" was done separately by stacking gelled layers to form a shorter composite plate, which was later joined with the outer part of the "A" using additional slurry. This shows another very interesting feature of this processing method, as it demonstrates how ionotropic gelation can be used to join ceramics.[11]

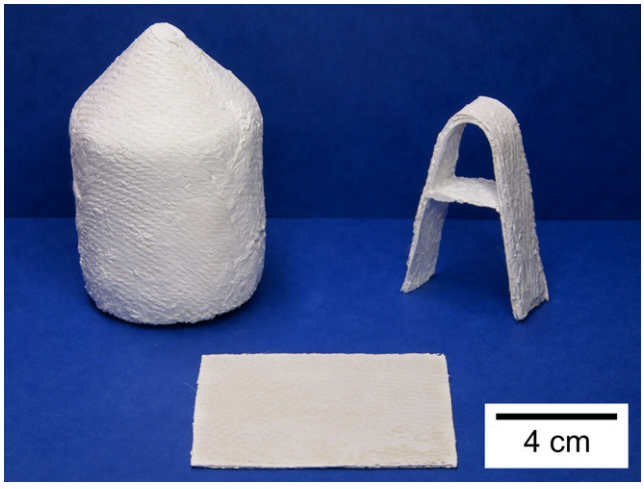

FIGURE 3 Examples of geometries of CMC components possible with ionotropic gelation [Color figure can be viewed at wile yonlinelibrary.com]

3 | CONCLUSION

In summary, Ox-CMCs with high strength and fracture toughness were successfully produced by ionotropic gelation. This method showed considerable improvement in the infiltration step since it allows use of slurries with high solid content and control of viscosity over time. Thus, composites produced with only one infiltration showed a good level of fiber infiltration and minimal matrix defects. This is perhaps one of the main features of this processing route since other methods for the production of complex-shaped CMCs

usually require further infiltration steps. In addition, the low amount of binder used in this method (<1 wt%) can be easily extracted during sintering without the necessity of an additional heat-treatment step. Another advantage of ionotropic gelation is related to the easy shaping, as well as the possibility to join two composite plates to achieve even more complex geometries. The produced Nextel 610/alumina-zirconia composites achieved mechanical properties similar to commercially available composites, but with all the additional advantages highlighted above.

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