INTRODUCTION

As the interest in components that can operate at higher temperatures and oxidizing atmospheres has increased over the last decades, all-oxide ceramic matrix composites (Ox-CMCs) have been developed. These composites normally contain alumina-based fibers reinforcing matrices composed of alumina, aluminosilicates and/or zirconia. The idea behind the reinforcement of oxide ceramics with oxide ceramic fibers is to increase their fracture toughness and damage tolerance while maintaining their high strength, as well as high thermal and chemical resistances. This is normally achieved by producing a porous matrix, in which cracks can be deflected before reaching the reinforcement fibers.\(^1\) Owing to this interesting combination of properties, Ox-CMCs are attractive for several industrial applications such as: gas turbine engines, thermal protection systems, and hot-gas filters.\(^2\) However, their further development is somewhat restricted by the available processing methods.

During the fabrication of Ox-CMCs, care should be taken not to impair the reinforcement fibers. Hence, several processing methods applicable for traditional ceramics with complex geometries cannot be adapted for the manufacturing of these fiber-reinforced composites. The most traditional way of preparing Ox-CMCs is by infiltrating fiber fabrics or preforms with a low-viscosity preceramic fluid.\(^3\) Infiltrated fabrics can be then stacked together and shaped with different techniques. Simple geometries are fabricated by pressing, whereas a higher degree of complexity can be achieved with a vacuum-assisted lamination process.\(^4\) Alternatively,
infiltrated fiber bundles can be wound to produce cylindrical geometries. Considering the current processing methods for OxCMCs, it is clear that joining techniques are required to reliably produce components with higher complexity such as the ones present in turbine engines, for instance. Furthermore, joining can also decrease the production cost of such components as it is cheaper to produce simpler shapes that can be later joined together.

Several authors have investigated different joining techniques for CMCs based on glass or ceramic joining, pyrolysis of preceramic polymers, and spark plasma sintering. However, these works are focused on joining of non-oxide CMCs. The literature on joining of OxCMCs is still very limited. The selection of a proper joining material for OxCMCs is difficult since it should have suitable wetting properties, similar coefficient of thermal expansion to the composite and should not react deleteriously with the composite during its application. Also, the functionality of the composite should not be hindered by the joint. In other words, the joining material should be stable at high temperatures (up to 1000°C) and oxidizing atmospheres, too. Commercial glass solders used for joining of oxide ceramics are not suitable for the joining of OxCMCs due to their low interaction with the composite surface. Akram et al. could successfully join OxCMCs using different brazing alloys and tailored glass-ceramics. The glass-ceramic joints are preferred since they showed higher shear strength and oxidation resistance than the brazing alloys. Nevertheless, the thermal stability of these joints is still lower than commercial OxCMCs. Blazing alloys oxidize at 550°C, whereas the softening temperature of these glasses is around 800°C-900°C.

Since the joining of OxCMCs is a very important topic, yet very little investigated, the objective of this work was to develop a joining methodology using the ionotropic gelation technique. Ionotropic gelation is a type of gel casting, in which ceramic suspensions with polysaccharide polymers are gelled. The polysaccharide chains can be cross-linked with multivalent metallic cations like Ca$^{2+}$ forming a gel. Thus, a ceramic green body can be shaped during this gelation reaction, which is later dried and sintered. In our previous study, we successfully produced high-strength OxCMCs using this technique for the consolidation of the matrix. Ionotropic gelation presents several advantages over traditional slurry infiltration methods, such as: the control of the slurry viscosity with the gelling reaction, a relatively high ceramic particle content of the slurry, a low content of binder and flexible shaping possibilities.

Furthermore, previous works from our research group showed that this technique can be used to join monolithic ceramics in the green state. Therefore, the focus of this work is to further develop this technique and to investigate its capabilities regarding the joining of OxCMCs. For that, composite plates containing Nextel 610 fibers and alumina-zirconia matrix (N610/AZ) were produced. The composites were united at different stages of processing using a ceramic suspension containing the polysaccharide polymer alginate as the binder. Composite plates were joined in the wet-gel and dry green-body state, as well as after sintering. The results are compared to the interlaminar shear strength (ILSS) and microstructure of the single composite plates.

## Experimental Procedures

### Composite processing

The methodology applied to produce the composites studied here was adapted from our previous work. Nextel 610 fiber fabrics DF-11 (3M) were used as the reinforcement. This fiber was chosen since it is the strongest oxide fiber commercially available, as well as being the most used reinforcement for OxCMCs. The matrix composition was 80 wt% alumina and 20 wt% yttria-stabilized zirconia. The ceramic powders used were: alumina CT 1200 (d$_{50}$ = 1200 nm; Almatis GmbH), alumina TM-DAR (d$_{50}$ = 200 nm; Taimei Chemicals), and zirconia TZ-3YS-E (d$_{50}$ = 40 nm; Tosoh Corporation). For the preparation of the ceramic suspension, 45 mL of double-deionized water with 5 mL of NH$_3$OH (pH = 9) was used as the solvent. Two different alginates were used as the binders: 0.6 g of Protanal LFR5/60 (FMC Corporation) and 0.6 g of Alginic acid sodium salt from brown algae medium viscosity (Sigma-Aldrich Chemie GmbH). 1 g of 5-sulfosalicylic acid dihydrate ReagentPlus® (Sigma-Aldrich Chemie GmbH) was used as dispersing agent. The prepared slurries had a solid content of 50 vol%. A detailed description of the suspension preparation is given in Ref. 17.

Before the infiltration step, the fiber fabrics were heat cleaned at 700°C for 2 hours using a high-temperature chamber furnace LHT 04/17 (Nabertherm GmbH). Subsequently, the fabrics underwent a cold-plasma surface treatment using a Femto low-pressure plasma system (Diener electronic GmbH + Co. KG). This was performed in an O$_2$ atmosphere with 3-4 mbar of pressure and 50 W of power for 2 minutes. The plasma treatment was done to clean the surface of the fibers and to improve the wetting properties. For the infiltration, 0.3 wt% regarding the slurry of aluminum acetate, basic (Honeywell Specialty Chemicals Seelze GmbH) was added to the suspension to start the cross-link reaction. While the gelling reaction took place, the fiber fabrics were infiltrated with the slurry and individually rolled between two metallic rolls for improving the infiltration. The infiltrated fabric layers were then gelled for 20 minutes at 50°C and at 80% of air humidity. Afterward, the gelled layers were laminated to the desired composite thickness simply by stacking them, that is, without any external pressure. After at least 2 days of
drying, the composites were sintered at 1200°C for 1 hour. The same oven used for the heat cleaning was used for the sintering step. The properties of the produced composites have been previously measured,\textsuperscript{17} and are displayed in Table 1.

### 2.2 Joining approaches

The joining capabilities of the ionotropic gelation method were assessed during different stages of composite processing. Figure 1 shows a schematic representation of the different joining approaches. For all types of joints, two composite plates were united with a basic single-lap joint. The composite plates were composed of five partially gelled layers stacked together resulting in a thickness of 2.0 ± 0.2 mm. Joining was performed using a new batch of ceramic suspension, which was mixed with the cross-linker shortly before the joining process. The suspension used for joining had the same composition and was prepared as previously described.

The first type of joint investigated was performed during the gel state. For that, the stacked layers were gelled for an additional time of 40 minutes under the same conditions (50°C and humidity of 80%). A thin layer of ceramic suspension was placed between two gelled plates and lightly pressed. The joined specimens were then dried for 2 days and, subsequently, sintered at 1200°C, as previously described. The second type of joint was done on green composite plates after drying. The joining region was lightly wetted with double-deionized water before the joining process. Just like the previous type of joint, the samples were dried for 2 days and then sintered. The third type of joining was performed after sintering the composite plates. To prepare the surface of the composites for joining, a cold-plasma surface treatment was performed. The composite plates were joined and dried for 2 days. In order to consolidate the joint, the joined composites were sintered again. This second sintering was also performed at 1200°C for 1 hour. For comparison, single composite plates were also produced and tested. The composite plates were fabricated using ten layers of fiber fabric, resulting in a thickness of 4.2 ± 0.2 mm. Details on the geometry of the tested samples are given below.

### 2.3 Characterization methods

To evaluate the quality of the joints, microstructural analyses were performed under scanning electron microscope (SEM). For that, samples were cut along the joint and embedded in epoxy resin. Surface preparation (grinding and polishing) was done using an automatic polishing machine Mecatech 234 (PRESI). Micrographs of the joints and composite plates were taken using a SEM Zeiss EVO 10 (ZEISS) with an acceleration voltage of 15 kV. For the single-composite plate, the matrix-rich region between the fabric layers was evaluated.

Single-lap compression shear test (CST) was used to characterize the shear strength of the joints. This testing method was chosen for a direct comparison with the values of composite ILSS measured by double-notch compression shear test (DNC), which is often used for the characterization of CMCs.\textsuperscript{19} Tests were performed in accordance to the standard DIN EN 658-4. The composite plates used for joined samples were cut in the dimensions of 20 mm × 10 mm. The joint length was 7.9 ± 0.8 mm, resulting in a joint area of approximately 80 mm². Hence, the length of the joint was much smaller than the length of the plates. This was done in order to ensure that, during shear tests, the failure would occur in the joint region instead of interlaminar failure between the composite layers. Tests were performed on an universal testing machine Zwick/Roell Z005 (Zwick GmbH) equipped with a U2B/5kN load cell (HBM Inc). The compressive load was applied in the direction parallel to the joint with a traveling speed of 1 mm/min until failure. Therefore, shear strength was calculated by dividing the maximum applied load by the joint area. A total of five samples were tested for each type of joint. As previously mentioned, the strength of the joints was compared to the ILSS of single composite plates. DNC samples were machined from composite plates with the dimensions of 30 mm × 10 mm. Notches were machined on opposite sides of the sample using a diamond-wire saw Well model 6234 (WELL Diamond Wire Saws SA). The distance between the notches was of 8.3 ± 0.2 mm and the notch depth was at least half of the plate thickness. DNC tests were performed with the same parameters used for CST. A picture of the samples exemplifying their geometries can be seen in Figure 2. After the tests, the fracture surfaces of the tested samples were analyzed via dark-field microscopy using a digital optical microscope VHX-6000 (KEYENCE Deutschland GmbH).

### 3 RESULTS

#### 3.1 Microstructural analysis

Figure 3A shows a micrograph of the studied N610/AZ composite. The picture was centered on the matrix-rich region,

| Fiber content (%) | Porosity (%) | Bending strength (MPa) | ILSS (MPa) | $K_{IC}$ (MPa m$^{0.5}$) |
|-------------------|--------------|------------------------|------------|--------------------------|
| 24                | 34.9 ± 0.8   | 194 ± 19               | 8.4 ± 0.6  | 11.4 ± 0.8               |

\textbf{Table 1} Properties of N610/AZ composite produced by ionotropic gelation\textsuperscript{17}
in-between the fabric layers, and exemplifies two types of defects that are occasionally seen in these composites: vertical cracks and spherical pores. The cracks observed are probably caused by matrix shrinkage during sintering. The pores in the matrix-rich region can be related to trapped air during the stacking procedure. Nevertheless, a very good degree of fiber infiltration was obtained as no macropores were observed within the fabric layers.

The microstructure of the joints is shown in Figure 3B-D. As it can be seen in the micrographs, the joining area for the gel joint (Figure 3B) and green joint (Figure 3C) are very similar to the matrix-rich region of the N610/AZ composites. In general, there are no discontinuities between the joint and the composite plates. Hence, it is not possible to identify where the CMC plates end and where the joint begins. Just like in the regions between the fabric layers, pores and vertical cracks are observed along the joint. Nevertheless, a different microstructure was observed for the composite plates connected after sintering, Figure 3D. It should be noted that the scale of this figure is different since the joint was thicker than the other cases. A few voids with irregular shape were observed between the composite plates and the joining area. Besides the vertical cracks, horizontal cracks (along the joint) were also detected. Still, some parts where the joint showed good adhesion (no discontinuities) can be observed as well. For instance, no big defects were detected between the lower composite plate and the sintering joint in Figure 3D.
3.2 Shear strength

The shear strength of the single composite plates and joints were measured by DNC and CST, respectively. The results of the tests are presented in Figure 4. Comparing results of ILSS of the composite presented below (7.8 ± 0.5 MPa) and the one given in Table 1, it can be seen that the results measured by DNC are slightly lower. The values presented in the table were measured with the short-beam bending test configuration (standard DIN EN 658-5). The difference between the results of these two techniques is somewhat expected since DNC tends to lead to more conservative ILSS values due to the presence of the notches. The strength of the joints is in accordance to the observations made on the micrographs (Figure 3), in which the gel and green joints are very similar to matrix-rich region of the composite plates, whereas the sintering joint showed several defects. Statistically speaking, the strength of the gel and green joint are equal to the ILSS of the composites. Then again, the sintering joint showed much lower shear strength, 0.8 ± 0.2 MPa.

Further differences were seen in the load-displacement curves. While the composite plates and other joined samples showed only linear deformation before failure, the sintering joint showed a few small load drops before the maximum load was achieved. Examples of the fracture surface of each type of sample can be seen in Figure 5. The micrographs were taken from both sides of the same broken samples. The patterns observed for the gel joint (Figure 5B) and green joint (Figure 5C) are rather similar to the one observed for the DNC sample (Figure 5A). In both cases, exposed fibers are seen along the fracture surface. This indicates that, during failure, the crack propagates through the joint and through the outer layer of the composite plates, that is, interfacial failure. In the case of the sintering joint (Figure 5D), the failure was primarily adhesive. In other words, the composite plates were intact and crack propagation happened at the composite-joint interface. Furthermore, several cracks with different directions were observed in the exposed joint of the fracture surface. This can be associated with the microstructural defects observed in Figure 3D. At lower loads, crack propagation from the pre-existing defects takes place. The small load drops detected in the load-displacement curves are probably due to cracks that stabilize after reaching the irregular voids at the composite-joint interface. As a result, this joint shows lower shear strength.
The quality of the investigated joints is directly related to the interactions between the alginate chains, present in the composite plates and joint, and the cross-linker. Alginate is a copolymer of β-D-mannuronic acid (M) and α-L-guluronic acid (G), whereas the cross-linker aluminum acetate is a chemical compound soluble in water with linear formula of Al(OH)(C₂H₃O₂)₂. When aluminum acetate is added to the water-based slurry, it slowly dissolves releasing Al³⁺ ions. Multivalent cations like Al³⁺ react with the G part of alginate chains inducing interchain associations. This forms the so-called "egg-box" structure, in which G blocks of opposing alginate chains are cross-linked by the cations, as shown in Figure 6. The cations are located in-between the G groups and are coordinated by the oxygen atoms of the G units. This interaction is what gives the gel properties of the infiltrated layers.

The same reaction is expected to occur when a suspension containing more alginate and aluminum acetate is used to bond two previously gelled composite plates (gel joint). Considering the modeled ratio between cross-linked G units and multivalent cations, and the amount of aluminum acetate added for the first cross-link reaction, it is safe to assume that there are alginate chains on the surface of the gelled composite plates, which are not saturated with Al³⁺ ions. It is therefore suggested that these chains can be then cross-linked with the ones present in the joint during this second cross-linking, see Figure 6. Hence, the gel formed in the joining area will create a bond between the gelled composite plates and have similar properties compared to them. As a consequence, the joint will be identical to matrix-rich regions of the composite plates after sintering, as seen in Figure 3. A similar reaction occurs during the green joint. By wetting the joining surfaces with water, the alginate chains of the green bodies can interact with the chains present in the joining suspension once more. It is worth mentioning that the green joint was initially performed without wetting the composite plates. However, the strength of the joint was low and irregular voids were perceived in the joint; similarly to the ones observed in the sintering joint (Figure 3D). Therefore, it can be assumed that a proper joint can only be formed if
the alginate chains of the surface can interact with the ones in the joint. Hence, partially dissolving the alginate chains of the composite plates with water can permit this interaction.

Several defects were detected in the sintering joint (Figure 3D) and its shear strength was lower than for the other types of joint (Figure 4). During the sintering of the composite plates at 1200°C, the alginate chains are burned out along with the other remaining organic compounds. Therefore, the suspension used for joining has a lower interaction with the sintered plates. As a result, irregular voids are seen between the joint and the composites. Still, regions without defects were also observed, for example, joint connection with the lower plate in Figure 3D. The previously performed plasma treatment can clean the surface of ceramic substrates and increase their hydrophilicity.25 Therefore, the joining suspension can properly wet the surface of the composite plates resulting in the regions without defects. During the second sintering step, the ceramic particles present in the joint are consolidated, whereas the matrices of the composite plates are further densified. Since the first sintering step was performed at a relatively low temperature and for a short time, the composite plates still show considerable sinterability. Hence, physical connections are formed between the joint and the plates due to diffusion. Since the composite plates were previously sintered, it can be expected that they will present lower densification/shrinkage than the joint. This difference in shrinkage leads to the development of internal stresses in the joint, which in turn, leads to the formation of the horizontal cracks seen at the composite-joint interface (Figure 3D). As a result, this type of joint shows much lower shear strength (Figure 4) and adhesive failure (Figure 5D). Therefore, it is here suggested that the quality of this type of joint can be improved by performing the first sintering step at a lower temperature. By performing only a presintering step before the joining, the composite plates and the joint can properly densify during the second sintering.

With the exception of the sintering joint, the joints manufactured in this work showed shear strengths of around 8 MPa, being comparable to the ILSS of the composite plates (Figure 4). As previously mentioned, the literature on joining of Ox-CMCs is very limited. For that reason, there are not that many values to compare them with the shear strength obtained in this work. The gel and green joints showed higher shear strength than metallic brazes based on AgCuTi, AgCuSnTi, ZrNiTiHf, and TiCuAl, which have average shear strength ranging from 2-5 MPa.12 Glass-ceramic joints like SACM12 and GOX6 show possibly higher shear strength than the joints presented here. In the works from Akram et al6,12 the shear strength of these glass-ceramic joints could not be measured since the used Ox-CMCs plates failed due to delamination before the joint. During our experiments, it was identified that the failure was indeed in the joint area. Nonetheless, the joint strength is similar to the ILSS of the produced composites. This means that even if the joint strength would be higher, the material would still fail in shear due to the delamination of the composite layers. Besides, our approach produces a joint with the same properties of the matrix of the composite plates. Hence, incompatibilities during service time at high temperatures are not to be expected, for example, differences in the coefficient of thermal expansion or thermal/chemical stability. Another advantage of joining Ox-CMCs in the green state is that it eliminates the necessity of an additional thermal treatment. In comparison, the joining with SACM and GOX glass-ceramics is performed at the temperatures of 930°C and 1010°C, respectively.6,12

5 | CONCLUSIONS

In this work, ionotropic gelation technique was used to produce and join Nextel 610/alumina-zirconia oxide ceramic matrix composites. The joining capabilities of this technique were tested by joining composite plates at different stages of processing: gel state, dry green body and after sintering. In general, joining in the gel or green state
proved to be very effective. No discontinuities were observed between the joint and the composite plates. As a result, the properties of the joint are similar to the matrix-rich region of the composite plates. In both cases, the alginate chains of the composites can interact with the chains of the joining suspension. Hence, the joined plates can be consolidated together with the joint during the sintering step. When joining was performed after sintering, however, voids and cracks were detected at the joint interface, which led to lower shear strength. To avoid the formation of shrinkage cracks in the joint, it is suggested that the sintering temperature of the Ox-CMCs should be adjusted to consider the further densification that occurs during the sintering of the joint. In summary, ionotropic gelation is not only a promising technique for a flexible processing/shaping of Ox-CMCs, but also for joining them.

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