Abstract
Silicon carbide-based fiber-bonded ceramics, obtained from hot pressing of woven silicon carbide fibers, are a cost-effective alternative to ceramic-matrix composites due to their ease of fabrication, involving few processing steps, and competitive thermomechanical properties. In this work, we studied the high-temperature strength and thermal shock resistance of Si-Al-C-O and Si-Ti-C-O fiber-bonded SiC ceramics obtained from hot pressing of two types of ceramic fibers, by mechanical testing in four-point bending. The bending strength of Si-Al-C-O-based fiber-bonded ceramics at room temperature is $\sim 250$–$260$ MPa and remains constant with temperature, while the bending strength of Si-Ti-C-O increases slightly from the initial $220$ to $\sim 250$ MPa for the highest temperature. Both materials retain up to $90\%$ of their room temperature strength after thermal shocks of $1400^\circ$C and show no reduction in elastic moduli. After thermal shock, failure mode is the same as in the case of as-received materials.

KEYWORDS
fibers, silicon carbide, strength, thermal shock/thermal shock resistance

1 | INTRODUCTION
Ceramic matrix composites (CMCs) are the subject of great interest due to their numerous potential applications as structural elements in high-temperature and extreme environment systems. Applications in areas related to energy production and the improvement of energy efficiency are also numerous, for example in heat exchangers and thermal management devices, high-temperature gas filtration, or in nuclear fusion reactors, due to their excellent fracture toughness and thermal shock resistance. The interest in ceramic materials in general and CMCs in particular is especially relevant in the aerospace industry, and are currently used in strategic applications, such as hot-zone structural components of gas combustion turbines and aerojets, thermal protection systems in aerospace vehicles (X-38 re-entry vehicle), and advanced friction systems, such as brake disks in commercial vehicles or emergency braking systems on railways.

The success of CMCs is determined by their microstructural design that makes them tolerant to the presence of cracks and defects, but also by the individual properties of the fiber and matrix that make up the material. It is possible, by selecting both appropriately, to obtain composites with tailored properties for specific applications. For example, all-oxide CMCs are resistant to oxidation,
but their properties at temperatures above 1200°C are relatively poor due to subcritical crack growth effects and low creep resistance.11–13 To operate at higher temperatures, it is necessary to use nonoxide phases, such as graphite or SiC. The most studied composites contain carbon fibers in a carbon matrix (C/C) or SiC matrix (SiC/SiC) or SiC fibers in a SiC matrix (SiC/SiC). C/C composites retain their properties at very high temperature (> 2000°C) but cannot be used in oxidizing environments without coatings. SiC/SiC composites on the contrary are relatively resistant to oxidation as the initial oxide layer that is formed acts as a diffusion barrier, and for this reason, they have received great attention.

The development of SiC/SiC CMCs has gone hand in hand with the emergence of new ceramic fibers with which to obtain composites with improved properties. There is currently a wide range of oxygen-free fibers available.14,15 Of these, Tyranno-SA fibers, produced by Ube Industries (Tokyo, Japan), stand out for their properties. These fibers, developed by T. Ishikawa in the early nineties, are highly crystalline, resulting in an improvement of their mechanical properties, and are resistant to oxidation and contamination by vitreous and alkaline deposits.16 CMCs made of Tyranno-SA fibers have superior properties to those made with other fibers, such as Nicalon, Hi-Nicalon, or Sylramic.3,5

Fiber-bonded ceramics are placed halfway between conventional CMCs and monolithic ceramics produced by powder processing. Examples of these materials are Si-Ti-C-O and Si-Al-C-O fiber-bonded ceramics obtained by hot-pressing fabrics made with Tyranno and Tyranno-SA fibers, respectively.17,18 Fiber-bonded ceramics are significantly cheaper than CMCs to process since their manufacturing involves fewer processing steps and can be made into relatively complex shapes and geometries by using molds during pressing. Thanks to their microstructure containing a very high density of interfaces, fiber-bonded ceramics exhibit good thermomechanical properties and high-fracture toughness, comparable to that of CMCs.

There are several reports in which different aspects of the mechanical behavior of these materials are studied, such as the work of Matsunaga et al.19 who performed creep-rupture tests in bending. Their findings for Si-Ti-C-O ceramics indicate that these materials can withstand a continuous tensile load of 175 MPa for 1000 h in the temperature range 500–1150°C. In the case of the Si-Al-C-O, this limit would be at 225 MPa in the same range, decreasing to a value of 175 MPa for temperatures above 1300°C. Kajii et al.18 studied the three-point bending strength and fracture behavior of Si-Ti-C-O-based fiber-bonded ceramics manufactured under different processing conditions up to 1500°C in air.

An important property for high-temperature applications of ceramics is their thermal shock resistance, as rapid thermal cycling and thermal gradients cause thermal stresses, which can result in a loss of mechanical properties. Schneider20 analyzes various types of tests to evaluate the resistance to thermal shock of materials, such as cooling experiments in a cold water or oil bath or the disk irradiation method, comparing their advantages and disadvantages. There are some studies of thermal shock resistance of CMCs in the literature: for example, Yin et al. evaluated the thermal shock resistance of C/SiC compounds by heating the samples in a flame-generated combustion atmosphere for a few seconds and then cooling them in air.21 Levine et al.22 studied the thermal shock resistance of ultra-high temperature ceramics by repeated heating cycles in a combustion chamber with a variable H:O ratio, which allows to reach different temperatures of the flame, in view of possible applications in aeropulsion systems.

In general, it is expected for composite materials to exhibit a higher resistance to thermal shock than monolithic materials because their microstructural design prevents catastrophic failure due to microcracks generated by thermal stresses.23 In these materials, not only the properties of the fiber and the matrix determine their resistance to thermal shock, but also the orientation of the fibers, making composites with a higher density present greater resistance to shock.24 It is expected that the composites studied in this work have a high resistance to thermal shock given their low porosity and their high density of fibers and interface.

In this work, we evaluate the high-temperature bending of Si-Ti-C-O and Si-Al-C-O fiber-bonded ceramics and evaluate their thermal shock resistance by determining the retained strength in four-point bending after exposing the material to rapid cooling.

2 MATERIALS AND METHODS

2.1 Processing of fiber-bonded ceramics

Si-Ti-C-O fiber-bonded ceramics were supplied by UBE Industries (Yamaguchi, Japan) under the Tyrannohex brand as bend bars 50 mm long with a cross section of 4 mm wide by 3 mm tall. Details of its processing have been published elsewhere.18,19 In brief, continuous yarns of Si-Ti-C-O fibers are obtained from a poly titanocarboasilane polymer precursor by melt spinning and then continuously pyrolyzed under N2. The resulting fiber is sold commercially by UBE industries under the Tyranno™ name, grade LoxM, and exhibits a tensile strength of 3.3 GPa and a tensile modulus of 187 GPa, along with a thermal expansion coefficient of 3.1·10−6 K−1 and a density of 2.48 g·cm−3.
Materials characterization and mechanical testing

2.2 Materials characterization and mechanical testing

Samples were prepared for observation under the scanning electron microscope (SEM, Jeol 6460LV) using conventional metallographic procedures involving sectioning, grinding, and polishing with diamond slurries. X-ray diffraction was performed in a Bruker D8 Advance A25 diffractometer in a Bragg-Brentano configuration using Cu radiation. All these observations were carried out at the CITIUS central research facilities of the University of Sevilla.

The obtained Si-Ti-C-O fibers are then oxidized in air at 1000–1100°C for 20 h to form a thermally grown oxide layer 200–300 nm thick. Oxidized fibers are then woven in 8-HS configuration, stacked, and hot-pressed at 1750°C in Ar. During hot pressing, a thin carbon layer appears at the interface between the SiC and the SiO2 thermally grown oxide layer, which is attributed to an excess of carbon in the fiber precursor that diffuses toward the outer surface of the fibers during sintering.18,25 The final, dense ceramic consists of pressed Si-Ti-C-O fibers surrounded by a mostly amorphous SiO2 layer with TiC precipitates.

The Si-Al-C-O fiber-bonded ceramics studied in this work were also supplied by UBE Industries under the SA-Tyrannohex commercial brand as bend bars 50 mm long with a cross section of 4 mm wide by 3 mm tall. Details of its processing have also been published elsewhere.15–17

In brief, a poly-aluminocarbosilane polymer is spun into a continuous yarn and cured in air at 160°C to promote cross-linking. Then, the fibers are continuously pyrolyzed at 1300°C in Ar to obtain amorphous SiC1.5O0.4Al0.014 fibers with about 12% weight of nonstoichiometric carbon and oxygen. The resulting fibers in this intermediate state can then be sintered at 1700–2000°C to produce highly crystalline SiC fibers, sold commercially under the Tyranno-SA™ name, with a tensile strength of 2.8 GPa and a tensile modulus of 410 GPa,15 along with a thermal expansion coefficient of 4.5×10⁻⁶ K⁻¹ and a density of 3.02 g cm⁻³.

For the fabrication of fiber-bonded ceramics, the fibers in the intermediate state (prior to sintering) are woven into 8-HS cloths and stacked into shapers and molds to obtain the desired part shape. Hot pressing is then performed at 2000°C to both produce densification and structurally modify the fibers: during sintering some excess carbon is oxidized to form CO while the rest migrates to the outer surface of the fibers. Finally, densification modifies the cross-sectional shape of the fibers from circular to roughly hexagonal. The unreacted carbon remains as a thin layer of carbon at the fiber’s interfaces.17,19,26

Mechanical properties were measured in four-point bending in air at room temperature, 1000, 1200, and 1400°C in an electromechanical universal testing machine (EM1/50/FR, Microtest) with an attached high-temperature furnace, using polycrystalline high purity Al₂O₃ rods to transfer the load. An in-house designed, articulated bending fixture made of Hexoloy™ SA (Saint Gobain Ceramic Materials) was used, with an outer span of 40 mm and an inner span of 20 mm. This fixture is compliant with ASTM standards for bending strength, thermal shock resistance, determination of subcritical crack growth, and toughness of ceramics: C1161, C1211, C1525, C1576, C1465, and C1421B.

After the tests, each sample was inspected optically and those where the failure occurred outside of the loading span or at the loading rods were deemed unsuccessful and the results discarded. At least three successful tests were performed for each fiber-bonded ceramic and each testing condition. The applied load was parallel to the direction of pressing of the material, that is, perpendicular to the ceramic fabrics that make up the materials. Thus, the load at the tensile face was parallel to the ceramic fabrics.

For thermal shock experiments, the ceramic bars were heated in a furnace with a manually actuated sample elevator to temperatures of 1025, 1275, and 1425°C. Once the desired temperature was reached, the system was allowed to stabilize for 40 min before opening the furnace. The samples were then lowered and thrown into a silicone oil bath at 25°C, its temperature monitored using a type K thermocouple. In all cases, the time elapsed between opening of the furnace and dropping the samples in the cold bath was below 10 s. In this way, three samples of each composition, subjected to thermal shocks of 1000, 1250, and 1400°C, respectively, were tested. Subsequently, the samples were ultrasonically cleaned in three consecutive baths of distilled water with soap, distilled water, and acetone. After cleaning, the samples were dried on a stove at 100°C for 3 h before being subjected to bending tests at room temperature.

3 RESULTS AND DISCUSSION

Figure 1 shows the microstructure of the fiber-bonded ceramics studied in this work. In the case of Si-Al-C-O ceramics, fibers show polygonal cross-sections that are the result of the hot-pressing processing stage. A compositional gradient is observed, as evidenced by darker backscattered electron contrast in the inside of the fibers. The carbon concentration in the fibers is largest at their axis and decreases toward the outside of the fibers, leaving a thin carbon layer at their interface. In the case of Si-Ti-C-O fiber-bonded ceramics, fibers retain their
circular cross-section and are surrounded by a matrix of amorphous SiO$_2$. X-ray diffraction analysis of the as-received materials also reveals differences in their microstructure and composition (Figure 2). In the case of Si-Ti-C-O fiber-bonded ceramics, the reflections corresponding to SiC are significantly broader than in the case of Si-Al-C-O ceramics, which is due to a difference in SiC crystallite size. The Si-Al-C-O fiber-bonded ceramic is highly crystalline with grain sizes over 200 nm, due to the presence of Al which acts as a grain growth promoter during sintering, whereas the Si-Ti-C-O shows much lower crystallinity and significant background scattering from the presence of amorphous SiO$_2$.

Figure 3 shows representative stress-strain curves in four-point bending at different temperatures for both materials. A nonlinear range is observed before fracture, characteristic of composite materials in which cracks are generated in the matrix before fiber failure occurs.$^{27}$ In the case of Si-Ti-C-O, the curve of the test performed at 1400$^\circ$C shows some initial plastic deformation probably at the amorphous matrix of SiO$_2$. Fracture in Si-Al-C-O fiber-bonded ceramics is catastrophic in most cases, typical of tensile fracture at the fiber planes.$^{24}$ In the case of Si-Ti-C-O, this load drop is staggered, typical of a delamination fracture, in which successive load drops are due to failures caused by shearing of different layers of the material.$^{28}$ This is not the case for samples tested at 1400$^\circ$C, which exhibit brittle fracture similar to that of Si-Al-C-O. The absence of an actual matrix in Si-Al-C-O fiber-bonded ceramics facilitates that the cracks spread more quickly along the weak C interface between the fibers to cause the failure of the material, while in the case of Si-Ti-C-O, the presence of the SiO$_2$ matrix, in addition to the C interface...
surrounding the fibers, causes fracture to occur in the form of delamination.

The bending strength is shown as a function of temperature in Figure 4. In tensile fracture, the properties of the fibers play an essential role, while the failure by delamination is determined mainly by the properties of the matrix or the fiber–matrix interface.\textsuperscript{29,30} Thus, in the case of Si-Al-C-O, the proven stability of Tyranno-SA fibers up to high temperature\textsuperscript{16} explains why it maintains its bending strength with increasing temperature. In addition, the SiO$_2$ layer that covers the bars of the studied compounds resulting from their preoxidation acts as a diffusional barrier for O$_2$, protecting the SiC fibers from oxidation and above all avoiding the burnout of the C interface that covers these fibers. The slight increase in strength with temperature in the case of Si-Ti-C-O can be attributed to a plasticity effect on the SiO$_2$ matrix for temperatures above 1200°C. Ishikawa et al.\textsuperscript{31} observed an increase in the toughness of Si-Ti-C-O, at 1300 and 1400°C with respect to its value at room temperature and attributed it to this softening effect. The fact that both compounds have similar values of flexural strength may be due to the fact that the tensile strength of Tyranno fibers and SA fibers is very similar, 3.3 and 2.8 GPa, respectively.\textsuperscript{15}

Figure 4 also shows optical photographs of specimens from both materials after being tested in bending at each of the temperatures studied. From the macroscopic point of view, delamination is clearly observed in the case of Si-Ti-C-O. The cracks that originate in the central area can be seen in greater detail in the Scanning Electron Microscope (SEM) micrographs in Figure 5 (panel A for Si-Al-C-O and panel B for Si-Ti-C-O). The fracture of fibers is clearly visible, as well fiber pull-out in the case of Si-Ti-C-O due to the presence of a weak carbon interface that surrounds these fibers, that causes cracks to propagate preferentially through it.\textsuperscript{32} The propagation of cracks along this carbon interface is also clearly observed in panel (F) of Figure 5. The presence of this weak interface makes it easier
for cracks to propagate through it than through the fibers or the SiO\textsubscript{2} matrix, except in areas closer to the beginning of the fracture where the propagation energy of the cracks is greater. It is this interface that is responsible for the non-fragile fracture of these compounds.\textsuperscript{30,33}

Figure 6 shows room-temperature stress-strain curves in bending after thermal-shock up to 1400°C. Although final strength is reduced, the fracture mode is similar to that of as-received materials tested at room temperature. There are also no significant differences between the slope
FIGURE 6 Stress-strain curves in four-point bending for samples tested at room-temperature after thermal shock. (top) Si-Ti-C-O fiber-bonded ceramics. (bottom) Si-Al-C-O fiber-bonded ceramics

of curves of compounds subjected to thermal shock with respect to the curves of as-received materials, meaning that there is no appreciable change in the Young’s modulus after thermal shock, suggesting that very few cracks are generated in the matrix from the rapid cooling.\textsuperscript{21,34}

If we compare the maximum values of room temperature strength, we see in Figure 7 that there is no significant difference in strength after thermal shock, especially if we consider the error bars, since both have a decrease in their resistance to bending for all the shock temperatures analyzed and the percentage of retained strength is very similar in both cases, and after a shock of 1400\textdegree C both retain 90\% of their initial strength. This can be attributed to the presence of the C interface surrounding the SiC fibers in both ceramics and the good mechanical strength of the fibers. The change in temperature suffered by the samples in the shock generates thermal stresses due on the one hand to the temperature difference between the surface of the samples and their interior, and on the other hand to the difference in the coefficients of thermal expansion

FIGURE 7 (top) Bending strength as a function of thermal-shock temperature drop, dashed lines are included only as a visual aid. (bottom) SEM micrographs of a Si-Ti-C-O sample subjected to thermal shock $\Delta T = 1000\,^\circ\text{C}$ and fractured in bending. The top one is from the region where fracture started, while the bottom one is obtained from a region away from the main fracture zone, where cracks propagate at the interface between fiber mats between the fibers and the matrix (in the case of the Si-Ti-C-O material) which can cause thermal stresses resulting in the formation of matrix cracks, which thanks to that C interface that surrounds the fibers is deflected with penetrating the fibers. This effect has been observed in carbon fiber composites, coated by a C interface of about .3 μm, in a SiC matrix.\textsuperscript{21}
Since in the process of thermal shock applied to the samples they remain several minutes at high temperature in air, oxidation should be considered as a possible cause of the deterioration of their resistance to bending. Wang et al. \textsuperscript{24} studied the thermal shock resistance of Nicalon/CVI SiC composites and distinguished between oxidation and thermal stress effects, concluding that the strength degradation is due to a combined effect of both factors. In our case, the oxidation would be harmful by affecting the C interface that covers the fibers, but the SiO\textsubscript{2} layer resulting from the preoxidation prior to the shock of the bars efficiently protects the material. Otherwise, its resistance to bending would have suffered further deterioration. Figure 7 also shows micrographs from Si-Ti-C-O after being subjected to a shock of 1000\textdegree{}C and fractured in bending. In this case, cracks propagate mainly between layers of fibers with different orientations. In SiC/reaction-bonded silicon nitride compounds, \textsuperscript{34} the loss in bending resistance after subjecting the materials to thermal shocks above 650\textdegree{}C is attributed to the possibility of loss of integrity between planes due to matrix fracture, which is consistent with our observations.

Although a quantitative measure for the thermal shock resistance of CMCs or fiber-bonded ceramics is difficult to establish because of crack deflection at the interfaces, a parameter was defined by Chawla and Chawla \textsuperscript{35} that depends on the thermoelastic properties of the material as well as the critical temperature \( \Delta T_c \), the sudden drop in temperature that results in a reduction of mechanical properties:

\[
R' = \Delta T_c \frac{\sigma_c \cdot k \cdot (1 - \nu)}{\alpha E},
\]

where \( \sigma_c \) is the bending strength, \( k \) is the thermal conductivity, \( \alpha \) is the coefficient of thermal expansion, and \( E, \nu \) are the Young's modulus and Poisson's ratio, respectively. Table 1 summarizes the thermoelastic properties of the two fiber-bonded ceramics studied in this work, including a commercial SiC ceramic for comparison. \textsuperscript{36,37} For Si-Ti-C-O and Si-Al-C-O, the critical temperature was chosen as 800\textdegree{}C, the smallest temperature drop studied in this work, while for Hexoloy, we used recent data on the thermal shock of tubular hexoloy specimens, \textsuperscript{38} showing cracking for a temperature drop of 400\textdegree{}C or higher, in agreement with other works. \textsuperscript{39} For fiber-bonded ceramics, the obtained thermal shock resistance represents an upper bound. A more interesting parameter would be the critical strength retention, the fraction of bending strength that is retained after a temperature drop equal to the critical temperature. In the case of Si-Ti-C-O and Si-Al-C-O, this would be \( \sim 90\% \) at \( \Delta T_c = 800 \textdegree{}C \), while for Hexoloy, it is \( \sim 50\% \) at \( \Delta T_c = 400 \textdegree{}C \).

\[\textbf{TABLE 1} \quad \text{Thermoelastic parameters for Si-Ti-C-O, Si-Al-C-O, and Hexoloy-SA}\]

<table>
<thead>
<tr>
<th></th>
<th>( \Delta T_c ) (K)</th>
<th>( E ) (GPa)</th>
<th>( \nu )</th>
<th>( \sigma_f ) (MPa)</th>
<th>( k ) (W m\textsuperscript{-1} K\textsuperscript{-1})</th>
<th>( \alpha ) (\texttimes{}10\textsuperscript{-6} K\textsuperscript{-1})</th>
<th>( R' ) (\texttimes{}10\textsuperscript{6} W K m\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Ti-C-O</td>
<td>800</td>
<td>115</td>
<td>.22</td>
<td>220</td>
<td>3.9</td>
<td>3.20</td>
<td>.9</td>
</tr>
<tr>
<td>Si-Al-C-O</td>
<td>800</td>
<td>300</td>
<td>.12</td>
<td>260</td>
<td>72</td>
<td>3.20</td>
<td>10.0</td>
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<tr>
<td>Hexoloy-SA</td>
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<td>430</td>
<td>.14</td>
<td>380</td>
<td>78</td>
<td>4</td>
<td>5.9</td>
</tr>
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\[4 \quad \text{CONCLUSIONS}\]

Four-point bending tests have been carried out on Si-Ti-C-O and Si-Al-C-O fiber-bonded ceramics at air temperatures of 25, 1000, 1200, and 1400\textdegree{}C. In the case of Si-Al-C-O ceramics, bending strength is \( \sim 250–260 \text{ MPa} \) and remains constant with temperature due to the high thermal stability of its fibers and the fact that initial oxidation protects the carbon layer at the interface between the fibers. The bending strength of Si-Ti-C-O increases slightly from the initial 220 to \( \sim 250 \text{ MPa} \) for the highest temperature, probably due to plastic flow SiO\textsubscript{2} matrix which reduces the stress concentration on defects. While the load drop after fracture of the Si-Al-C-O ceramic is abrupt, in the case of Si-Ti-C-O, it occurs in a staggered manner, due to fracture by delamination. The absence of a matrix in the case of Si-Al-C-O may explain this difference. In both cases, the carbon interface surrounding the fibers influences the propagation of cracks.

We have subjected both composites to a thermal shock of 1000, 1250, and 1400\textdegree{}C with respect to room temperature, cooling in a cold bath of silicone oil after heating in a furnace for 1 h. These thermal shocks do not significantly affect the bending strength at room temperature. In the stress-strain curves of the bending tests of both materials, there is no change in the fracture mode or appreciable difference in the elastic moduli when compared to the as-received materials. Both fiber-bonded ceramics retain \( \sim 90\% \) of their room temperature bending strength after being subjected to thermal shock of up to 1400\textdegree{}C. This high resistance to thermal shock can be attributed to the presence of the carbon interface surrounding the fibers, which efficiently deflects the cracks generated from thermal stresses.

\[\textbf{ACKNOWLEDGMENTS}\]

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REFERENCES


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