

High temperature oxidation of multilayered SiC processed by tape casting and sintering

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Abstract

The oxidation behaviour of a multilayer SiC ceramic was investigated at high temperatures. The ceramic samples were processed by tape casting of a slurry containing α -SiC powders, forming of green tubular components and sintering without pressure. The oxidation resistance of this ceramic material was investigated by temperature programmed oxidation (TPO); the gaseous oxidation products were analysed by mass spectrometry. Thermal gravimetric analyses (TGA) were also performed. Buckles, machined from the multilayer ceramic tubes, were submitted to long-term oxidation treatments carried out at 1200, 1400 and 1600 °C in air. The microstructure and the radial compressive strength of these specimens were compared before and after oxidation. Microstructure was investigated by SEM–EDS and X-ray diffraction. The multilayered SiC showed increased toughness with respect to conventional ceramics, owing to delamination phenomena occurring before failure. Oxidation mainly affected the material surface, where a thin layer of silica grew. Oxidation treatments did not suppress the energy adsorbing mechanism occurring during the fracture process. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ceramics might be attractive materials for high temperature applications provided that both their reliability and toughness could be improved. Monolithic ceramics show a catastrophic fracture behaviour under applied stress due to the lack of energy absorbing mechanisms in the failure process. Several tough composites and multilayer ceramics were, however, developed in recent years. The key factor improving the toughness of these materials is the presence of weak interfaces between fibres and the composite matrix or between the ceramic layers. These interfaces allow for energy dissipation before fracture through mechanisms of crack deflection, crack bridging, fibre pull out and interface delamination. Fibre debonding and pull out are frequently achieved by putting a thin interphase layer on the fibre surface. For instance, interphases, generally less than 1 μm thick, made of carbon or boron nitride, were successfully used

in SiC/SiC_f composites.^{1–3} Unfortunately, a pyrocarbon interphase easily undergoes oxidation, thus preventing many structural applications of SiC/SiC_f at high temperatures.^{4–7} Several kinds of oxidation barriers deposited on the composite surface have been investigated.^{6,8–13} Even though these surface coatings delay the oxidation process, the composite degradation in oxidising environment still remains one of the more important problems to be overcome.¹⁴ Another problem preventing widespread ceramic/ceramic composite applications is their high cost due to the prohibitively expensive fabrication technologies.

Multilayered ceramics, generally processed by tape casting and firing or hot pressing,^{15–20} are cheaper materials than fibre reinforced composites. Several multilayer ceramics, formed by stacking of layers, differing in chemical composition or porosity, have been investigated: Al₂O₃/ZrO₂;^{19–21} Al₂O₃/SiC;²² Si₃N₄ or Si₃N₄/BN;^{23,24} Al₂O₃/TiC/MoSi₂;¹⁷ C/SiC;²⁵ Al₂O₃/MoSi₂;²⁶ 3Al₂O₃ 2SiO₂/ZrO₂;²⁷ SiC/C/SiC.¹⁸ Also in the case of these laminates an enhanced toughness over conventional ceramics was achieved by the introduction of weak interfaces. The presence of the different layers controls

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the crack path, frequently avoiding completely brittle behaviour.²⁸ When the layers are strongly bonded together, a crack in one layer can propagate readily into the adjacent layer, and then the material behaves as a conventional ceramic. In contrast, if the sliding resistance of the interface is poor, sliding of the layers past one other, that is delamination, occurs before cracking. Finally, even where the interface is sufficiently strong to avoid sliding, crack deflection at the interface, with crack growth along the interface and further delamination may occur. When a crack enters a porous or weak layer, deflection can also occur, thus increasing fracture work.^{17,18,23,26} An alternative strategy to obtain crack deviation is to exploit residual stresses at interfaces.^{29,30,31} Stresses can arise, during the processing of hybrid ceramic laminates composed of alternating layers of two or more different ceramic materials, owing to differential drying, differential densification and shrinkage or differential thermal expansion during cooling.^{27,31} However, for these reasons, unwanted cracks may form already during material fabrication. Furthermore, the mismatch in thermal expansion between the different layers makes the material prone to damage by thermal fatigue, thus preventing high temperature applications. For similar applications in oxidative environment the adoption of carbon layers should also be avoided.

This paper deals with the processing of a multilayered SiC ceramic fabricated by a simple way, involving tape casting and sintering without pressure. The high temperature oxidation resistance of this SiC multilayer is investigated by using thermoanalytical techniques as well as by comparing the microstructure and mechanical behaviour before and after long-term oxidation treatments.

2. Experimental

2.1. Materials and methods

2.1.1. Material processing

Multilayered SiC tubular specimens were prepared in F.N (S.p. Nuove Tecnologie e Servizi Avanzati, Boscomarengo, Italy). The processing method involved several steps: slurry preparation, tape casting, solvent evaporation, specimen forming, debinding and sintering.

The slurry was obtained by dispersing α -SiC powder (15 m²/g, produced by Starck) in a mixture of organic solvents, plasticisers and binders (the slurry composition is detailed in Table 1). Boron and carbon (about 2 wt.%) were added, in order to aid the final sintering treatment. Thin sheets were produced by casting the slurry on a moving plastic support (Mylar film). The layer thickness was controlled by a blade, obtaining a deposited layer about 0.8–1 mm thick. The organic solvents were then slowly removed by controlled evaporation in air. The 0.3 mm thick SiC green tape was carefully detached from

Table 1
Slurry composition

| | | % Weight | % Weight after solvents evaporation |
|-----------|---|----------|-------------------------------------|
| Powder | 15 m ² /g α -SiC powder | 33.98 | 69.22 |
| Binder | (poly)vinyl butyral | 9.75 | 19.86 |
| Solvents | Ethanol | 11.88 | |
| | Butanol | 18.24 | |
| | Tetrachloroethylene | 20.79 | |
| Additives | Plasticizer | 5.09 | 10.37 |
| | Anti foaming agent | 0.27 | 0.55 |

the plastic support and wrapped on a mandrel to obtain tubular specimens. Tubular specimens were submitted to a debinding treatment, carried out by slow heating up to 500 °C under an argon atmosphere. The final pressureless sintering step was performed at 2180 °C under argon. A severe shrinkage (about 20%) occurred during sintering; ceramic tubes 100 mm long with an external diameter of 36 mm were obtained. The final thickness of the tube wall, made of the lay up of seven SiC layers, was about 1.5 mm. Buckles (rings) 10 mm long were machined from the tubes by using diamond tools.

Microstructure, Mechanical strength and oxidation resistance of the multilayered material were investigated.

2.1.2. Oxidation tests

Firstly, the material oxidation resistance was studied by temperature programmed oxidation (TPO) and thermal gravimetric analysis (TGA). A Thermoquest TPD/R/O 1100 instrument, equipped with a mass spectrometer (Balzer Quadstar 422), and a Setaram TGA92 analyser were respectively used for these tests.

Samples of ceramic material (0.5–1 g in weight, obtained by cutting sectors of the multilayered SiC rings) were put in the TPO sample holder and then kept at 300 °C for 3 h in a helium gas flow, with the aim of removing moisture and any other adsorbed gaseous species. Afterwards, these samples were cooled down to ambient temperature and then heated up to 1100 °C (heating rate of 10 °C/min) under a gaseous oxidising stream (oxygen/helium, 5% vol. of oxygen, flow = 2 ml/min). Contemporaneously, the gas stream, flowing out from the TPD/R/O reactor during a programmed temperature scan, was analysed by the mass spectrometer. This analyser measured the content in the gaseous flow of the species with mass of 44, 28 and 12 (that is the amounts of CO₂, CO and C). The content variations of these species allowed study of the multilayer oxidation process.

Small samples of multilayered SiC (few tenths of a milligram in weight, machined by a diamond wheel from the multilayered rings) were submitted to TGA up to 1350 °C. After a preliminary isothermal treatment (10 min long) at 120 °C under helium, these samples

were heated (rate 10 °C/min) in the TGA equipment under an air flow (33 ml/min). The sample weight variation was related to oxidation of the SiC and carbon present in the sample respectively to silica or carbon dioxide.

Long-term oxidation treatments were also carried out in calm air at high temperatures. Buckles 10 mm long were kept at 1200 °C for 100 and 200 h, at 1400 °C for 100 and 200 h or at 1600 °C for 100 h. After these treatments both the specimen microstructure and mechanical strength were investigated.

2.1.3. Material characterisation

The microstructure of the ceramic samples was studied by microscopy and X-ray diffraction. A Philips 515 scanning electron microscope equipped with an energy dispersive spectrometer (PV9900) and a Philips PW1710 diffractometer (CuK_α radiation) were used. The XRD patterns of both buckle surface and buckle core were compared before and after the oxidising treatments. To this purpose, the surface layers of the specimens were removed by grinding, thus obtaining a powder sample representative of the sample surface. After the removal of the more external SiC layers, the remaining material was milled. The powders arising from both the external layers and multilayer core were submitted to XRD analysis.

The mechanical strength of the buckles was investigated by radial compression tests, carried out according to the ISO 2739 specification. This test is not specifically designed for ceramic buckles, but it was suitable for

investigating the effect of oxidation on strength. At least three samples for each oxidising condition were examined and the corresponding compression test results were averaged. Compression tests were performed by pressing the specimens between two flat plates at ambient temperature, using a Sintech 10D equipment. These experiments, performed at constant strain rate with a displacement rate of 0.5 mm/min, made it possible to obtain the stress/displacement curve as well as to calculate the compression strength according to the equation:

$$\text{Compression strength} = \frac{F(D - e)}{Le^2}$$

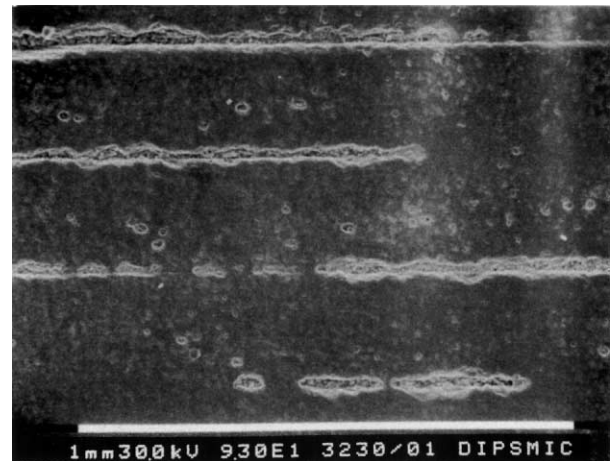


Fig. 1. Stacking of SiC layers in the multilayered SiC ceramic.

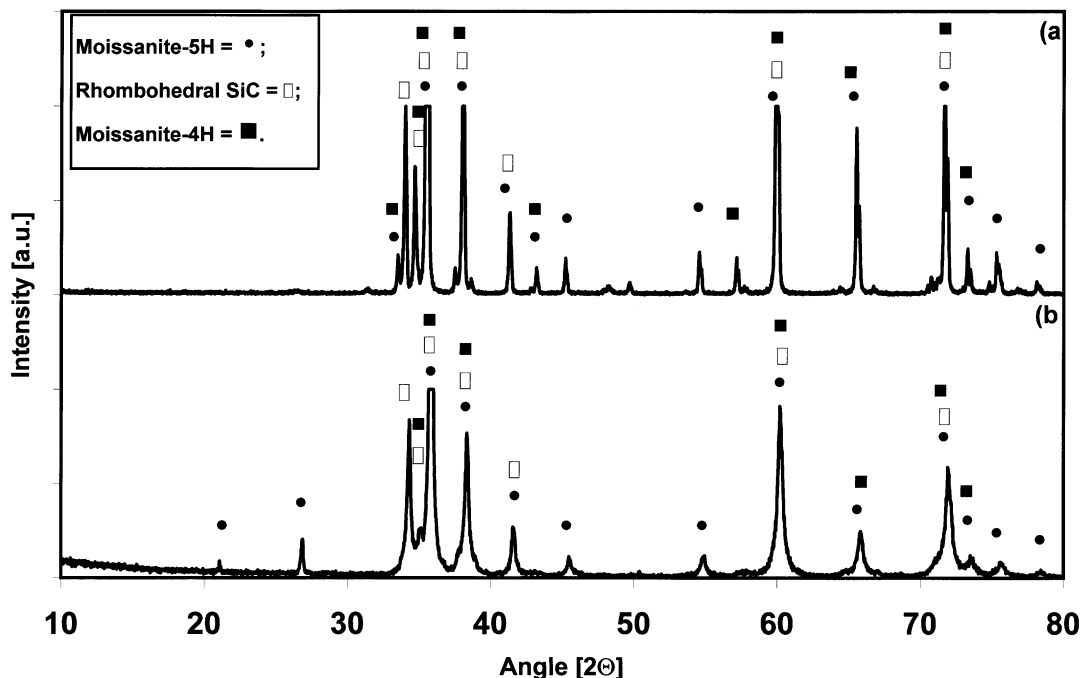


Fig. 2. XRD patterns of (a) powdered multilayered SiC; (b) SiC powder used for material preparation.

where: F = load at failure, L = buckle length, D = buckle external diameter, and e = thickness of the buckle wall. The fracture surfaces were examined by SEM.

Indentation tests were carried out in order to investigate crack propagation inside the multilayer ceramic. Vickers indentations were performed (with loads ranging between 3 and 10 kg) on buckle sections taken both in the parallel and transversal direction with respect to the buckle axis.

2.2. Results and discussion

2.2.1. As-processed material microstructure

The multilayered structure consists of seven SiC layers 190–220 μm thick. As all these layers are made of the same material, the interface between two neighbouring single layers is clearly distinguished only after delamination. Fig. 1 shows the interfaces between the layers, observed after partial delamination on the cross section of

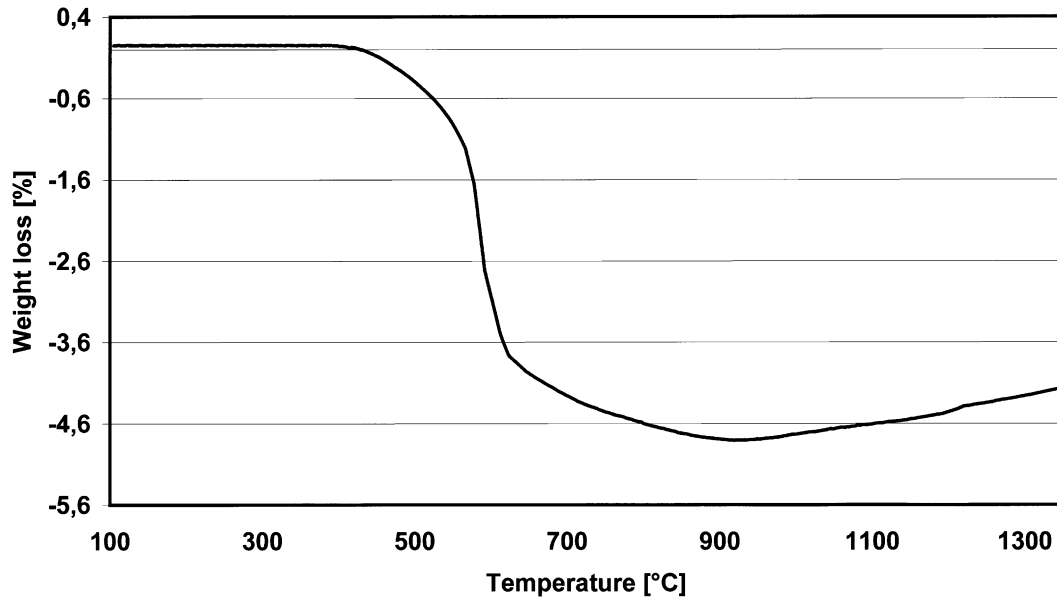


Fig. 3. TGA curve of the as-processed multilayered SiC ceramic.

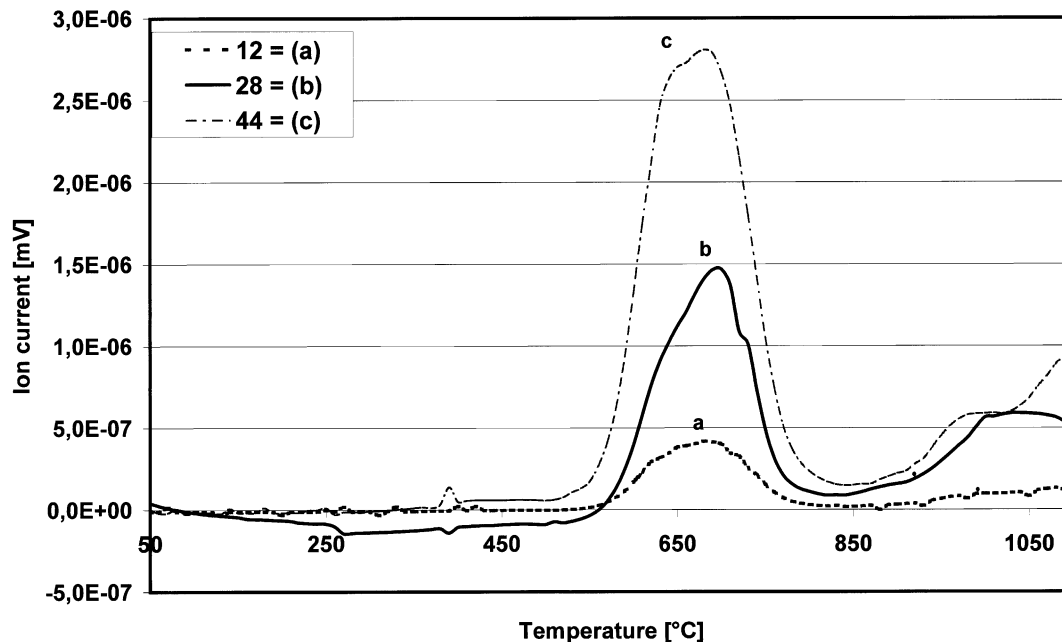


Fig. 4. TPO curves of the as-processed multilayered ceramic: (a) carbon; (b) carbon oxide; (c) carbon dioxide.

a tubular sample, previously submitted to a compressive load. Small pores have been detected close to the interfaces between adjacent SiC layers. The XRD pattern of the as processed material shows reflexes belonging to alpha SiC (Fig. 2a); in this figure the laminate diffraction spectrum is compared with that of the alpha SiC powder used for slurry preparation (Fig. 2b). All the peaks showing appreciable intensity in these two spectra can be

attributed to different polytypes of α SiC: moissanite-5H, moissanite-4H and rhombohedral silicon carbide (ICDD card Nos. 42-1360, 29-1127 and 4-0756, respectively). The powders sampled from both the specimen surface and the multilayer core showed the same diffraction pattern, which demonstrates that each single layer is made of α -SiC only and that no new phase (detectable by XRD) forms during material processing.

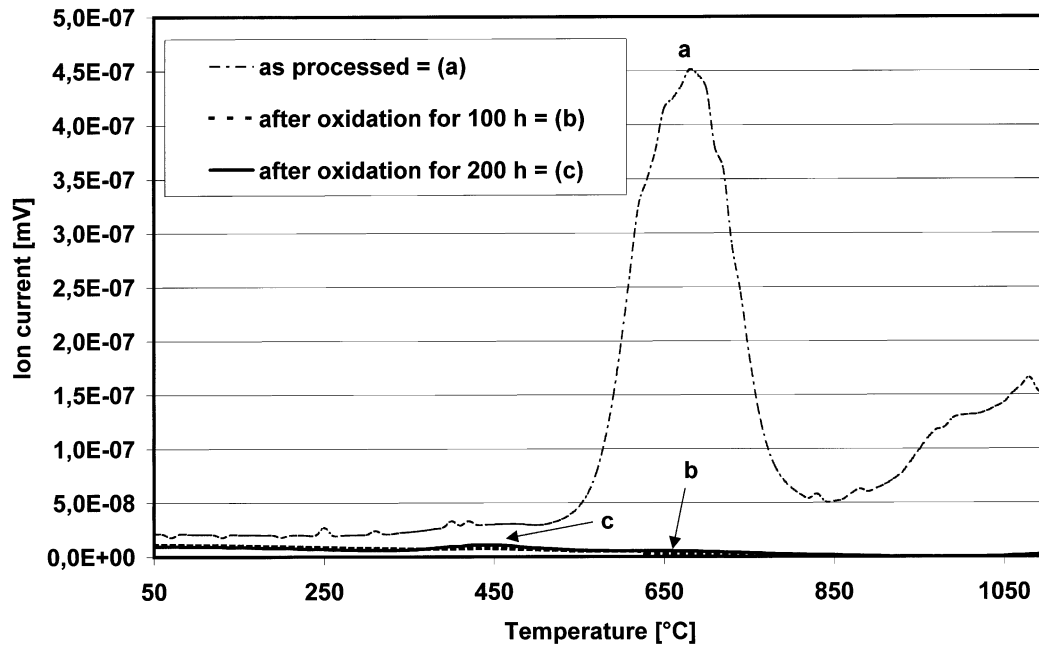


Fig. 5. TPO curves showing CO_2 formation versus temperature; comparison of curves belonging to: (a) as-processed material; (b) material after oxidation in air at 1200°C for 100 h; (c) material after oxidation in air at 1200°C for 200 h.

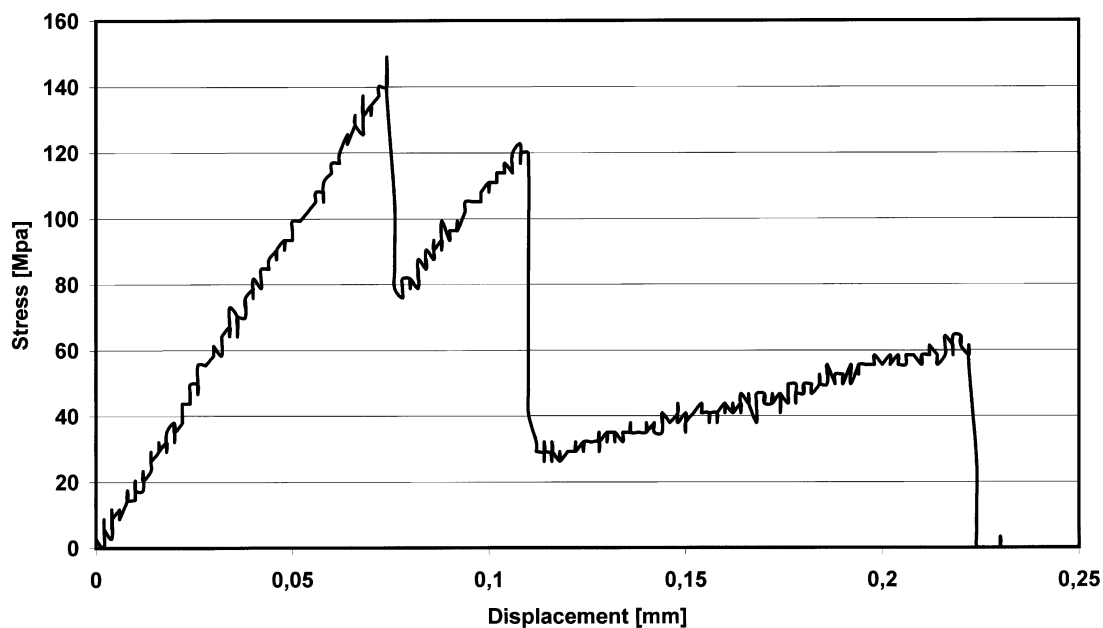


Fig. 6. Stress-displacement compression curve of the as-processed material.

2.3. TGA and TPO tests

TGA analysis shows that the ceramic material undergoes a significant progressive loss of weight during heating in air in the temperature range between 400 and 900 °C, after which the sample weight only slightly increases with temperature up to 1350 °C (Fig. 3). The weight loss is very likely due to the oxidation of carbon contained in the material (carbon was added to the slurry in order to help sintering and an additional amount of carbon also forms owing to the pyrolysis of plasticisers and binders), while the sample weight

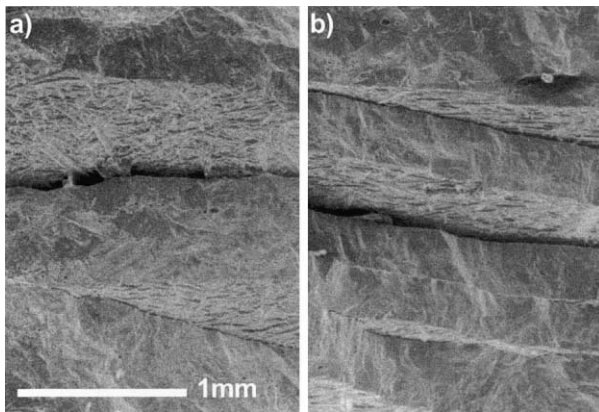


Fig. 7. Fracture surfaces showing delamination: (a) as-processed buckle; (b) buckle previously submitted to oxidation in air for 200 h at 1200 °C.

slightly increases above 900 °C probably because of the slow oxidation of SiC to SiO₂.

TPO results are reported in Fig. 4: in this figure the curves related with the presence of CO₂, CO and C in the gas flowing outlet from the TPO reactor are plotted against the sample temperature (CO and C species very likely form from carbon dioxide within the mass spectrometer). The CO₂ emission reaches its maximum at about 650 °C, which is the temperature corresponding to rapid air combustion of carbon, thus confirming that the carbon contained in the ceramic sample is responsible for the most important phenomena detected by TGA and TPO during the temperature scan. A subsequent increase of CO₂ emission was observed starting from about 900 °C, showing that SiC oxidation starts at this temperature.

The SiC samples treated in air at 1200 °C for 100 and 200 h were also submitted to TPO experiments. The TPO curves showing the CO₂ emission from these two samples are compared with that characteristic of the as-processed material in Fig. 5. This figure demonstrates that the CO₂ trace in a TPO curve is almost completely suppressed after a long-term oxidation treatment, because this allows for either combustion of carbon or SiC surface oxidation.

2.4. Compression and indentation tests

A buckle average compressive strength of 135 MPa was measured for the as-processed material (Table 2). A typical stress-displacement curve for this material is

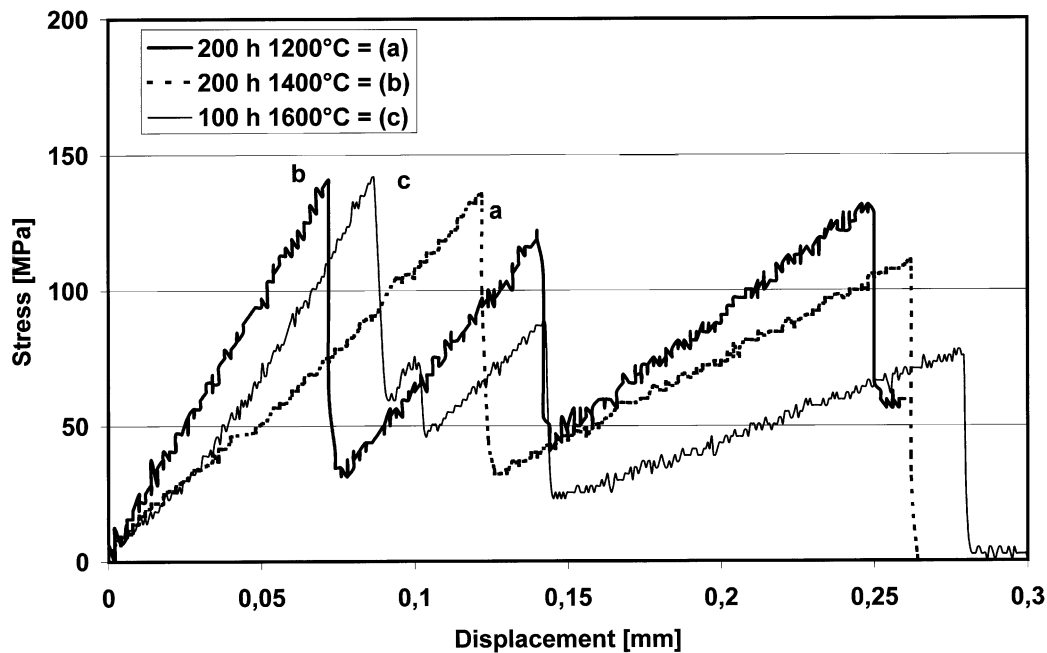


Fig. 8. Stress-displacement compression curves characteristic of specimens oxidised in air for 200 h at 1200 °C (a), 200 h at 1400 °C (b) and 100 h at 1600 °C (c).

Table 2
Compressive strength of buckles before and after oxidation treatments

| Oxidation treatment | | Compressive strength (MPa) |
|---------------------|----------|----------------------------|
| Temperature (°C) | Time (h) | |
| – | – | 135 |
| 1200 | 100 | 132 |
| 1200 | 200 | 142 |
| 1400 | 100 | 126 |
| 1400 | 200 | 141 |
| 1600 | 100 | 137 |

shown in Fig. 6. This curve has a particular trend. The stress/displacement response is linear elastic up to a maximum, occurring at the failure of any SiC layers, then the stress abruptly falls, but without resulting in the specimen breaking. The multilayer ceramic still can sustain stresses after the onset of fracture. The SiC layers not yet damaged support a further stress increase, generally up to about the 70% of the maximum value previously reached; meanwhile the delamination phenomena allow for significant sample deformation before the final breaking. The delamination mechanism, which provides a toughening effect, is most evident when the fracture surfaces are examined (Fig. 7).

Long-term oxidation treatments carried out in severe conditions (1200, 1400 and 1600 °C) did not appreciably change either the compressive strength of the buckles (Table 1) or their failure mode. These oxidation treatments may even result in an increase of displacement at failure (Fig. 8). The toughening delamination phenomena still occur after oxidation, as shown by the shape of the stress-displacement curves and the fracture surface morphology of oxidised specimens (Figs. 7 and 8).

Vickers indentation, performed on the cross sections of the buckles, resulted in radial cracks of unequal length, indicating the presence of residual stresses. Actually, cracks preferentially travel in the direction parallel to the buckle axis, which is the direction parallel to the interfaces between adjacent layers. Furthermore, if the indentation is performed inside one of the SiC layers constituting the walls of the buckle, these cracks are deflected towards the sample surface: they stop at the concave or the convex buckle surface, when the indentation is made inside the SiC layer constituting the inner or the outer buckle wall respectively (Fig. 9a). Indentations affecting an intermediate SiC layer (placed at the multilayer core) chiefly cause the formation of cracks parallel to this layer (Fig. 9b). The shorter cracks growing in other directions are frequently deflected, for instance when they reach the interface between two layers. Conclusively, indentation tests performed on both parallel and cross buckle sections suggest that cracks preferentially form parallel to the layer interfaces, which hinders the fracture propagation from one SiC layer to its neighbour.

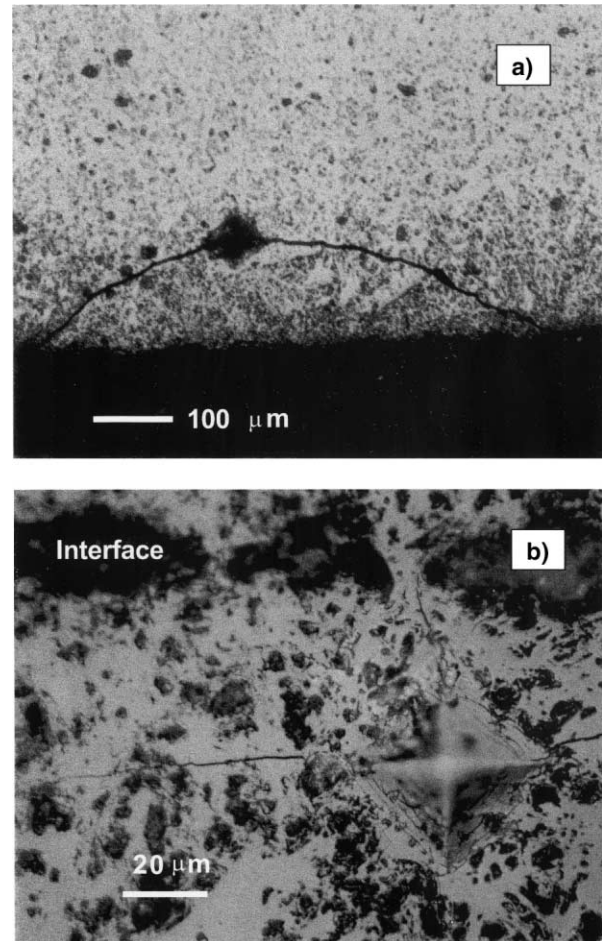


Fig. 9. Indentation cracks: (a) deflection towards the sample surface of cracks growing in an external SiC layer; (b) indentation of an intermediate SiC layer with cracks growing in the direction parallel to interfaces.

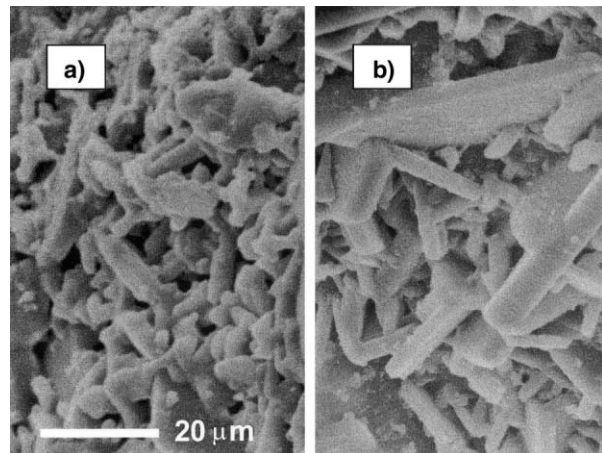


Fig. 10. Fracture surfaces: size of SiC grains in the as-processed material (a) and after oxidation in air for 200 h at 1200 °C (b).

2.5. Microstructure of oxidised specimens

As expected, a high temperature thermal treatment in an oxidative environment resulted in the growth of the

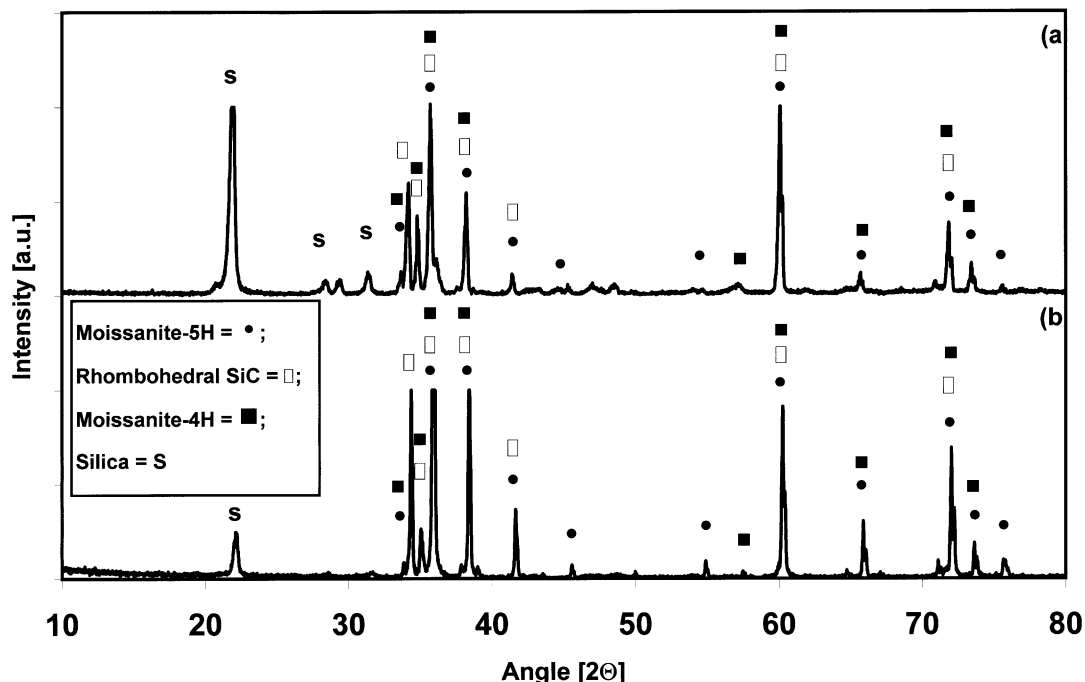


Fig. 11. XRD patterns of powders taken from different parts of a buckle oxidised at 1600 °C for 100 h: (a) buckle surface; (b) buckle core.

SiC grains (Fig. 10). XRD patterns put in evidence that silicon carbide suffers oxidation to silica. However, it is chiefly the buckle surface which undergoes this reaction; reflections belonging to silica are most evident in the powders sampled from the specimen surface, while the powders taken after the removal of the more external SiC layer show an XRD pattern containing all the peaks characteristic of silicon carbide and only a low-intensity peak pertaining to silica (Fig. 11, patterns a and b). A silica layer with thickness ranging between 35 and 50 μm was observed by SEM on the fracture surface of samples oxidised in the most severe conditions (1600 °C for 100 h) (Fig. 12). In this figure the EDS spectrum of the oxide scale is also reported, showing the contemporaneous presence of silicon and oxygen. This last

element was not detected by EDS in this specimen below the oxidation layer. Conclusively, the oxidation of multi-layered SiC mainly regards a fraction of the more external SiC layer. Firstly, a silica coating, well adherent to SiC, forms; afterwards, this layer greatly slows down oxygen diffusion, thus preventing the oxidation of the sample core. However, due to the geometry of the examined specimens (short buckles), gaseous oxygen penetrates between adjacent layers, diffusing in the direction parallel to the buckle axis and thus causing oxidation at the layer interfaces. Oxygen was detected in the interfacial zones, at distances from the buckle extremity up to about 1 mm, by EDS analysis. In these interfacial zones a higher oxygen concentration was observed in concomitance with the presence of voids of major dimension.

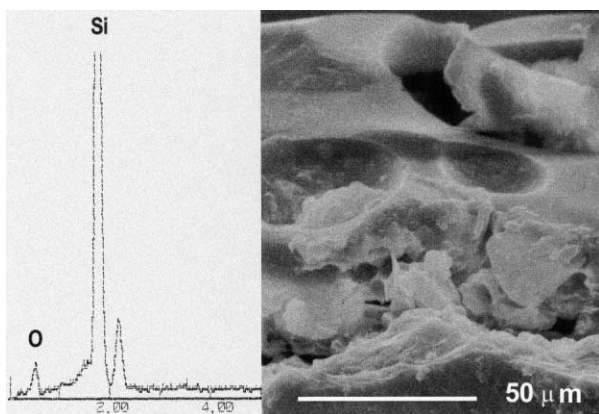


Fig. 12. Silica scale grown on the surface of a sample kept for 100 h at 1600 °C in air; EDS spectrum of this area.

3. Conclusions

Tubular components of α -SiC with a multilayer structure were produced by tape casting and sintering without pressure. This simple processing method is suitable for making a tough SiC ceramic.

Compression tests indicated that the multilayer toughness is increased over that of a conventional ceramic owing to delamination phenomena.

Indentation tests showed that residual stresses control the crack path.

During a temperature scan in an oxidative environment, firstly carbon (added to the slurry in order to help sintering and arising from pyrolysis of the slurry additives too) burns, afterwards, the SiC sample surface is

oxidised to silica starting from about 900 °C. A continuous silica coating, which acts as a barrier for a further oxygen penetration, forms.

Oxygen diffusion along the interfaces between the layers and, consequently, oxidation in these zones were observed too.

In spite of the oxidative reactions, both the compressive strength and the fracture behaviour of the multilayer ceramic were found unchanged, even after oxidation treatments carried out in very severe conditions (up to 100 h at 1600 °C).

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