Proceedings of CIEC 16 European Inter-regional Conference on Ceramics - Torino, 9-11 September 2018

(Article begins on next page)

19 April 2024

Ceramic laminates integrating ZrB$_2$/SiC and SiC layers for TPS applications.

E. Padovano[1*], F. Trevisan[1], S. Biamino[1], O. Ostrovskaya[1] and C. Badini[1]

[1] *Politecnico di Torino, Department of Applied Science and Technology, Corso Duca degli Abruzzi 24, 10129 Torino.*
[*] *Corresponding author. E-mail: elisa.padovano@polito.it*

Abstract

Multilayer structures integrating ZrB$_2$-SiC layers stacked in between SiC ones were successfully prepared using tape casting technique and pressureless sintering. Thin cracks propagated in the composite layers without affecting SiC ones; their formation was due to residual stresses developed in the two materials because of the differences in their CTEs and shrinkage during the cooling from sintering temperature. The measurement of the elastic modulus and the flexural strength of hybrid multilayer evidenced that the presence of these cracks do not significantly affect the mechanical behavior of laminates.

Keywords

Tape casting; Mechanical properties testing; Ceramics; Residual Stresses

Introduction

High temperature ceramics, ultra-high temperature ceramics and their composites are considered the most promising candidates for use in sharp leading edges and nose cones of atmospheric re-entry vehicles. These materials show in fact rather good mechanical properties combined with high melting temperatures and high resistance to environmental degradation. Among them SiC and ZrB$_2$-SiC composites are widely used for aerospace applications. It is well known that SiC shows excellent oxidation resistance up to 1600°C since a thin silica passive layer forms on its surface. However at high temperatures and under very low oxygen partial pressure the passive layer can be destroyed owing to active oxidation [3]. In addition cristobalite melts at 1725°C and then it evaporates, while the sharp profiles of space vehicles and hypersonic aircraft demand materials able to sustain temperatures up to around 2000°C. Differently the oxidation of ZrB$_2$ and ZrB$_2$-SiC composites results in the formation of a glassy phase that easily volatilizes, and solid zirconia which melts well above 2000°C. Therefore ZrB$_2$-based ceramics can be used under extreme temperature conditions, but unfortunately their oxidation resistance is much worse than that of SiC below 1700°C [4]. Then it is not possible using a single material showing superior oxidation resistance all over the range of temperatures that are experienced by TPSs. In this paper multilayer structures comprising ZrB$_2$-SiC layers stacked in between SiC ones have been successfully prepared by tape casting and pressureless sintering. The advantage of using laminates is related to their improved toughness with respect to conventional ceramics and the possibility of adjusting their

_____

architecture and chemical composition. Such a kind of structure would allow to hinder the quick recession of TPS when the temperature exceeds 1700°C, thus providing structures able to sustain oxidation in a very wide temperature range. Two kinds of specimens were obtained: multilayer containing ten SiC or ZrB_2/SiC composite sheets and hybrid laminates comprising alternating layers of SiC and ZrB_2/SiC. They were designed according to the following symmetric structure: 3 SiC layers–1ZrB_2/SiC layer-2SiC layers–1ZrB_2/SiC layer-3SiC layers. The effect of composite thickness layers in hybrid structures (ZS-1 and ZS-2) was studied. Moreover the microstructure and the mechanical behaviour of laminates were investigated.

Results and discussion

Laminates	Layer thickness after sintering [µm]	Relative density [% of the theoretical]	Elastic modulus [GPa]	Flexural strength [MPa]
SiC	163 ± 5	91.9 ± 0.1	339 ± 19	324 ± 24
80ZrB_2-20SiC	105 ± 5	97.3 ± 0.2	444 ± 10	277 ± 29
ZS-1	SiC= 163; ZrB_2/SiC= 75	92.9 ± 1.8	297 ± 14	313 ± 10
ZS-2	SiC= 163; ZrB_2/SiC= 105	93.1 ± 1.0	319 ± 22	289 ± 56

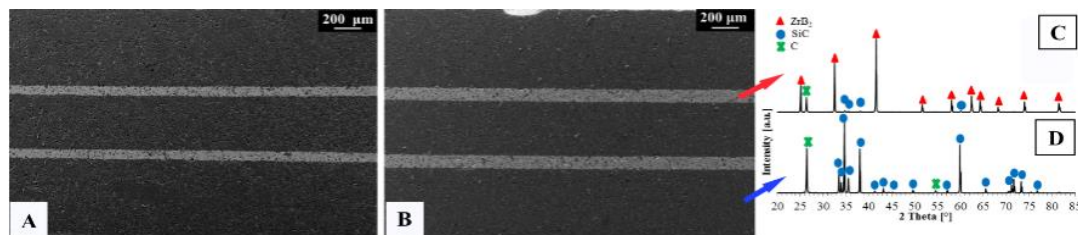Tab I. Composition and mechanical properties of laminates

Fig. 1. SEM images of multilayer polished cross section for sample ZS-1 (A) and ZS-2 (B); XRD patterns of the two materials constituent the multilayer (C) and (D).

Table I reports the thickness of SiC and ZrB_2/SiC layers in the different kinds of laminates. The interfaces between the two materials are clearly distinguishable; the thickness of the two composite layers is constant and uniform. Figure 1A and 1B show the microstructure of the hybrid laminates ZS-1 and ZS-2. It was observed a remarkable decrement of layers thickness during the sintering: cross section analysis showed that SiC layers shrank by 32% while the shrinkage observed for ZrB_2-SiC ranged between 45 and 46%. Figure 1C and 1D show the XRD patterns obtained by analysing the layers with different composition contained in the hybrid laminates. No difference was observed with respect to the XRD spectra recorded for laminates fully constituted by identical layers. The only additional phase with respect to SiC and ZrB_2 was carbon; its peak was due to the graphite flakes added as sintering aid and to the residuals of degradation of the organic compounds occurring during the de-binding. Figure 2A and 2B show some cracks propagating in the composite layer without appreciably affecting the neighbouring SiC ones. These

_____

_____

cracks were very thin and they could be observed in both ZS-1 and ZS-2 specimens.
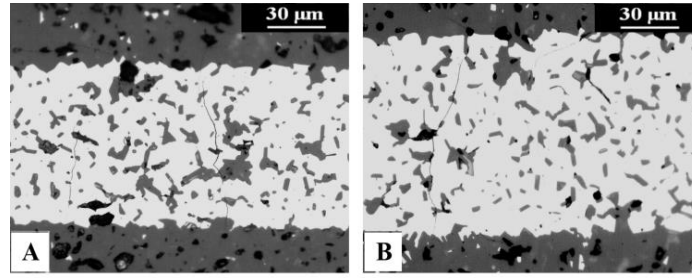

Fig. 2. Microstructure of hybrid laminates: optical images of polished cross section of laminates ZS-1 (A) and ZS-2 (B), detail of the composite layer.

They propagated inside the ZrB_2 matrix in a twisted manner, moving preferentially towards carbon and SiC particles. The presence of cracks was caused by residual stresses which arose from the different sintering shrinkage occurring for SiC and composite layers. In fact the shrinkage of composite layers was higher with respect to the SiC ones, which resulted in tensile residual stresses inside the composite sheets. In addition the presence of cracks was also very likely caused by residual stresses which developed during the cooling from the sintering temperature.

Hybrid laminates integrate SiC and ZrB_2-based composite which show different coefficient of thermal expansion. In fact the CTE of SiC is $5.9 \cdot 10^{-6}$ °C^{-1} (25-2500°C) while that of ZrB_2 is $8.3 \cdot 10^{-6}$ °C^{-1} (25-2500°C) [5,6]. The composite 80%ZrB_2-20%SiC has CTE value, calculated by the mixture rule, of 7.8·10-6 °C-1 (25-2500°C). The composite shows higher CTE and consequently its contraction during the cooling from the sintering temperature is higher than for SiC. The mismatch between SiC and composite CTEs causes thermal stresses at the interface between layers with different chemical composition. This results in compressive stresses within layers with lower CTE, that is SiC layers, while tensile stresses develop in composite layers with higher CTE. The extent of the residual stresses depends on the composition of neighbouring layers, their properties (such as elastic modulus and Poisson's ratio) and the thickness of each layer.

For this kind of architecture the tensile residual stress sustained by the composite sheets can be evaluated according to the equation (1) [7]:

$$\sigma_2 = \frac{n_2 \, E_1 \, E_2 h_1 (\alpha_2 - \alpha_1) \, \Delta T}{n_1 \, (1 - \nu_1) E_2 \, h_2 + n_2 (1 - \nu_2) E_1 h_1} \qquad (1)$$

Where 1 and 2 are SiC and ZrB_2/SiC respectively, n_i is the number of layers, E_i and ν_i are the Elastic modulus and Poisson's ratio of the ith component, h_i is the thickness of the two kinds of layers, α_i their CTEs (from sintering to room temperature).

The residual stresses in the 75 μm thick composite was found to be around 450 MPa and was only slightly lower for the 105 μm thick layers. Since this value is higher than the flexural strength of ZrB_2-SiC laminates, the presence of cracks is not surprising.

The mechanical properties of laminates integrating different materials are compared in Table I with those of laminates made with all layers of the same composition.

The relative bulk density of multicomponent laminates was comparable to that of

_____

_____

multilayer prepared by using only SiC or ZrB$_2$/SiC sheets. Probably due to the presence of micro cracks inside the composite sheets, the elastic modulus of hybrid multilayer was slightly lower with respect to the value of both one-constituent samples. These modulus values were however closer to those of SiC which represented the main component of ZS-1 and ZS-2 samples.

The flexural strength of hybrid laminates were very similar showing values of 313 MPa and 289 MPa for specimens containing respectively 75 μm and 105 μm thick composite sheets. The flexural strength values of hybrid laminates were close to that containing all layers with composition 80vol%ZrB$_2$-20vol%SiC. The presence of micro cracks crossing the composite layers without affecting the SiC material did not significantly affect the mechanical properties of the hybrid laminates.

Conclusions

Laminates integrating ZrB$_2$-SiC layers in between SiC ones were successfully prepared by the tape casting technique and pressureless sintering. The laminates showed the formation of thin cracks propagating only in the composite layers independently from their relative thickness with respect to SiC ones. These cracks were caused by residual stresses that may have arisen owing to various factors: the different sintering shrinkage of SiC and ZrB$_2$-SiC composite and the different contraction of these two materials occurring during the cooling from sintering temperature. The presence of these cracks weakly affected the mechanical properties of the hybrid laminates.

Acknowledgements

References

[1]   S. T. Pichon, R. Barreteau, P. Soyris, A. Foucault, J.M. Parenteau, Prel Y., Guedron, CMC thermal protection system for future reusable launch vehicles, Acta Astronaut. 65 (2009) 165–176.

[2]   J. Barcena, M. Lagos, I. Agote, C. Jimenez, X. Hernandez, C. Badini, E. Padovano, S. Gianella, SMARTEES FP7 Space Project – Towards a New TPS Reusable Concept for Atmospheric Reentry from Low Earth Orbit, in: 7th Eur. Work. Therm. Prot. Syst. Hot Struct., Noordwijk, The Netherland, 2013.

[3]   E.A. Gulbransen, S.A. Jansson, The high-temperature oxidation, reduction, and volatilization reactions of Si and SiC, Oxid. Met. 4 (1972) 181–201.

[4]   E. Padovano, C. Badini, E. Celasco, S. Biamino, M. Pavese, P. Fino, Oxidation behavior of ZrB$_2$/SiC laminates: Effect of composition on microstructure and mechanical strength, J. Eur. Ceram. Soc. 35 (2015) 1699–1714.

[5]   J.F. Shackelford, W. Alexander, CRC Materials science and engineering handbook, in: New York, 2001: pp. 1557–1558.

[6]   P.N. Bansal, Handbook of Ceramic Composites, Vol 200, 2006.

[7]   X. Zhang, P. Zhou, P. Hu, W. Han, Toughening of laminated ZrB$_2$-SiC ceramics with residual surface compression, J. Eur. Ceram. Soc. 31 (2011) 2415–2423.

_____