ELSEVIER

Journal of Nuclear Materials 307–311 (2002) 1196–1199

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Development of 2D and 3D Hi-Nicalon fibres/SiC matrix composites manufactured by a combined CVI–PIP route

C.A. Nannetti [a,*], B. Riccardi [b], A. Ortona [c], A. La Barbera [a], E. Scafè [d], G. Vekinis [e]

[a] *ENEA Casaccia, 00060 S. Maria di Galeria, RM, Italy*
[b] *ENEA Frascati, P.O. Box 65, I-00044 Frascati, RM, Italy*
[c] *FN S.p.A., 15062 Bosco Marengo, AL, Italy*
[d] *Eni Tecnologie, 00016 Monterotondo Scalo, RM, Italy*
[e] *DEMOKRITOS, Aghia Paraskevi Attikis, 15310 Athens, Greece*

Abstract

SiC_f/SiC composites with true 3D textures were manufactured in order to investigate the effects of the texture on thermal and mechanical properties. Hi-Nicalon^{TM} fibre preforms having a total fibre volume content of about 40% with 25 and 50% relative fibre content through the thickness were infiltrated using a mixed chemical vapour infiltration–polymer infiltration and pyrolysis technique. The issues and the main characteristics of the obtained 3D composites are presented and compared with the ones of 2D composites prepared employing the same materials and process.

1. Introduction

SiC_f/SiC composites are under development worldwide because of their attracting high temperature properties and increased mechanical reliability in comparison with SiC fibre un-reinforced SiC. Due to low activation under irradiation, their use in future fusion reactors has been recognised as very promising [1–3] provided that some critical issues such as stability under neutron and particle irradiation, quite low thermal conductivity, lack of gas tightness and of reliable joining techniques may be overcome.

Concerning the manufacturing processes for the densification of fibre preforms, the most developed ones are chemical vapour infiltration (CVI) [4] and polymer infiltration and pyrolysis (PIP) [5–7].

Both techniques are based on the common principle of filling the porosity inside the fibre preforms with a SiC matrix resulting from decomposition of gaseous precursors (CVI) or pre-ceramic polymer precursors (PIP).

Apart from raw materials and process costs, CVI appears less suitable for the manufacturing of high thickness components (>4 mm), PIP generally results in a less pure and crystalline SiC matrix which impairs somewhat the thermomechanical properties.

Nevertheless the recent availability of almost stoichiometric SiC fibres with improved thermal stability together with new pre-ceramic polymers which result into almost stoichiometric SiC upon pyrolysis, may open new perspectives to PIP process since also the matrix crystallinity, may be improved with the use of higher pyrolysis temperatures.

Moreover the availability of true 3D preforms with a significant amount of fibres in the thickness direction may, in principle, give a further contribution to the development of composites with improved thermal conductivity and interlaminar shear strength.

In this work, the last results concerning the preparation of SiC_f/SiC composites using a combined CVI/PIP process, already described in previous works [5,7], are reported.

---

[*] Corresponding author. Tel.: +39-6 3048 3297; fax: +39-6 3048 3327.

E-mail address: carlo.nannetti@casaccia.enea.it (C.A. Nannetti).

0022-3115/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(02)00956-X

In particular CVI was used to deposit onto the fibres a thin carbon coating and a subsequent somewhat thicker SiC layer. PIP was then employed to densify the preforms (flat panels) and finally CVI was sometimes used to obtain a final SiC coating on the densified preforms.

The main aim was to investigate the effects of the use of true 3D Hi-Nicalon fibres preforms having a significant amount of fibres in the thickness direction and of a new pre-ceramic polymer for the PIP process, on the thermal and mechanical properties of the obtained composites.

To get a more significant picture of the results, the characteristics of the obtained 3D composites were compared with the characteristics of 2D composites (eight harness satin texture) prepared using the same materials and process.

2. Experimental

2.1. Materials

Two types of 3D preforms (100 × 100 × 4 mm) were woven by Albany Int. Techniweave (USA) using Hi-Nicalon fibres from Nippon carbon (Japan). Compared to the previous Nicalon ceramic grade fibres, these new ones are still characterized by excess carbon but present rather low oxygen content (about 1%) and consequently improved thermal stability.

Details about the weaving process are not yet available. The fibres volume fraction was about 39% for T1 type preforms and 41% for T2 type preforms, while the fibres distributions along the three main directions are listed in Table 1.

For the PIP process both polycarbosilane (PCS) from Nippon carbon and allylhydridopolycarbosilane (AHPCS) from Starfire (USA) were employed.

2.2. Preforms densification

CVI carbon interlayer was deposited using a mixture of nitrogen and methane at 1200 °C and 1 mbar pressure. The operating conditions were chosen to obtain a slow deposition rate of approximately 0.01 μm/h.

SiC was deposited using a mixture of methyltrichlorosilane and hydrogen at 950 °C and 1 mbar pressure in condition to get the same deposition rate of the carbon coating.

Each panel was subjected to 10 h of carbon deposition and 30 h of SiC deposition.

Pre-ceramic PIP procedures had already been described elsewhere [5,7]. All the panels were subjected to seven PIP steps using PCS polymer and to three additional steps using AHPCS. Matrix densification was then stopped since no significant improvements were foreseen by performing additional PIP cycles.

Table 1
Fibres distribution along the 3D preforms main directions

Preform type	Yarn direction	Fibre volume fraction	Fibre distribution (%)
T1	*X*	0.113	28.7
	Y	0.093	23.8
	Z (thickness)	0.187	47.5
T2	*X*	0.113	27.5
	Y	0.198	48.3
	Z (thickness)	0.099	24.2

2.3. Characterization

Apparent density was determined by mass and geometric volume. To minimize the errors on thickness, the specimen surface was ground up to almost constant density because the surface had coarse weaviness and roughness.

Porosity was estimated by computing the theoretical density by the masses and respective densities of the constituent materials, assuming volumes additivity.

The modulus of rupture (MOR) was measured by three point bending tests at room temperature (span 40 mm, cross-head speed 1 mm/min).

Elastic constant was determined by measuring the fundamental flexural frequencies by means of an E-Meter resonant frequency tester (James Instr. Inc.).

Straight-edge notch beam (SENB) 3-point bending test was also performed to investigate the fracture behaviour in flexure of the materials and their crack-arrest capabilities. Due to the different fibre amounts along the main directions (X, Y) of the 3D preforms, the tests were carried out on specimens cut and prepared in two orthogonal directions.

Crack propagation was monitored to investigate the *R*-curve behaviour of the materials.

The thermal diffusivity was measured by the laser-pulse method under vacuum to reduce heat losses. A 40 J Nd-glass laser (Lumonics Ltd.) with a pulse width of about 500 μs and a wavelength of 1.06 μm was used. Details of the measures are reported in [8].

3. Results and discussion

The results of the characterizations concerning mean apparent densities, residual porosities and bending tests are collected in Table 2 for the two types of 3D panels, in comparison with the results obtained for the 2D composites prepared using the same materials and process.

Table 2
Typical characteristics of the obtained 3D and 2D composites

Composite identification	Apparent density (g/cm^3)	Porosity (%)	MOR (MPa)
3D T1	2.19 ± 0.02	17.4	627 ± 40
3D T2	2.31 ± 0.02	13.3	701 ± 60
2D	2.23 ± 0.02	15.9	555 ± 10

Possibly due to the different weaving texture, T2 type panels, characterized by a lower fraction of fibres across the thickness (*Z* direction, Table 1) showed higher apparent density than that of T1 type panels; The 2D specimens showed intermediate density values; of course the porosity follows an opposite trend since the theoretical density is almost the same for all the materials. The average densification level of the fibre preforms may be considered quite satisfactory, at least for the 2D and 3D T2 type panels.

A typical cross-section of a 3D T2 composite, evidencing fibre texture across the thickness, has already been presented in [11].

Concerning the bending tests, the measured MOR values result quite satisfactory for all the tested materials. It is to be pointed out that the MOR values of the 3D composites refer to specimens loaded in the direction characterised by the highest amount of fibres.

Typical stress–displacement curves of the 3D T2 and 2D materials are presented in Fig. 1.

The displacement at failure is quite high, reasonably due to the low stiffness of the matrix material as evidenced by the values of the elastic constants (Table 3), which are rather low in comparison with typical SiC_f/SiC composites densified by CVI. The failure of the 3D T2 composite shows a very limited region of energy dissipation after initial fracture, followed by a much more abrupt load drop in comparison with the 2D material which presents a very graceful fracture. Conversely the same 3D material loaded in the orthogonal direction behaves similarly to the 2D specimens even if the maximum stress before initial failure is lower.

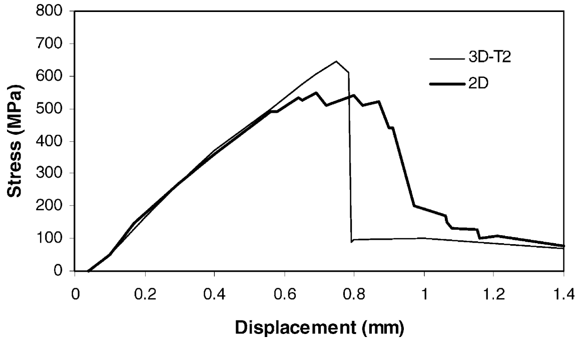

Fig. 1. Hi-Nicalon 3D and 2D composites typical stress–displacement curves.

Table 3 shows the results obtained from both the SENB tests, and the elastic modulus measurement.

The 2D material and the 3D T2 material (orthogonal orientation) display pronounced pseudo plastic behaviour and very significant energy dissipation during the cracking.

3D T1 specimens displayed only limited energy dissipation and less pseudo plastic behaviour. As already observed in the bending tests, the 3D T2 specimen (in the other orientation) behaved as the most brittle one with almost no energy dissipation.

The main mechanism of energy dissipation in all cases was observed to be crack bifurcation, crack jumping and wandering giving strong interlocking between fibre bundles.

These mechanisms give good crack arrest capabilities, a very important parameter in achieving flaw-tolerance and high reliability during the service.

In addition fibre pull-out was generally observed on fractured specimens.

The initial matrix cracking level could not be clearly determined in 2D specimens, as the stress–displacement curves did not show any pronounced change in gradient until fibre bundle deformation. 3D specimens showed a clear change in gradient and displayed clear matrix cracking.

Because of the pronounced crack wandering, clear crack extensions in all specimens could not be determined with certainty and thus quantitative *R*-curves could not be obtained. However, the specimens' compliance during the testing indicated that in almost all materials, the *R*-curves were steep or medium-steep.

The toughness and the fracture behaviour of 2D and 3D specimens were generally very promising and indicated that these materials may offer sufficient flaw tolerance and reliability for engineering applications.

The measured thermal diffusivity α of the two 3D SiC–SiC composites samples (Table 4) were somewhat lower than those reported in the literature [9,10] for a 2D SEP material (densified by CVI), and they follow a similar trend as a function of density.

Table 4 also shows the temperature dependence of the 3D composites. T2 and T1 samples exhibit the expected decrease in the thermal diffusivity as a function of temperature, even if the decrease is less steep with respect to typical composites densified by CVI, probably due to an higher degree of inhomogeneities in the present 3D composites (free carbon, amorphous or nanocrystalline phases, etc.).

Although the application of the diffusion technique to obtain the thermal conductivity is not always reliable. For heterogeneous structures, such as these composites, we made a rough estimate of room temperature thermal

Table 3
Results of SENB tests and elastic constants measurements

Specimen	Notching and loading orientation	Initial matrix cracking stress (MPa)	Apparent energy dissipation after initial fracture (J/m^2)	Apparent ΔK_{IC} due to toughening (MPa m$^{1/2}$)	Flexural modulus by resonance (GPa)
3D T1		79	800	12	86
3D T1	Orthogonal	35	1430	14	94
3D T2		114	–	–	124
3D T2	Orthogonal	92	3600	23	79
2D		–	6700	38	131

Table 4
Thermal diffusivities results

Sample	T (°C)	$\alpha \times 10^{-2}$ (cm^2/s)
3D T2	20.9	3.08 ± 0.06
	327.0	2.13 ± 0.11
	592.8	1.91 ± 0.03
3D T1	22.9	2.37 ± 0.06
	314.0	1.91 ± 0.09
	621.8	1.75 ± 0.06

conductivity obtaining 5.2 and 3.8 $\mathrm{W\,m^{-1}\,K^{-1}}$ for T2 and T1 composite respectively [11].

4. Conclusions

The 3D texture appears very promising to get high strength $\mathrm{SiC_f/SiC}$ composites with improved thermal conductivity. Concerning the weaving texture it was observed that a very high fraction of fibres (about 50%) across the thickness does not seem useful since none of the measured properties was improved with respect to the composites having less fibres (about 25%) through the thickness. In addition different amounts of fibres in the in-plane (X, Y) directions induced properties anisotropy perhaps larger than expected.

The mechanical properties of all the tested materials were satisfactory, particularly in terms of room temperature MOR; moreover the fracture behaviour of both 2D and 3D composites generally indicated enough flaw tolerance and reliability for structural applications.

The thermal conductivities were still low, even if sensibly improved with respect to previous 2D Nicalon CG composites prepared with our combined CVI–PIP process. How much this improvement may be attributed to the use of Hi-Nicalon fibres, to the 3D texture or to the partial use of the new AHPCS pre-ceramic polymer for the PIP process is still to be investigated.

Apart from the availability of fibres with much more improved intrinsic thermal conductivity, we expect that, through the optimization of the densification process, the improvement of the purity, crystallinity and stiffness of the matrix material, which is to be pursued using only the new pre ceramic polymer (AHPCS) and higher pyrolysis temperatures, further remarkably improvements of the thermal and mechanical properties may be achieved.

References

[1] S. Sharafat, F. Najmabadi, C.P.C. Wong, and the ARIES Team, Fus. Eng. Des. 18 (1991) 215.

[2] S. Ueda, S. Nishio, Y. Seki, R. Kurihara, J. Adachi, S. Yamazaki and DREAM design team, J. Nucl. Mater. 258–263 (1998) 1589.

[3] A.S. Peres Ramirez, A. Caso, L. Giancarli, N. Le Bars, G. Chaumat, J.F. Salavy, J. Szczepanski, J. Nucl. Mater. 233–237 (1996) 1257.

[4] T.M. Besmann, HT-CMC II Ceram. Trans. 58 (1995) 1.

[5] A. Donato, A. Ortona, C.A. Nannetti, S. Casadio, SiC/SiC fibre ceramic composites for fusion application: a new manufacturing process, Proceedings of the 19th Symposium on Fusion Technology (SOFT), September 1996, Lisbon, Portugal.

[6] S. Casadio, A. Donato, A. Nannetti, A. Ortona, M.R. Rescio, HT-CMC 2 Ceram. Trans. 58 (1995) 193.

[7] A. Licciulli, A. Ortona, C.A. Nannetti, S. Botti, Key Eng. Mater. 127–131 (1997) 279.

[8] L. Fabbri, E. Scafè, J. Nucl. Mater. 212–215 (1994) 835.

[9] H. Tawil, L.D. Bentsen, S. Baskaran, D.P.H. Hasselman, J. Mater. Sci. 28 (1985) 3201.

[10] D.P.H. Hasselman, A. Venkateswaran, M. Yu, H. Tawil, J. Mater. Sci. Lett. 28 (1991) 1037.

[11] C.A. Nannetti, B. Riccardi, A. Ortona, A. La Barbera, E. Scafè, 4th IEA Workshop on $\mathrm{SiC_f/SiC}$ Ceramic Composites for Fusion Application, 12–13 October 2000, Frascati, Italy.