Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 30 (2010) 1751–1759
www.elsevier.com/locate/jeurceramsoc

Study of joining of carbon/carbon composites for ultra stable structures

M. Salvo [a,*], V. Casalegno [a], Y. Vitupier [b], L. Cornillon [b], L. Pambaguian [c], M. Ferraris [a]

[a] *Materials Science and Chemical Engineering, Politecnico di Torino, Corso Duca degli Abruzzi, 24, Torino, Italy*
[b] *Thales Alenia Space, Cannes, France*
[c] *European Space Agency (ESA) Noordwijk, The Netherlands*

Received 30 July 2009; received in revised form 23 November 2009; accepted 18 December 2009
Available online 18 January 2010

Abstract

The aim of this work is to study joining materials and innovative bonding technologies for ultra stable joints of carbon/carbon composite (C/C) sandwich panels for the manufacturing of next generation space instruments. The proposed solutions have low coefficient of thermal expansion (CTE) and coefficient of moisture expansion (CME), and a good mechanical strength, in order to guarantee the dimensional stability and mechanical reliability of the joined C/C panels.

Keywords: A. Joining; B. Composites; C. Mechanical properties; E. Space instruments

1. Introduction

Future large optical instruments will be based on interferometric and optical aperture synthesis (according to the ESA science program for 2015–2025 named "Cosmic Vision"[1]). Such instruments will require ultra high stability large structures (some square meters) and a near to zero CTE is necessary for both in-orbit and ground-and-orbit operations.

Carbon/carbon composites (C/C) have been selected as key materials for the future instruments as their properties can be tailored to the application requirements detailed below[2]:

- very high thermo-elastic stability: C/C CTE is close to zero (in a quasi isotropic lay-up configuration);
- low density with good mechanical properties: they are not brittle materials and allow simple and reliable design;
- moisture insensitivity (null coefficient of moisture expansion, CME);
- various architectural possibilities: thin and large size cylinders, skins and honeycomb sandwiches, which can be adapted to several efficient structural concepts;
- industrial maturity: large industrial facilities up to 2.5 m^2.

To fully benefit from the potential given by C/C, it is important to select a joining material having the same properties of C/C, in particular a quasi-zero CTE and CME, in addition to a good mechanical strength.

With this purpose, several joining materials and technologies have been selected. The requirements for the joining materials are mainly given by the strict dimensional stability requirements of the future high performance space instruments.

The requirements of the joints established by the end-user are reported in Table 1.

Several types of bonding materials and technologies between honeycomb C/C cores and C/C skins (sandwich panels) have been tested at Thales Alenia Space (TAS). Although pyrolitic bonding, obtained through co-densification of C/C skins and honeycomb C/C core, gave promising results at small sample level, the mechanical strength of such bonding was low on large samples.[3]

Consequently, for large size panels, the assembly of C/C skins and honeycomb C/C cores relies today on organic bonding. Organic bonding is applicable to whatever size of sandwich and skins thickness, but the resulting assembly is sensitive to moisture absorption, leading to distortion of the structure.

The aim of this work is to study joining materials and innovative bonding technologies for ultra stable joints of C/C sandwich panels for the manufacturing of next generation space instru-

* Corresponding author.
E-mail address: milena.salvo@polito.it (M. Salvo).

0955-2219/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2009.12.013

Table 1
Requirements set by end-user for the joints.

Preferred joining process temperature (°C)	<300 °C[a]
Operating T range (°C)	from −50 to 50
CTE ($\times 10^{-6}$ °C^{-1}) in [−50 °C, 50 °C]	≤5
Shear strength at RT (MPa)	≥12
Young modulus, E (GPa)	1–30
Coefficient of moisture expansion (CME)	0
Joint thickness (μm)	100–200
CTE × E × thickness ($\times 10^{-6}$ °C^{-1} GPa mm)	<120[b]

[a] Compatible with end-user standard processing equipments.
[b] From Ref. 11.

ments. The results obtained by using different joining materials (metals and adhesives) are described and discussed.

2. Experimental

2.1. Sandwich sample description

The C/C to be joined are sandwich panels composed of two C/C skins joined to a honeycomb C/C core (Fig. 1).

2.1.1. C/C skins and honeycomb C/C cores

C/C skins are produced by Chemical Vapour Infiltration (CVI) of a quasi-isotropic lay-up (0°/45°/−45°/90°) of ex-PAN fibres; an adequate high temperature treatment confers to the material a quasi-null CTE.

The typical properties of C/C skins, measured at room temperature, are about 60 GPa (tensile modulus) and about 160 MPa (tensile strength).

During the CVI process a 10–15 μm pyrocarbon "seal coat" grows at the surface of the C/C skin, with a smooth laminar orientated structure. The coating is usually removed by polishing C/C skins before joining them to honeycomb C/C cores, nevertheless, its influence on the joining material wettability and shear strength of joined samples was investigated for comparison purposes. Some C/C skins were polished to remove the coating before wettability and joining tests and the results were compared with those obtained on as-received samples.

Honeycomb C/C cores are made of ex-PAN T300 fibres, fabric plain weave and lay-up 45°/−45°.

2.2. Joining materials

The joining materials selected, taking into account the requirements in Table 1, are listed below:

- Metal brazing
  (i) TiCuNi brazing alloy (70 wt.% Ti, 15 wt.% Cu, 15 wt.% Ni) supplied by Wesgo Metals;
  (ii) Si (silicon powder <150 μm supplied by MERCK); Si was applied on C/C substrates as a slurry (Si powder/ethanol).

- Adhesives (polymeric precursors of ceramic)
  (i) Carbon fibre reinforced commercial adhesive (CFA);
  (ii) CFA + 65 vol.% (5 wt.%) of fumed silica (99.8% supplied by Aldrich);
  (iii) CFA + 25 vol.% (40 wt.%) negative CTE glass–ceramic powder (GC).

The composition of GC is BaO 33.3 mol.%, B_2O_3 33.3 mol.% and Al_2O_3 33.3 mol.%.[4,5]

The GC was produced as a glass material by melt/quenching at 1500 °C for 1 h then heat treated (720 °C, dwelling time 24 h + 780 °C, dwelling time 8 h) to obtain a glass–ceramic.

GC has been added to CFA as follows: CFA + 25 vol.% glass–ceramic powder (<105 or <44 μm).

2.3. Wetting tests

The wetting tests were performed by heating microscopy (hot stage microscope Leitz GmbH AII) equipped with a Leica DBP (Ernst Leitz GmbH, Wetzlar, Germany) camera; the wetting behaviour on C/C skins was studied by contact angle measurements from pictures acquired by the camera. The authors characterized the wettability parameters basically to meet the practical demands of brazing rather than for a study of the wetting mechanisms or ceramic–metal interactions.

Table 2
Joining materials, their CTE and Young modulus, the thermal treatment used to obtain the joined structures and the average shear strength of joints (C/C skin without seal coat).

Joining material	Coefficient of thermal expansion ($\times 10^{-6}$ °C^{-1})	Young modulus (GPa)	Thermal treatment for the joining process	Average shear strength (MPa)
TiCuNi brazing alloy	20.3[a,9]	144[a,9]	1000 °C, 10 min, 10 °C/min, Ar flow	24 ± 2
Pure Si	3.6[16]	112[17]	1450 °C, 10 min, Ar flow	15 ± 4
CFA (carbon fiber reinforced adhesive)	<8[b]	18 ± 3	130 °C, 4 h + 260 °C, 2 h; in air	14 ± 3
CFA + 65 vol.% silica	2.9[c]	–	130 °C, 4 h + 260 °C, 2 h; in air	9 ± 3
CFA + GC[d]	5.3[c]	17	130 °C, 4 h + 260 °C 2 h; in air	17 ± 3

[a] Properties of TiCuNi before brazing process, from Ref. 9.
[b] Supplier data sheet.
[c] Calculated by using the rule of mixture.
[d] Negative CTE glass–ceramic powders.

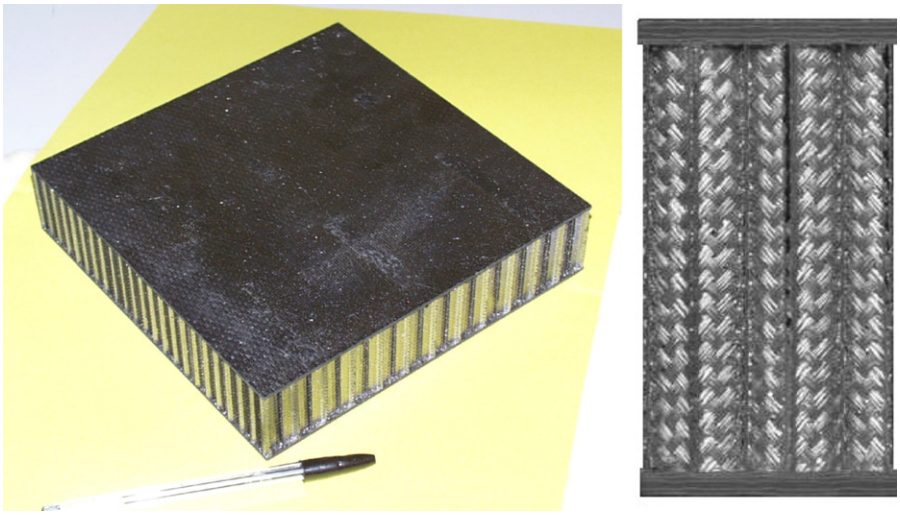

Fig. 1. C/C sandwich panel (on the left) and side view (on the right).

2.4. Joining process

Table 2 shows the chosen joining materials, their CTE and Young modulus, the thermal treatment used to obtain the joined structures and the measured average apparent shear strength of joints.

2.5. Joined sample characterisation

Polished cross-sections of the joined samples C/C skins were characterised by optical microscopy (REICHERT-JUNG MEF-3 metallographic optical microscope, with a Sony High Resolution camera and Leica QWinPro image analysis program) and scanning electron microscopy, SEM (scanning electron microscopy Philips 525M) equipped with EDS analyzer (Philips SW9100 EDAX). The crystalline phases in the joined areas were identified by X-ray diffraction analysis (X'Pert Philips diffractometer) using the Bragg Brentano camera geometry and the Cu Kα incident radiation.

2.6. Mechanical and thermo-mechanical testing

The apparent shear strength of joined C/C skins was measured at room temperature with compression tests performed on an universal mechanical testing machine (SINTEC D/10), according to the method described in Ref. 6 as single lap test, adapted from ASTM D1002-05.

The single lap tests were carried out on at least five samples for each kind of joint.

The joined C/C skins were glued to the fixtures by an epoxy adhesive (Araldite AV 119). Dimensions of the tested samples were about 6 mm × 10 mm × 1.5 mm.

After mechanical test, the fracture surface morphology was qualitatively examined to observe the fracture propagation mechanisms.

Young modulus of the CFA joint area was measured by a Nanoindenter XP (depth limit 2000 nm).

CTE measurements have been performed on a test facility equipped with a Michelson interferometer (Doppler effect laser) to measure the length change of the samples. Thermocouples are attached to the specimen surface at multiple points. The measurement is made under secondary vacuum. The length change and the mean temperature are measured every 30 s.

Thermal-gravimetric analysis (TGA Mettler-Toledo) was used for investigating the thermal stability of cured CFA joining material up to 150 °C (in air) with a heating rate of 10 °C/min.

Ageing in climate chamber (VOTSCH VC 4010) at 45 °C, 95% relative humidity (RH) for 7 days was performed on CFA joined C/C.

3. Results and discussion

3.1. Metal brazing

3.1.1. TiCuNi brazing alloy

The active metal brazing process is a "one-step" brazing process used to join ceramics to metals. During brazing the "active" elements (for example Ti) form a reaction layer on the ceramic which is readily wetted by the active metal braze. The active metal braze process provides a strong joint and is ideally suitable for joining large ceramics and composites parts.[7]

TiCuNi foil comprises three material layers: the external layers are made of Ti while the core layer is made of a CuNi alloy. TiCuNi was successfully used by the authors to braze C/C to copper in a previous work.[8]

The dimensional stability of a TiCuNi based assembly may be adversely impacted due to the high CTE and high Young modulus (E) (CTE = 20.3×10^{-6} °C^{-1} and E = 144 GPa from Ref. 9). These properties were given by the supplier and refer to the as prepared TiCuNi: they can thus be different after brazing.

Wetting tests (heat treatment: 1000 °C, 10 min, 10 °C/min, Ar atmosphere) were performed on seal coated C/C; the wettability of TiCuNi on C/C is very high, as can be observed in Fig. 2.

After wetting test, some joined samples were manufactured using one TiCuNi foil. The brazing process was carried out as

Fig. 2. Macrographs of as-received C/C skins before (on the left) and after (on the right) the wettability tests by TiCuNi.

described in Table 2; joined C/C samples were manufactured by using as-received C/C skins or C/C skins after seal coat removal by polishing.

SEM characterization was performed on the cross-section of C/C joined skins. The joint thickness is about 30–35 μm; the interface between the C/C (both with and without seal coat) and the brazing alloy is continuous, free of micro-defects, independently from carbon fibre orientation (parallel or perpendicular to the surface) (Fig. 3). A thin titanium carbide layer of about 2 μm was detected close to C/C interface resulting from the reaction between C and Ti (Fig. 4). Such carbide forming reaction causes beneficial near-interfacial changes which promote wetting and bonding.[9]

SEM and EDS analysis (Fig. 5) on the joint area showed that TiCuNi after brazing process results in a multiphase material. The two-phase microstructure of TiCuNi shows two Ti-rich phases: a light-gray Ti-rich phase containing also Cu and Ni, and a dark-gray Ti-rich phase containing a very small amount of Cu. Details on Ti–Cu–Ni system can be found in Ref. 10.

Shear tests were performed on C/C skins (without seal coat) brazed by one TiCuNi foil; the average shear strength was 24 ± 2 MPa, but the joint thickness ranges between

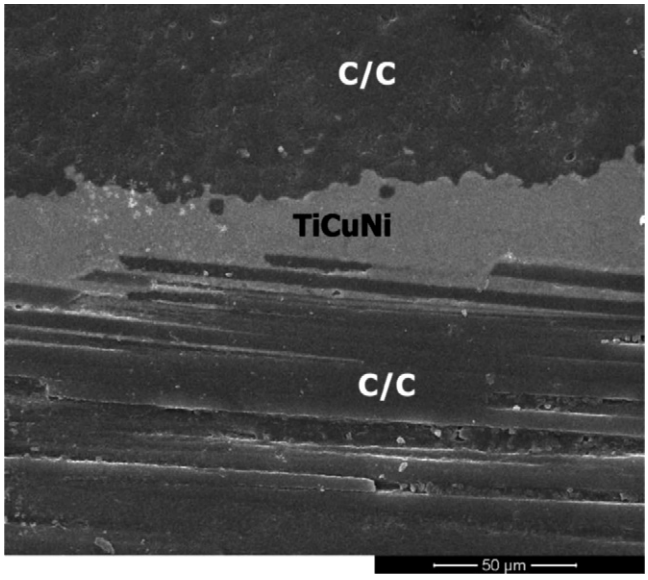

Fig. 3. C/C skin (without seal coat) brazed by TiCuNi.

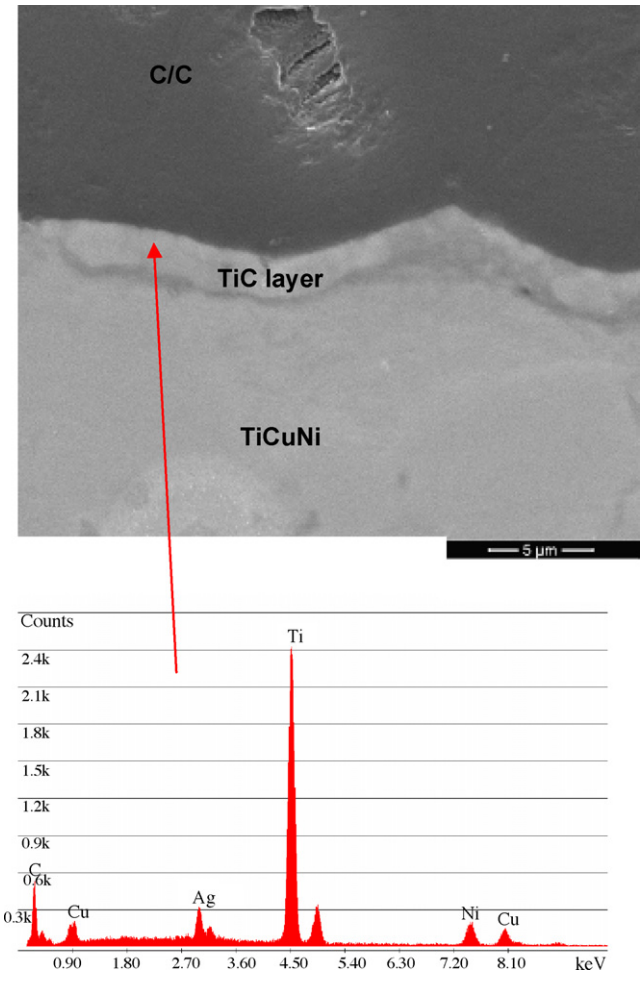

Fig. 4. SEM magnification and corresponding EDS analysis of the interface between the joining material (TiCuNi) and the C/C skin; a thin carbide layer can be observed on the C/C skin surface (Ag from sample metallization).

30 and 35 μm, lower than 100–200 μm as requested in Table 1.

Other C/C skins (without seal coat) were joined by using three foils of TiCuNi as brazing material in order to satisfy the thickness requirements in Table 1 (thickness of 100–200 μm) and to test the effect of the higher thickness on the joint mechanical strength. Three brazing alloy foils can also improve the homogeneous distribution of the joining material and avoid lack of braze in the joint area.

The joint thickness in samples brazed by three TiCuNi foils was about 90–100 μm and the average apparent shear strength was 17 ± 3 MPa: it is 30% lower than the shear strength measured on the thinner joints (30–35 μm), but still within the requirements of Table 1.

Some sandwiches made by one honeycomb C/C core joined by one TiCuNi foil to two C/C skins were prepared, as shown in Fig. 6.

TiCuNi alloy was effective to join C/C samples, the compatibility with different C/C substrates (honeycomb C/C cores and C/C skins) was demonstrated and the bonding strength of the joints was higher than the interlaminar shear strength of C/C (12 MPa).[2] The main drawback is the high value of CTE and *E*.

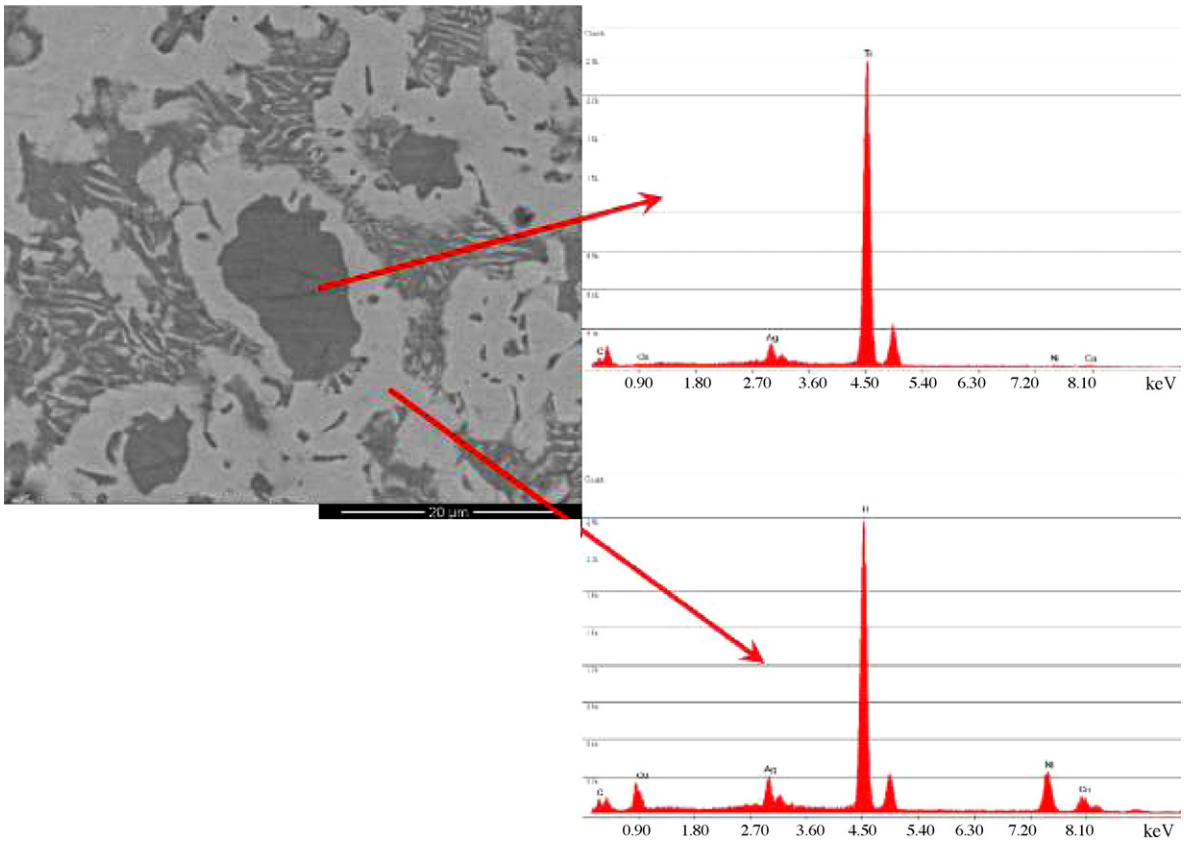

Fig. 5. SEM picture and corresponding EDS analysis in the joining material (TiCuNi) (Ag from sample metallization).

Fig. 6. Sandwich panel brazed by one foil of TiCuNi.

The product CTE × E × thickness of the bonding layer has to be matched to the C/C skin one, in order to limit the strains in the sandwich panel and to guarantee its stability. A low value of the parameter (CTE × E × thickness) is necessary in order to obtain a low averaged coefficient of thermal expansion of the whole structure (skins, adhesive and honeycomb).[11]

For the selection of a bonding technology it has been calculated[12] that the maximum allowable value for the product CTE × E × thickness should be $120 \times 10^{-6}\,^{\circ}C^{-1}$ GPa mm. For TiCuNi brazing layer both CTE and E are high, leading to a CTE × E × thickness product between 292 and $584 \times 10^{-6}\,^{\circ}C^{-1}$ GPa mm (depending on the joint thickness), so the impact of thermo-elastic mismatch between the joint and the C/C would be quite important; according to these results and considering the temperature of the joining process (much higher than 300 °C), the TiCuNi brazing process has not been considered as the most suitable solution for ultra stable structures.

3.1.2. Silicon

Silicon as joining material for SiC/SiC and C/C composites is a well known solution, as reported in Refs. 13–15. Silicon was expected to be suitable as joining material for C/C as its CTE ($\alpha_{(20–250\,^{\circ}C)} = 3.6 \times 10^{-6}\,^{\circ}C^{-1}$) fulfils the requirement in Table 1, it can be easily applied as a slurry on the surfaces to be joined and molten silicon reacts with the C/C to form silicon carbide at the interface, thus improving wettability and adhesion.[16]

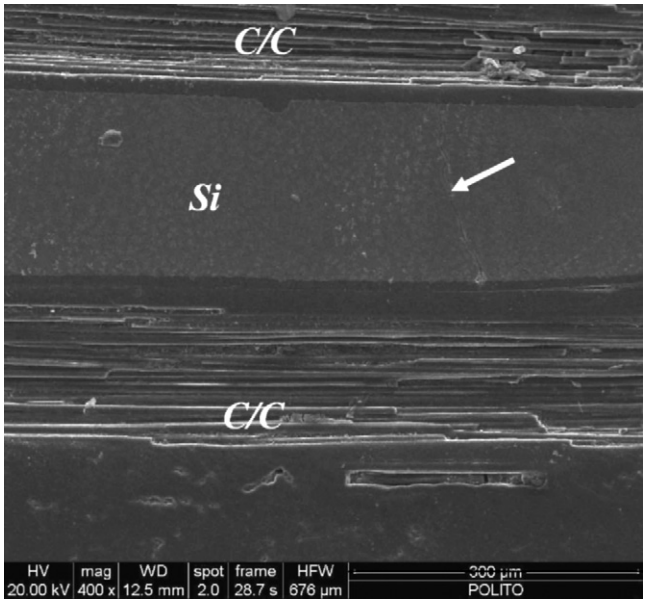

Fig. 7. Silicon joined C/C skins: crack induced by internal stress is arrowed.

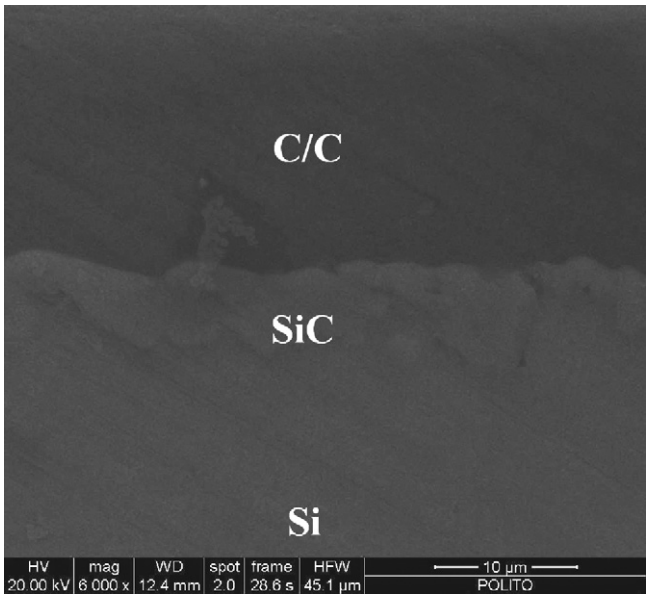

Fig. 8. Silicon joined C/C skins: a layer of SiC of approximately 10 μm can be seen at C/C-joint interface.

Wettability tests were performed on as-received C/C skins with a heat treatment at 1450 °C, a dwelling time of 10 min, under Ar flow. The wettability test results confirmed that the contact angle on seal coated C/C skins is consistent with the equilibrium contact angles reported in the literature ($\theta = 30$–$35°$), measured for liquid Si on C substrates when reactive wetting occurs with SiC formation at interface. The low contact angle value at the equilibrium characterizes the chemical interactions across the liquid-silicon/SiC interface[16] and the molten silicon spreading on C/C substrates.

The formation of silicon carbide on the C/C surface during the wetting experiment was also confirmed by X-ray diffraction analysis, not reported here.

Some silicon joined C/C were manufactured with as-received C/C skins and C/C skins without seal coat. The joining process parameters are reported in Table 2. SEM analysis on silicon joined sample cross-sections showed defect free and continuous interfaces between the molten Si and the C/C substrates (Fig. 7); a layer of SiC of approximately 10 μm can be seen at C/C-joint interface (Fig. 8). The thickness of the joint is about 190 μm as shown in Fig. 7; the vertical crack arrowed in Fig. 7 was caused by the tensile residual stresses developed during the cooling to room temperature, resulting from the CTE mismatch between C/C and Si.

The average apparent shear strength of the silicon joined samples obtained with as-received C/C skins and C/C skins without seal coat was 16 ± 5 and 15 ± 4 MPa, respectively. The fracture always occurred in the C/C composites, thus indicating a joint strength higher than the interlaminar shear strength of the composite itself. The presence of cracks perpendicular to the Si/composite interface was therefore not detrimental for the joint mechanical strength.

The possibility to join honeycomb C/C core to C/C skin has been tested with silicon. The joined sample appeared without macroscopic defects.

In conclusion, despite its Young modulus of 112 GPa,[17] higher than the requirement established in Table 1, silicon was effective to join C/C samples; the low CTE of silicon compensates its high stiffness and leads to an acceptable value of CTE × E × thickness of 76×10^{-6} °C^{-1} GPa mm.

The main drawback of this bonding solution is that silicon melting point is at about 1410 °C and the brazing process must be performed at 1450 °C under controlled atmosphere. This is a major drawback in terms of manufacturing cost, as a large furnace under vacuum is necessary to avoid C/C degradation.

3.2. Adhesives

3.2.1. Carbon fibre reinforced commercial adhesive (CFA)

The carbon fibre reinforced commercial adhesive (CFA) used to join C/C was chosen because of its carbon based composition after curing process and its low CTE ($<8 \times 10^{-6}$ °C^{-1}). The CTE is higher than the requirement established by end-user (see Table 1), but the material has been tested due to its other promising properties (i.e. Young modulus, density, joining process temperature). Both as-received and without seal coat C/C skins were joined by CFA.

Different modifications of the joining process were carried out in order to decrease the porosity of the joint areas and to improve shear strength, i.e. the heating rate was reduced to allow an easier elimination of gases produced during the curing process.

The best results in terms of lower porosity and higher shear strength were obtained on C/C without seal coat and with the following optimised joining parameters: 2–4 h at room temperature; 0.1–0.6 °C s^{-1} heating up to 130 °C, followed by a dwelling time, final curing at 260 °C (in air) and a low external pressure (<1 kPa) applied during the joining process. The apparent shear strength of joined samples produced as described above was

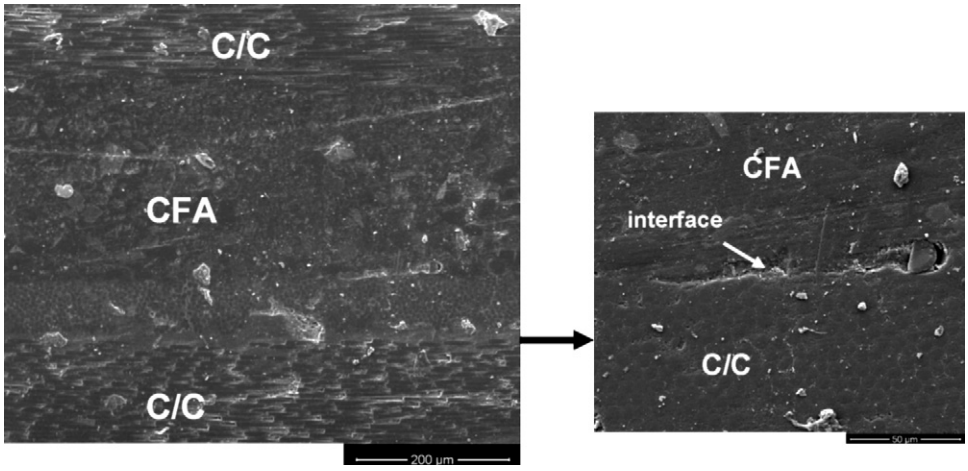

Fig. 9. SEM of CFA joined C/C skins (without seal coat).

14 ± 3 MPa for C/C without seal coat, while only 7 ± 4 MPa was obtained for joined samples produced with as-received C/C.

During the mechanical tests of the joined C/C without seal coat, the failure always occurred in the composite materials, thus indicating an apparent joint shear strength higher than the C/C interlaminar shear strength. The lower adhesion between the joining material and the as-received (coated) C/C resulted in lower apparent shear strength and failure at CFA/composite interface.

Morphological analysis was performed on CFA joined C/C (Fig. 9), the interface is continuous and free of defects such as microvoids and porosity, while residual porosity is still present in the joint area; the dispersion of graphite fibres inside the joining material can be observed.

Joining of honeycomb C/C core to C/C skins by CFA was also successfully performed (picture not reported here).

The average modulus of the CFA, measured by nano-indentation tests (4 nano-indentation tests and 15 values from each test) in the joint area, is 18 ± 3 GPa: this value fulfils the requirement for E in Table 1.

X-ray diffraction analysis on CFA after joining process showed that graphite is the only crystalline phase present in the joint (Fig. 10).

In order to evaluate the joining material outgassing, thermo-gravimetric analysis up to 150 °C (Fig. 11) was performed on CFA after joining process: the weight loss of the CFA up to 150 °C was found to be negligible.

Furthermore, the influence of thermal ageing on joined samples was studied. Ageing in climate chamber at 45 °C, 95% relative humidity (RH) for 7 days was performed on CFA joined C/C: this thermal ageing treatment is currently used in space qualification tests, to evaluate the behaviour of the material during long terms storage. Apparent shear strength of joined samples before and after 7 days at 45 °C at 95% RH is 14 ± 3 and 15 ± 2 MPa, respectively. Thus, it can be concluded that CFA joined samples showed an excellent moisture resistance.

Coefficient of thermal expansion was measured on as-received C/C skins and CFA joined C/C skins (length of 200 mm): CTE for as-received C/C and CFA joined C/C skins was the same ($-0.3 \times 10^{-6}\,°C^{-1}$), thus indicating that CFA joining material has no influence on the CTE of joined materials of this size (the accuracy of the test is $0.1 \times 10^{-6}\,°C^{-1}$).

The joining process performed by using CFA satisfies all the conditions as stated in Table 1, with the exception of the CTE value, which can be an issue for large joined structures. In order to reduce the CTE of the bonding material, low CTE fillers were added: fumed silica (CTE = $0.55 \times 10^{-6}\,°C^{-1}$) and bar-

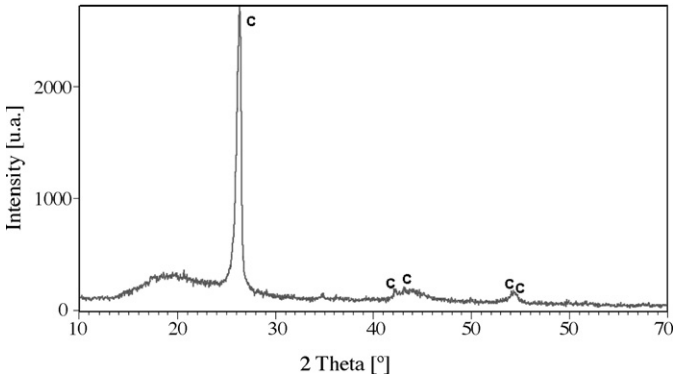

Fig. 10. XRD pattern of CFA after curing process.

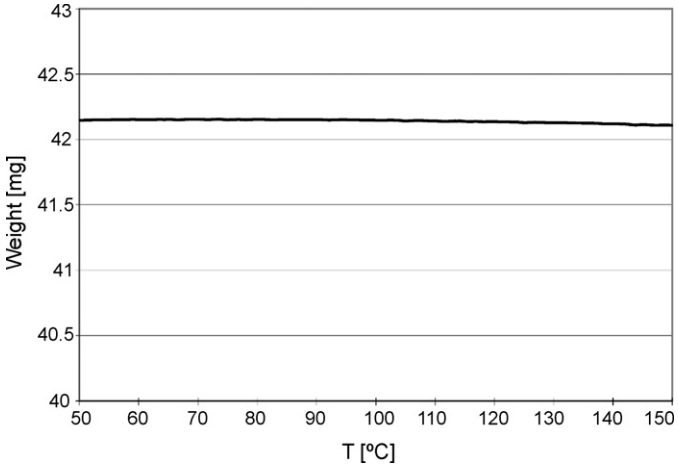

Fig. 11. TGA curve for cured CFA from 50 °C to 150 °C in air (10 °C/min).

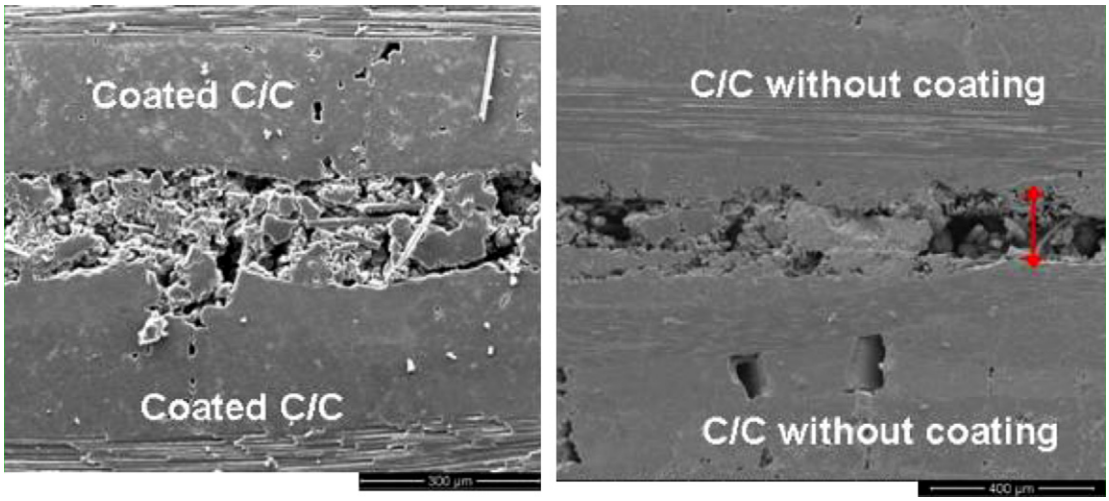

Fig. 12. SEM of C/C skins joined by CFA + 65 vol.% fumed silica.

ium, boron and aluminium oxide based glass–ceramic powder, GC (CTE = $-1.2 \times 10^{-6}\,^{\circ}C^{-1}$).

3.2.2. CFA with fumed silica filler

Fumed fillers are usually added to reduce CTE in polymeric resins for packaging technology[18]: here a compromise between CTE reduction and suitable viscosity was found by adding 65 vol.% (5 wt.%) fumed silica to CFA.

The heat treatment used to obtain the joined sample is the same as for pure CFA as joining material.

Micrographs of the cross-section of joined (coated and uncoated) C/C skins are shown in Fig. 12. The joint thickness is about 100–150 μm. The joined area is porous with a discontinuous interface with C/C.

The average apparent shear strength of the joined C/C skins by CFA +65 vol.% SiO_2 is 9 ± 3 MPa (C/C skin without seal coat) and 2 ± 0.5 MPa (C/C skin with seal coat). The obtained apparent shear strength for C/C without seal coat is lower than the requirement set in Table 1 and significantly lower than the one obtained by using pure CFA without SiO_2 addition.

The viscosity increases too much by adding more than 65 vol.% silica filler to CFA resulting in a poor feasibility of the whole process.

3.2.3. CFA with glass–ceramic powder (GC) filler

This glass–ceramic was selected for its negative CTE of $-1.2 \times 10^{-6}\,^{\circ}C^{-1}$ (100–300 °C)[4,5]; 25 vol.% GC glass–ceramic powder (<105 or <44 μm) has been added to CFA. The heat treatment used to obtain the joined sample is the same as for pure CFA (see Section 3.2.1).

Figs. 13 and 14 show SEM cross-section of joined samples. The morphological analysis of the joining material showed that the GC particles are very sharp, which could induce cracks propagation; some micrographs show also that most of all large particles are located at the bottom of the joining area; it is probably due to sedimentation phenomena and can induce problems of homogeneity of the bonding layer. The average E obtained from the nano-indentation tests performed in the joint area is 17 GPa.

The joined C/C skins without seal coat resulted in higher mechanical strengths: 17 ± 3 MPa by using the coarse GC filler (<105 μm) and 5 ± 1 MPa with the fine GC filler (<44 μm). The addition of coarser powder seems to be more effective in reducing CFA porosity, thus obtaining a denser and stronger joining material. CTE measurement was performed on C/C (without seal coat) joined by CFA + 25 vol.% GC (<105 μm). CTE of the joined sample was $-0.2 \times 10^{-6}\,^{\circ}C^{-1}$ thus indicating that the joining material has no influence on the CTE of joined materials of this size (the accuracy of the test is $0.1 \times 10^{-6}\,^{\circ}C^{-1}$). Both morphology and dispersion of GC filler need to be optimized to fully exploit this joining material.

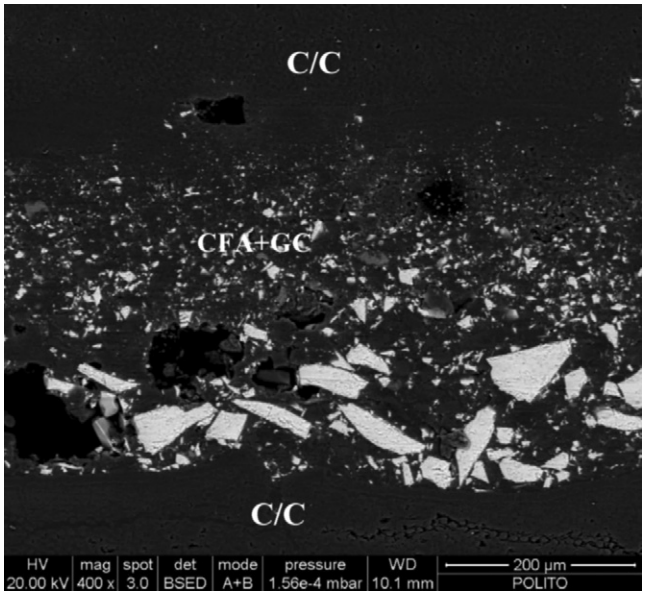

Fig. 13. SEM (back scattering) of as-received C/C skins joined by CFA + 25 vol.% GC (<105 μm).

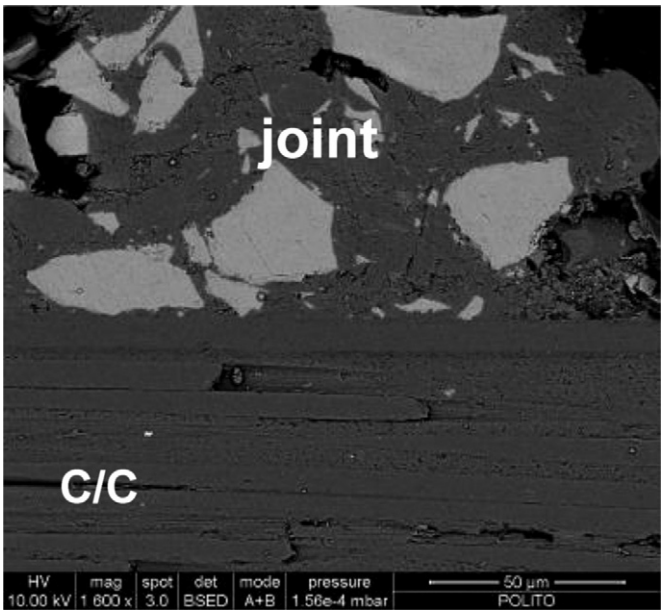

Fig. 14. SEM (back scattering) of as-received C/C skins joined by CFA + 25 vol.% GC (<44 μm).

4. Conclusions

Two brazing materials (TiCuNi, a commercial active brazing alloy, and pure silicon) and carbon fibre adhesive (CFA) have been tested as joining materials for ultra stable joints of carbon/carbon composite (C/C) sandwich.

TiCuNi brazing alloy was effective to join C/C samples and the bonding strength of the joints was higher than the interlaminar shear strength of C/C. However, the product CTE × E × thickness is too high to obtain an ultra stable assembled structure and the joining temperature is much higher than the desired value.

Pure silicon was successfully used to join C/C samples. Silicon has a low CTE and a high E, the product CTE × E × thickness would be acceptable for the envisaged application. However, the brazing process must be performed at very high temperature (1450 °C) under controlled atmosphere, thus leading to process issues.

The joining process performed by using CFA (carbon fibre adhesive) satisfies all the conditions as in Table 1, with the exception of the CTE value. In order to reduce its CTE, low CTE fillers were added: fumed silica (CTE = 0.55×10^{-6} °C^{-1}) and a barium, boron and aluminium oxide based glass–ceramic powder, GC (CTE = -1.2×10^{-6} °C^{-1}).

In conclusion, CFA and CFA + GC were found to be the most promising materials to join C/C samples.

Acknowledgements

Thales Alenia Space France and Politecnico di Torino, Italy, collaborated to this activity within the frame of ESA contract no. 20479/06/NL/Sfex.

References

1. *Cosmic Vision: Space Science for Europe 2015-2025, ESA, ESA Brochure*, vol. BR-247. 2005. p. 1–111.
2. Devilliers C, Nivet M, Copperet H. Advanced carbon/carbon materials for space telescopes structures. In: *52nd International Astronautical Congress*. 2001.
3. Panin F, Lutz-Nivet M, Lemaire H. Development of carbon/carbon sandwich panels. In: *European Conference on Spacecraft Structures, Materials and Mechanical Testing*. 2002.
4. Tauch D, Russel C. Glass–ceramics with zero thermal expansion in the system $BaO/Al_2O_3/B_2O_3$. *J Non-Cryst Solid* 2005;**351**:2294–8.
5. Tauch D, Rüssel C. Thermal expansion of glass–ceramics in the system $BaO/Al_2O_3/B_2O_3$. *J Non-Cryst Solid* 2005;**351**:3483–9.
6. Ferraris M, Salvo M, Isola C, Appendino Montorsi M, Kohyama A. Glass–ceramic joining and coating of SiC/SiC for fusion applications. *J Nucl Mater* 1998;**258–263**:1546–50.
7. Singh M, Shpargel TP, Morscher GN, Asthana R. Active metal brazing and characterization of brazed joints in titanium to carbon–carbon composites. *Mater Sci Eng A* 2005;**412**:123–8.
8. Appendino P, Casalegno V, Ferraris M, Grattarola M, Merola M, Salvo M. Joining of C/C composites to copper. *Fus Eng Design* 2003;**66–68**:225–9.
9. Singh M, Asthana R, Shpargel TP. Brazing of carbon–carbon composites to Cu-clad molybdenum for thermal management applications. *Mater Sci Eng A* 2007;**452–453**:699–704.
10. Gupta P. The Cu–Ni–Ti (Copper–Nickel–Titanium) system. *J Phase Equilib* 2002;**23**:541–7.
11. Iancu OT, Munz D, Eigenmann B, Scholtes B, Macherauch E. Residual stress state of brazed ceramic/metal compounds, determined by analytical methods and X-ray residual stress measurements. *J Am Ceram Soc* 1990;**73**(5):1144–9.
12. Thales Alenia Space private communication.
13. Lemoine P, Ferraris M, Salvo M, Montorsi M. Fracture characterization of silicon joined ceramic matrix composites. *Ceram Trans* 1995;**57**:459.
14. Salvo M, Ferraris M, Lemoine P, Montorsi M, Merola M. Joining of CMCs for thermonuclear fusion applications. *J Nucl Mater* 1996;**233–237**:949–53.
15. Salvo M, Lemoine P, Ferraris M, Montorsi M. Joining of carbon/carbon composites for thermonuclear fusion applications. *J Am Ceram Soc* 1997;**80**:206–12.
16. Dezellus O, Jacques S, Hodaj F, Eustathopoulos N. Wetting and infiltration of carbon by liquid silicon. *J Mater Sci* 2005;**40**:2307–11.
17. www.matweb.com.
18. Jang KW, Kwon WS, Yim MJ, Paik KW. Effects of silica filler and diluent on material properties and reliability of nonconductive pastes (NCPs) for flip-chip applications. *IEEE Trans Comp Pack Tech* 2004;**27**:1–8.