Novel Hybrid Ablative/Ceramic Layered Composite for Earth Re-entry Thermal Protection: Microstructural and Mechanical Performance

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In view of spacecraft re-entry applications into planetary atmospheres, hybrid thermal protection systems based on layered composites of ablative materials and ceramic matrix composites are investigated. Joints of ASTERTM lightweight ablative material with C_f/SiC (SICARBONTM) were fabricated using commercial high temperature inorganic adhesives. Sound joints without defects are produced and very good bonding of the adhesive with both base materials is observed. Mechanical shear tests under ambient conditions and in liquid nitrogen show that mechanical failure always takes place inside the ablative material with no decohesion of the interface of the adhesive layer with the bonded materials. Surface treatment of the ablative surface prior to bonding enhances both the shear strength and the ultimate shear strain by up to about 60%.

Keywords adhesives, aerospace, ceramic, composites, mechanical, microscopy, optical metallography, static, x-ray

1. Introduction

Original approaches based on ablative materials for novel thermal protection systems (TPS) are required for space applications, where resistance to extreme oxidative environments and high temperatures are required. For future space exploration, the demands for thermal shielding during very high speed atmospheric re-entry go beyond the current state-of-the-art (Ref 1–3). In addition, a new scenario has appeared due to a worldwide change in space mission planning strategies, with entry vehicles going back to capsule designs and as a result ablators are re-gaining attention. Therefore, the development of new thermal protection materials and systems at a reasonable mass budget is absolutely essential to ensure the feasibility of the envisaged missions.

Hybrid TPS heat-shields for atmospheric earth re-entry comprising an ablative material and a ceramic matrix were first reported about 10 years ago (Ref 4–6). Recently, layered ablator-ceramic composite materials have been investigated (Ref 7–9) for the protection of the metallic substructure in oxidative and high temperature environment experienced by the space vehicles (Fig. 1a). Their prospective advantages arise from the employment of a thinner, than usual, ablative layer able to withstand very high surface heat loads, while the tough ceramic composite underneath provides structural support. This results in the enhancement of the stability of the shield shape

which is an asset for the aerodynamic performance of the re-entry capsule. Since heat loads during re-entry are characterized by a heat flux peak profile (Fig. 1b) a thinner ablator can dissipate the high heat loads during the peaking time, while the underlying ceramic composite can withstand higher temperatures without sacrificing structural support.

The main challenge for the layered hybrid TPS heat-shield, described above, is to achieve a sound bonding among the two layers. In this paper, the bonding of a low density ablative outer-shield on top of a ceramic matrix composite layer (see Fig. 1a) is reported with respect to its microstructure and mechanical performance at liquid nitrogen and room temperature. The bonding of the two parts is based on the use of commercial high temperature inorganic adhesives.

2. Materials and Methods

2.1 Materials

The C_f/SiC (SICARBONTM) ceramic matrix composite (CMC) was delivered as plates by AIRBUS DEFENCE & SPACE, Germany (Ref 10). They consist of carbon fibers embedded in a silicon carbide matrix. The production process of this material is based on the Polymer Infiltration Pyrolysis process (PIP). The infiltration of the carbon fibers with a pre-ceramic polymer-based and powder-filled slurry system is performed by liquid polymer infiltration (LPI) via filament winding. The thickness of the C_f/SiC material used in the current study was 2.3 mm.

The ablative material examined was ASTERTM delivered by AIRBUS DEFENCE & SPACE, France, and it consists of carbon fibers (55–80%) and phenolic resin (20–45%) (Ref 11, 12). It is manufactured by impregnating compacted graphite felt with phenolic resin, followed by a polymerisation process and final machining. The manufacturing approach allows a wide range of final material densities from 0.2 to 0.55 g/cm³ and its decomposition point is about 235 °C while its porosity is between 75 and 80%.

For the bonding of C_f/SiC with the ablative material, three commercial adhesives were selected with a potential service

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temperature up to 1650 °C (Table 1). These adhesives were selected after initial screening of six commercial adhesives based on alumina, zirconia-zirconia silicate, and graphite in sodium and potassium solutions having high and low viscosities. The selected adhesives were supplied from Aremco Products, Inc. The identification, composition, and properties of the adhesives are presented in Table 1.

2.2 Adhesive Bonding Process

Joints of SICARBON™/ASTERM™ using the adhesives described in Table 1 were fabricated. The surface of the CMC specimens to be bonded was roughened by SiC abrasive paper. Both materials to be joined were ultrasonically cleaned using isopropanol and acetone and dried after each cleaning step. The amount of the adhesive applied was controlled by weighing. The adhesive was applied on both surfaces to be bonded. The fiber layers of the ablative material were placed parallel to the bonding area. A jig was constructed to assure the parallel alignment of the two pieces to be bonded and the homogeneous thickness of the adhesive. The bonded sandwiches were cured at room temperature for three hours and then at 94 °C for another three hours. During curing, a small load was applied on the bonded specimens. The final adhesive thickness, after adhesive curing, was 50-200 μm.

Since for good bonding, one should aim at an adhesive thickness between 50 and 200 μm, in order to prevent cohesive failure inside the adhesion layer, in the determination of the

adhesive mass to be applied on the materials, the weight loss for each adhesive during curing was taken into account.

In some of the joints prior to bonding, a silicate thinner was applied on the area on the ASTERM™ material to be bonded and it was cured at the required temperature. This was done in order to prevent separation of the adhesive constituents and absorption of the adhesive binder in the pores of the ablative material.

2.3 Structural and Thermal Characterization

X-ray diffraction (XRD) was performed for the base materials and for the adhesives. The latter, in order to perform the XRD measurements, were dried and ground into powder. Both the base materials and the cross section of the bonded specimens were investigated by scanning electron microscopy (SEM, JEOL) with EDX analysis.

The thermal stability of the adhesives was examined using thermo-gravimetric analysis (TGA) in the range 25 to 1300 °C at a heating rate of 10 °C/min in He gas atmosphere. For the TGA analysis of the adhesives, a certain quantity (few milligrams) of each adhesive was dried at 150 °C for 1 h and then ground.

2.4 Mechanical Tests

Bonded structure specimens for the mechanical tests at room and liquid nitrogen temperature were fabricated having a

Fig. 1 Schematic of the hybrid concept: (a) Thin ablative layer on top of a ceramic matrix composite and (b) The peak heat load profile of very fast re-entry scenario

Fig. 2 Schematic representation of the jig and the joint geometry used in the pure shear tests

Table 1 Identification, composition, and properties of adhesives (Ref 14)

Tradename	670 Ceramabond™	835 Ceramabond™	669 Graphi-bond™
Description	White, viscous and odorless paste	Tan, viscous and odorless paste	Black, viscous and odorless paste
FILLER major constituent	Al ₂ O ₃	ZrO ₂ -ZrSiO ₄	Graphite
Ingredients	Aluminum oxide, silicate solution	Zirconium oxide, zirconium silicate, aluminum silicate, silicate solution	Graphite, aluminum oxide, silicate solution
Viscosity, cP	2,500-5,000	20,000-40,000	20,000-40,000
Specific gravity, g/cm ³	1.80-1.95	2.25-2.35	1.45-1.50
Temperature use limit, °C	1650	1371	760
CTE, °C × 10 ⁻⁶	7.7	7.2	7.6

bonded area of $10 \times 10 \text{ mm}^2$. The shear strength of the joints was evaluated by pure shear loading, using the configuration shown in Fig. 2. The tests were carried out on an INSTRON 5982 Universal Testing Machine at a displacement rate of 0.1 mm/min. The values of maximum load and displacement at maximum load were obtained from the load-displacement

curves. In addition, the following properties were calculated; ultimate shear strength (determined as the ratio of the maximum load to the area under shear) and the % ultimate shear strain (determined as the ratio of displacement at ultimate shear strength to the original length). The values obtained for each adhesive joint is an average of three up to five tests. After

Fig. 3 XRD pattern of C/SiC (left) and $ASTERM^{TM}$ (right)

Fig. 4 SEM micrographs of the surface of the C/SiC to be bonded with magnification $\times 600$ (a) and $\times 2400$ (b). SEM micrographs of the cross section of the C/SiC at magnification $\times 300$ (c) and $\times 1200$ (d)

Fig. 5 SEM (backscattered electrons) micrographs of the ablative material of the surface to be bonded at magnification $\times 50$ (a) and $\times 400$ (b)

Fig. 6 XRD patterns of the adhesives

testing, the morphology of the fractured surfaces was examined and the general mode of failure was assessed.

3. Results and Discussion

3.1 XRD and Metallographic Analysis of the Base Materials

The XRD pattern of C_f/SiC corresponds to the compounds (a) Rhombo.R.axes carbon (C) in the R-3m space group, (b) hexagonal silicon carbide (SiC) of the P63mc space group and (c) cubic silicon carbide (SiC) in the F-43m space group (Fig. 3a). The XRD pattern of the ablative material corresponds to hexagonal graphite in the P63mc(186) space group (Fig. 3b).

Carbon fibers embedded in the SiC matrix are observed on the surface SEM micrographs (Fig. 4a, b) of the CMC. In the cross-sectional micrographs (Fig. 4c, d), alternate interlayers having the carbon fibers longitudinally and transversely ($0/90^\circ$) are observed. The dark dots in Fig. 4(c), (d) are the carbon fibers vertical to the paper. The gray light area around the fibers is the SiC matrix.

Micrographs, in backscattered electron mode, of the ASTERMTM material with its surface parallel to the bonding area of the joints are depicted in Fig. 5(a), (b). Batches of

Fig. 7 TGA (a) and DTG (b) thermal curves of the adhesives

carbon fibers can be observed with random orientation, as well as some randomly oriented carbon fiber bundles.

3.2 XRD and TGA Analyses of the Adhesives

The XRD patterns of the adhesives are given in Fig. 6. The Al_2O_3 -based adhesive corresponds to Rhombo.H.axes

Aluminum Oxide (Al_2O_3) with space group: R-3c(167). The ZrO_2 - ZrSiO_4 -based adhesive contains monoclinic zirconium Oxide (ZrO_2) with P21/c(14) space group and tetragonal ZrSiO_4 with I41/amd(141) space group. The analysis of the graphite-based adhesive shows that the pattern corresponds to hexagonal graphite of P63/mmc(194) space group.

The TGA and DTG diagrams of the adhesives are presented in Fig. 7. The weight loss during TGA is almost identical for the Al_2O_3 -based (5%), and ZrO_2 - ZrSiO_4 -based (3%) adhesives. However, the graphite-based adhesive exhibits much higher weight loss (32%). Specifically, between 25 and 1000 °C, the adhesive lost 12% of its initial mass and an additional 20% between 1000 and 1330 °C. The weight loss reflects the evolution of water loss since no organic binders, which would create volatiles, are present in the samples (Ref 13). The release of structural water, in the form of -OH groups, is most likely the mechanism for the abrupt change of weight loss in the graphite-based adhesive. It is noted that the $\text{SiO}_2\text{:X}_2\text{O}$ (X: K or Na) molar ratio varies, among the commercial used adhesives, in a not known way. The peaks of the derivative indicate the point of greatest rate of change on weight loss curves.

3.3 Metallographic Analysis of the Joints

In all the fabricated joints, the thickness of the adhesive was determined before the curing, by measuring the mass applied on both surfaces, and after the curing by the thickness of the sandwich structure compared to that of the base materials. A

decrease in the thickness is determined for all adhesives with an average value of 22% for Al_2O_3 , 47% for ZrO_2 - ZrSiO_4 and 74% for graphite, due to water loss and shrinkage.

3.3.1 Al_2O_3 -Based Adhesive. The cross section of the joint with the Al_2O_3 -based adhesive is presented in Fig. 8. The adhesive exhibits good bonding with both ASTERM™ and C_f/SiC material, presenting no cracks or voids. The cavities at the ASTERM™/adhesive interface are due to the ASTERM™ inherent porosity which is observed all over ASTERM™ cross section. Some micro-porosity that seems to be present in the bonding layer is typical of the adhesives after curing. According to the EDX analysis (Table 2), the adhesive includes the phases of aluminum oxide, aluminum silicate, and potassium silicate. The particles, “A1” areas, that are observed in the adhesive zone (Fig. 8b) are rich in aluminum oxide and aluminum silicate. In the ablative material, apart from the carbon fibers and phenolic resin, potassium silicate was detected through its whole thickness of 4.5 mm. The potassium silicate is due to the binder of the adhesive penetrating the porous ablative material. Also, in the first interlayers of the CMC in the vicinity of the adhesive a small quantity of potassium silicate is detected which originates from its diffusion in the CMC during curing.

3.3.2 ZrO_2 - ZrSiO_4 -Based Adhesive. The cross-sectional micrographs of the joint with ZrO_2 - ZrSiO_4 -based adhesive (Fig. 9) present a good bonding with both ASTERM™ and C_f/SiC materials. The interfaces are crack and void-free. Again some micro-porosity is observed inside the bonding layer

Fig. 8 SEM micrographs of the cross section of the Al_2O_3 -based joint at magnification $\times 100$ (a) and $\times 800$ (b)

Table 2 Results from EDX analysis in at.% for the joint's cross section with Al_2O_3 -based adhesive

	C	O	Al	Si	K	Main phases
Adhesive layer	...	52-53	18-22	21-22	4-6	Aluminum oxide, aluminum silicate, potassium silicate
“A1” areas (Fig. 8b)	...	51-55	21-22	24-26	≤ 1	Aluminum oxide, aluminum silicate
ASTERM™ near the adhesive (at ≈ 250 - $300 \mu\text{m}$)	60-68	21-27	...	7-9	4	Carbon, phenolic resin, potassium silicate
ASTERM™ near the free surface	67	23	...	7	3	Carbon, phenolic resin, potassium silicate
C_f/SiC in the 1st and 2nd interlayers at the vicinity with the adhesive	77-80	5-7	...	12-18	0.6	Carbon, SiC

Fig. 9 SEM micrographs of the cross section of the $\text{ZrO}_2\text{-ZrSiO}_4$ -based adhesive at magnification $\times 100$ (a) and $\times 800$ (b). (c-g) Elemental mapping of the (b) micrograph

which is not detrimental for the adhesive's performance. The elemental mapping of the Zr, O, Al, Si, and K is presented in Fig. 8(c)-(g). EDX analysis in the adhesive layer indicates the presence of zirconium oxide, zirconium silicate, aluminum silicate, and potassium silicate (Table 3). From the EDX analysis of the ablative material near its free surface, potassium silicate is found as in the case of the joints with Al_2O_3 -based adhesive. The same applies for the CMC in which K concentration of about 1 at.% is found through its whole thickness.

3.3.3 Graphite-Based Adhesive. The cross section of the joint with graphite-based adhesive is depicted in Fig. 10. The bonding with both base materials is sound and its bonding with ASTERM™ shows better adhesion than the other adhesives. The EDX analysis of the adhesive layer shows the presence of graphite and potassium silicate (Table 4). The latter is found in considerable concentration up to the free surface of ASTERM™ as in the case of the other two adhesives. Potassium silicate diffuses also in the first two interlayers of the CMC at the vicinity with the adhesive layer.

The examination of the cross section of the joint with graphite-based adhesive and thinner applied, prior to bonding, on ASTERM™ reveals penetration of the thinner at a depth of about 1.3 mm (gray area in Fig. 11).

3.4 Mechanical Tests

Shear tests were carried out on the ASTERM™/SICAR-BON™ joints for the three adhesives at room (RT) and liquid nitrogen (LN) temperature with and without previous thinner application on the ASTERM surface. Particular care was taken to ensure that only the adhesive layer was subjected to shear loading by careful construction of the jig, the compression anvils and the sliding shims supporting the specimens.

In all the joints, the failure takes place inside the ASTERM™ bulk material as it is observed in Fig. 12. Part of the ASTERM™ remains bonded with the adhesive.

The stress-strain curves at RT and without thinner application on the ASTERM™ surface are depicted in Fig. 13. These show that for all the adhesives tested, the joints present similar

Table 3 Results from EDX analysis in at.% for the joint's cross section with ZrO₂-ZrSiO₄ adhesive

	C	O	Al	Si	Zr	K	Main phases
Adhesive layer	...	57-67	≤ 2	19-24	11-15	2-5	Zirconium oxide, zirconium silicate, aluminum silicate, potassium silicate
ASTERM™ near the adhesive	60	28	...	8	...	4	Carbon, phenolic resin, potassium silicate
ASTERM™ near the free surface	67-73	18-25	...	5-6	...	3-4	Carbon, phenolic resin, potassium silicate
C _f /SiC in the 1st interlayer at the vicinity with the adhesive	80.8	11.5	...	7	...	0.7	Carbon, SiC, potassium silicate

Fig. 10 SEM micrographs of the cross section of the graphite-based adhesive at magnification ×100 (a) and ×800 (b)**Table 4 Results from EDX analysis in at.% for the joint's cross section graphite adhesive**

	C	O	Al	Si	K	Main Phases
graphite adhesive layer	54-64	21-27	≤ 1	11-13	3-5	Graphite, potassium silicate
ASTERM™ at 500 μm from the adhesive	58-67	21-30	≤ 0.1	8-10	3-6	Carbon, phenolic resin, potassium silicate
ASTERM™ near the free surface	66	24	≤ 0.1	8	2	Carbon, phenolic resin, potassium silicate
C _f /SiC in the 1st and 2nd interlayers at the vicinity with the adhesive	77-82	5-8	...	13-14	0.65	Carbon, SiC

shear strength which reflects the shear strength of the ASTERM™ material. The joints with ZrO₂-ZrSiO₄-based adhesives present the highest ultimate shear strain.

An additional series of mechanical tests were carried out, with thinner applied on the ASTERM™ surface prior to bonding, with the ZrO₂-ZrSiO₄ and graphite-based adhesives (Fig. 14). Again, fracture takes place inside the ASTERM™ material but in this case the ASTERM™ can bear a much larger load. This is attributed to some strengthening of the material due to the thinner penetrating into the porous ASTERM™. Also the ultimate shear strain appears enhanced by the application of the thinner on the ablative material.

At LN temperature (Fig. 15a, b), joints were tested with ZrO₂-ZrSiO₄ and graphite-based adhesives without thinner application. For ZrO₂-ZrSiO₄ adhesive, some samples were also tested at LN with thinner applied on the ASTERM™ surface (Fig. 15c). In all cases, the fracture takes place inside the ASTERM™ material as before. For both adhesives, the maximum load measured increases compared with those at RT, probably due to hardening of the phenolic at LN temperatures. This increase is more pronounced for the graphite adhesive.

Fig. 11 SEM (backscattered electrons) micrograph of the cross section of the graphite-based adhesive with application of the thinner on the ablative material

Fig. 12 Fractured surfaces of a joint using $\text{ZrO}_2\text{-ZrSiO}_4$ -based adhesive

Fig. 13 Stress-strain curves at ambient conditions of the joints with Al_2O_3 -based adhesive (a), $\text{ZrO}_2\text{-ZrSiO}_4$ -based adhesive (b) and graphite-based adhesive (c) without thinner application on the ablative material

This may be attributed to enhance strengthening of the ASTERM™ material by the graphite thinner (the thinner is different for each adhesive). In addition, as observed at RT tests, the use of the thinner increases drastically the maximum load at LN temperature by about 100% whereas it reduces the ultimate shear strain by about 50%.

From an analysis of the results, the predominant mechanism of failure during shear testing of the sandwich specimens

Fig. 14 Stress-strain curves at ambient conditions of the joints with $\text{ZrO}_2\text{-ZrSiO}_4$ -based adhesive (a) and graphite-based adhesive (b) with thinner application on the ablative material

appears to be gradual tearing of the ASTERM™ adjacent to the adhesive. The apparent beneficial influence of prior treatment with thinner is therefore due to the added load-bearing capacity provided by the thinner penetrating a small distance into the ASTERM™ (Fig. 11).

The values of maximum load, ultimate shear strength, displacement at maximum load, and ultimate shear strain together with the standard deviations are given in Table 5. At ambient conditions, the shear strength is similar for all the adhesives with an average value of 0.70 MPa, reflecting the shear strength of the ASTERM™ material. Joints with $\text{ZrO}_2\text{-ZrSiO}_4$ present the highest ultimate shear strain of $4.9 \pm 1.3\%$. This is attributed to the highest ductility of the $\text{ZrO}_2\text{-ZrSiO}_4$ -based adhesive. The application of thinner on the ablative material prior to bonding increases the shear strength of the joints by about 62% for both $\text{ZrO}_2\text{-ZrSiO}_4$ and graphite-based adhesives and this is attributed to the strengthening of the ASTERM™ material by the thinner. Similar increase is observed for the displacement at maximum load. At LN temperature, the shear strength, increases from 25%, for $\text{ZrO}_2\text{-ZrSiO}_4$, up to 100% for graphite adhesive, compared to that at ambient conditions. This is due to the stiffening of the phenolic resin in the ASTERM™ at LN temperature. The thinner applied on the ablative material had a positive effect, increasing the shear strength at LN.

Fig. 15 Stress-strain curves at liquid nitrogen temperature of the joints with ZrO₂-ZrSiO₄-based adhesive without thinner application (a), graphite-based adhesive without thinner application (b) and ZrO₂-ZrSiO₄-based adhesive with thinner application on the ablative material (c)

4. Conclusions

In view of the development of hybrid Thermal Protection Systems for atmospheric re-entry applications, layered joints of ASTERTM ablator with C_f/SiC (SICARBONTM) ceramic matrix composite using high temperature commercial inorganic adhesives were investigated. The metallographic analysis of the joints showed that sound joints without defects are produced. For all the adhesives tested, the shear strength of the joints is similar and reflects the strength of the ablative material since in all tests the failure takes place inside the ASTERTM material. This indicates a good compatibility between the adhesive and both the CMC and the ablative material, and shows that the defined and applied surface treatment is the correct procedure leading to the base material failure. The application of thinner on the ASTERTM surface prior to bonding strengthens the ablative material and this results in an increase of both the shear strength and the ultimate shear strain. At liquid nitrogen temperature, the mechanical shear strength is further enhanced due to the stiffening of the ablative material at this temperature.

A full verification campaign, including mechanical properties determination at high temperatures and plasma-jet tests is on-going and the results are to be published in a future paper.

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Table 5 Summary results of the mechanical tests

Adhesive	Maximum load, N	Ultimate shear strength, MPa	Displacement at maximum load, mm	Ultimate shear strain, %
Ambient conditions				
Al ₂ O ₃	74 ± 18	0.75 ± 0.18	0.28 ± 0.09	2.7 ± 0.9
ZrO ₂ -ZrSiO ₄	68 ± 9	0.68 ± 0.10	0.50 ± 0.13	4.9 ± 1.3
Graphite	64 ± 8	0.65 ± 0.08	0.31 ± 0.07	3.2 ± 0.6
ZrO ₂ -ZrSiO ₄ and thinner	111 ± 43	1.11 ± 0.43	0.80 ± 0.26	8.0 ± 2.6
Graphite and thinner	103 ± 28	1.05 ± 0.28	0.41 ± 0.06	4.2 ± 0.5
Liquid nitrogen				
ZrO ₂ -ZrSiO ₄	79 ± 15	0.80 ± 0.16	0.42 ± 0.26	4.2 ± 2.6
Graphite	127 ± 32	1.3 ± 0.32	0.37 ± 0.07	3.7 ± 0.7
ZrO ₂ -ZrSiO ₄ and thinner	181 ± 34	1.82 ± 0.33	0.22 ± 0.09	2.2 ± 0.9

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