Thermal Performance of Ablative/ Ceramic Composite

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Abstract: *A hybrid thermal protection system for atmospheric earth re-entry based on ablative materials on top of ceramic matrix composites is investigated for the protection of the metallic structure in oxidative and high temperature environment of the space vehicles. The paper focuses on the joints of ablative material (carbon fiber based CALCARB® or cork based NORCOAT™) and Ceramic Matrix Composite (CMC) material (carbon fibers embedded in silicon carbide matrix, Cf/SiC, SICARBON™ or C/C-SiC) using commercial high temperature inorganic adhesives. To study the thermal performance of the bonded materials the joints were tested under thermal shock at the QTS facility. For carrying out the test, the sample is mounted into a holder and transferred from outside the oven at room temperature, inside the oven at the set testing temperature (1100°C), at a heating rate that was determined during the calibration stage. The dwell time at the test temperature is up to 2 min at 1100ºC at an increasing rate of temperature up to ~ 9,5°C/s. Evaluating the atmospheric re-entry real conditions we found that the most suited cooling method is the natural cooling in air environment as the materials re-entering the Earth atmosphere are subjected to similar*

conditions. The average weigh loss was calculated for all the samples from one set, without differentiating the adhesive used as the weight loss is due to the ablative material consumption that is the same in all the samples and is up to 2%. The thermal shock test proves that, thermally, all joints behaved similarly, the two parts withstanding the test successfully and the assembly maintaining its integrity.

Key Words: *thermal shock, ablative materials, silicon carbide matrix composites, inorganic adhesives*

1. INTRODUCTION

The aim of the FP7 project HYDRA is the development of a hybrid thermal protection system to be used in extreme oxidative environments space applications that require high temperature resistance, such as hot parts of space vehicles for orbital entry (CTS/ARV), planetary probes and NEO exploration. The project focuses on designing, integration and verification of a hybrid heat shield based on ablative and ceramic components. The novelty of the solution consists in the integration of a low density ablative outer-shield on top of an advanced thermo-structural ceramic composite layer (Fig.1).

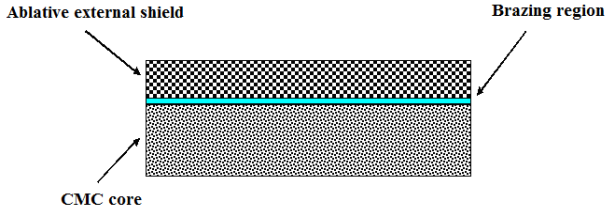

Fig. 1 − Hybrid concept scheme

This assembly is designed to have the ability to withstand extreme heat loads and to form a hybrid solution with enhanced shock absorbance, insulation, light-weight, oxidation protection, high toughness and damage tolerance properties.

The ablative material role is to bear the high thermal peak loads that the CMC cannot withstand. On the other hand, the ceramic composite layer underneath has several advantages, such as the fact that it acts as a "heat shield" for the long-term integral thermal loads during re-entry missions, it provides structural support as well as the assembly shape stability that contributes to the aerodynamic performance enhancement of the vehicles, and last but not least ensures lower contamination during re-entry phase in particular [3, 4].

Several past space missions have been analyzed in order to establish the environmental conditions during Earth re-entry stages. The parameters setting was performed on the basis of CTV/ARV(LEO) and CSTS (LLO) earth re-entry missions, taking into consideration entry environment, mass and thermal performance, eventual ablation performance, mechanical, environmental, interfacial, physical, design and programmatic requirements, as well as product assurance. Main aero-thermal requirements are summarized in the table below:

Table 1. Selected mission requirements

Mission	Total flux (max – $kW \cdot m^{-2}$)	Max Stagnation Pressure (Pa)	Total Heat Load ($MJ \cdot m^{-2}$)
CSTS (LLO)	5700	60600	416
CTV / ARV	700 – 1700	~15000 to 20000	140 – 270

During the space mission, the temperature varies from -100ºC in outer space to 1200ºC during the re-entry stage [2].

The main challenge regarding this hybrid solution is represented by the bonding of the two parts ablator and CMC that has to be able to withstand the extreme conditions during re-entry, namely a temperature peak up to 1200ºC and still perform when the ablator is fully charred. Taking into consideration these aspects, the use of inorganic adhesives appears to be most suitable choice. For the selection of the appropriate adhesive the following are taken into account [1]:

1. Thermomechanical performance of the adhesive bonding at the different phases (launching, ascent, re-entry).
2. Nature of the inorganic main adhesive constituent (alumina, zirconia, graphite, all at low and high viscosity grades).
3. Wettability of the adhesive with the surfaces of the base materials.
4. Curing temperature.
5. Ablator/ceramic interface temperature (aided by modeling).
6. Thermal properties (CTE, thermal conductivity).

The thermal shock test follows a procedure that has both qualitative and quantitative nature and the procedure aims to accomplish a hierarchy of various types of materials relative to the behavior during quick thermal shock tests by counting the number of fast thermal shock cycles and temperatures at which the tests were carried out until the appearance of damage, cracks or exfoliation of the layers [5, 6]. The procedure allows highlighting the microstructural changes in multilayer materials by optic and electron microscopy investigations (focusing on layer thickness, thickness uniformity, degree of porosity, cracks form and position in layer and boundary layer, formation of new layers by oxidation constitutive elements and their thickness, layer evolution with testing temperature, shape and size of component materials).

The thermal shock test performed in HYDRA project involved testing the joints, based on high temperatures adhesive, between the ablative and ceramic matrix part of the thermal protection assembly. The testing temperature was 1200ºC and the dwell time 2 minutes.

2. EXPERIMENTAL SECTION

2.1 Materials

The samples tested have two main components: the ablative material represented by CALCARB (CALCARB CBCF 18-2000- MERSEN- consisting of short cut carbon fibers, interconnected in a matrix produced by the carbonization of phenolic resin) and two types of ceramic matrix material (CMC) a) SICARBON^{TM} supplied by Airbus Group Innovations and b) C/C-SiC supplied by DLR. The two main components were joined using commercial adhesives supplied by AREMCO. Three types of adhesives were selected based on initial microstructural investigation of cross sections and pull off tests, namely a) CERAMABOND 669 based on graphite, b) CERAMABOND 670 based on Al_2O_3 and c) CERAMABOND 835 based on ZrO_2-$ZrSiO_4$.

2.2 Method and instrumentation

The thermal shock tests were performed using a facility designed and conceived by INCAS. For the performance of the test, the TPS sample is mounted into a holder and shifted form outside the oven from room temperature, inside the oven at the testing temperature of 1100°C and at a heating rate that was determined during the calibration stage. The testing program involved subjecting the samples to the set temperature for a period of time up to 2

minutes, weighting each sample before and after testing. The temperature measurement on the sample surface inside and outside the oven as well as in the cooling area is performed using 3 pyrometers. Evaluating the atmospheric re-entry real conditions, the most suited cooling method is the natural cooling in air environment as materials re-entering the Earth atmosphere are subjected to similar conditions.

The experimental setup, QTS facility, comprises a heating system composed of a vertical oven, provided with two holes, one at the lower part of the oven for the entrance of the specimen and the second on the lateral part to permit the reading of the surface specimen temperature in the oven during the quick thermal shock test. The movement of the specimen in and out the oven, and in the cooling area is achieved with 4 robot arms, three horizontal and one vertical. The specimen is mounted into a special ceramic holder provided with holes for passing of the thermocouple wire and insulated appropriately. The data acquisition system registers the testing parameters continuously, with lab View program. The data parameters recorded are: specimen temperature outside and inside of the oven during the test, environment temperature, water cooling temperature, heating time, dwell time, cooling time for air cooling. The testing parameters can be settled as per requirements in a large range of parameters: oven temperature between 900°C and 1400°C, the movement speed of the robot arms between 0 and 400mm/s, position precision 0.01 mm, data registration at 1 second, dwell time from 0 to 60 minutes, air pressure cooling from 2 to 9 bar.

QTS conceived by INCAS is a versatile facility that can perform a wide range of test parameters and values that include high heating and cooling rates up to 70°C/s, testing temperature up to 1500°C, which correspond to extreme operational conditions; Tests can be performed at progressive temperatures, with rate of 50°C, 25- 50 cycles, sequential analysis of visual and / or microstructure and weighing; the sample cooling is made in air. A specimen of parallelepiped shape is moved from the ambient temperature in the preheated facility furnace. The specimen is maintained at the set temperature for a period of time and then moved outside, where cooling can be performed using compressed air from or at room temperature. QTS facility possesses the following characteristics:

- Variable heating rates depending on the structure and chemical composition of the tested materials and constructive solution of the test installation,
- Maximum cooling rate 70°C/s,
- Precise positioning of the specimen in heating and cooling zone,
- Specimen dimensions: 1.5÷2.5 x 30 x 50 mm (for the HYDRA project, the specimen holder was adjusted for 10 x 30 x 50 mm specimens),
- Measurement temperature of specimen with quick response time radiation pyrometers,
- Vertical cylindrical furnace with Super Kanthal type resistances,
- Lab View data acquisition system,
- Ensuring the reproduction of extreme functional conditions of industrial parts.

The cross sections of the tested samples were investigated using Scanning Electron Microscopy (SEM, JEOL) with Energy Dispersive X-ray (EDX) analysis. Prior to the examination of the cross section, the sample was embedded in resin, then cut and polished.

2.3 Thermal shock testing parameter set up

The specimen was mounted into a special refractory ceramic support (holder) provided with holes for wire thermocouple passing and insulated against the metallic support. The thermocouple wires (+ and -) were mounted directly into the Lab View special adapter.

The established test temperature is set (1100°C), afterwards there is a time frame in which the oven reaches this value. The sample is maintained at 1100°C for approximately 2 minutes (timed since the sample thermocouple started recording this value), at the end of which, the robot arm removes the sample from inside the oven, the cooling being performed in atmospheric environment.

The nanocomposites were subjected to spectroscopy analysis using Thermo iN10 MX Mid Infrared FT-IR Microscope and scanning electron microscopy using HITACHI S2600N microscope.

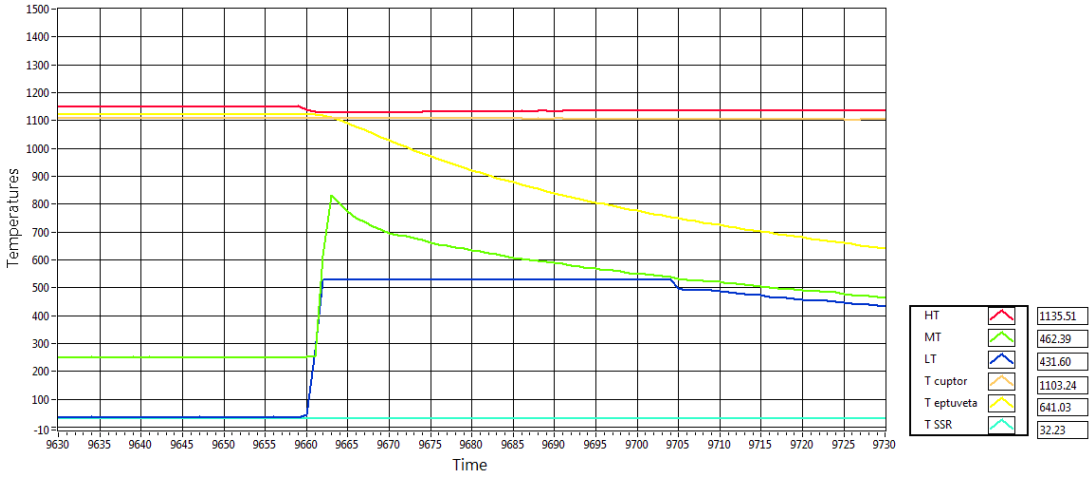

Fig. 1 – Set up parameters

Table 2 below presents a comparison between the sample weight before testing at 1100°C and after testing and cooling to room temperature respectively. A 0.5g decrease in weight can be observed.

Table 2. Gravimetric analyses of the E=ST specimen after thermal testing at 1100°C

Sample	Initial weight (g)	Final weight (g)
E=ST	40	39,5

The 0.5g weight loss that represents 1.25% of the initial weight is due to the consumption of the ablative material, which can be optically observed; the CALCARB edges are burned and rounded.

Setting the optimum parameters of the QTS2 facility previous to testing covered the following issues:

- The emissivity of the pyrometers were set up at 0.9- program Data Temp Multidrop Raytek delivered with the pyrometers,
- The oven temperature was set with a multifunction calibrator BEAMEX MC5 type and thermocouple B type Pt30Rh/Pt6R,
- The oven temperature was stabilized with GEFRAN equipment 1200 / W312 type,
- High temperature HT pyrometers – measurement range (500ºC÷2000ºC) – red color on graphic,
- Medium temperature MT pyrometers – measurement range (250ºC÷1650ºC) – green color on graphic,

- Low temperature LT pyrometers – measurement range (0ºC÷800ºC) – blue color on graphic,
- Oven temperature-range (400ºC÷1750ºC) – orange color on graphic,
- Specimen thermocouple temperature (K type range -100ºC÷1372ºC) – yellow color on graphic,
- GEFRAN SSPC-W312 external radiator temperature-(thermocouple range -100ºC÷400ºC) –turquoise color on graphic.

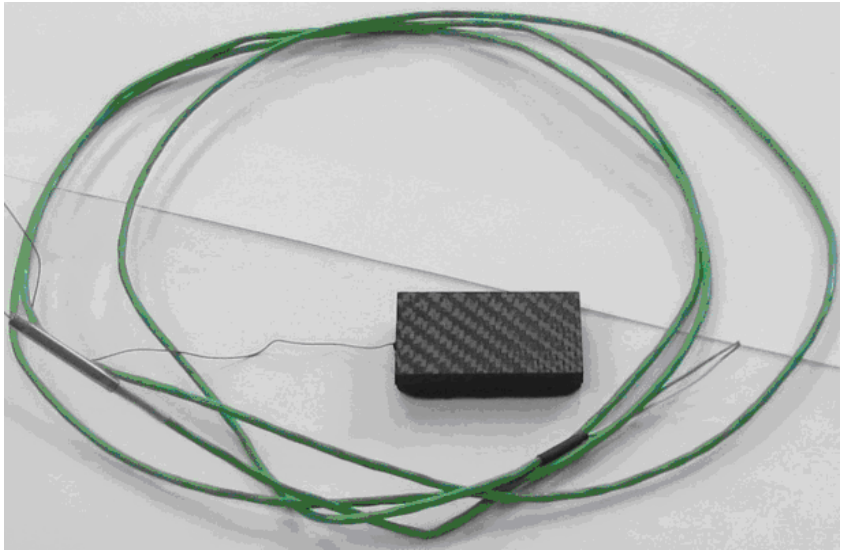

Fig. 2 – Specimen with thermocouple before testing

3. RESULTS AND DISCUSSION

After the calibration stage, the testing parameters were set: Testing temperature: 1100°C; Sample temperature increase speed rate: ~ 9,5°C/sec; Time interval for maintaining at test temperature: ~ 2 minutes; Cooling in atmospheric environment up to room temperature.

3.1 CALCARB/adhesive/CMC C/C-SiC series

There were tested 2 sets of TPS specimens according to the established testing program; the data recorded during testing as well as the results are presented in this section. The results are presented for the two types of CMC material and then by the adhesive type.

For the testing of the samples, the measurement ranges for the thermocouples used to cover the entire measurement domain:

- High temperature HT pyrometers – measurement range (500ºC÷2000ºC) – red line,
- Medium temperature MT pyrometers – measurement range (250ºC÷800ºC) – green line,
- Low temperature LT pyrometers – measurement range (0ºC÷500ºC) – blue line.

Three samples of each adhesive were tested. The samples components were CALCARB as ablative material and C/C-SIC as CMC layer.

There were 3 samples based on CERAMABOND 669 (graphite based) adhesive (Sample#1,#2, #3), 3 samples based on CERAMABOND 835 (de ZrO_2-$ZrSiO_4$based) adhesive (Sample#4,#5, #6), and 3 samples based on CERAMABOND 670 (Al_2O_3 based) adhesive (Sample#7,#8, #9).

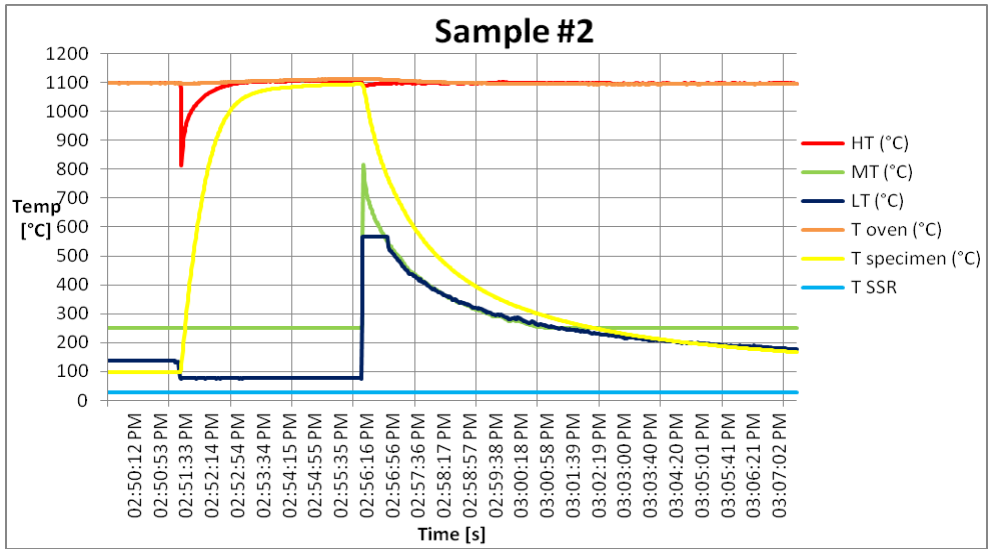

Fig. 3 – Thermal shock test of Sample #2 at 1100°C

Table 3. Temperatures recorded during thermal shock test of Sample #2

Sample #2	Time	HT (°C)	MT (°C)	LT (°C)	T_{oven} (°C)	$T_{specimen}$ (°C)	T SSR (°C)
Sample introduction into the oven	02:51:26 PM	1093.7	250.8	76.7	1097	99.9	28.4
The sample reaches the oven temperature	02:55:11 PM	1106.7	250.3	76.7	1110.5	1090.8	28.5
Sample removal from the oven	02:56:11 PM	1090.6	557	567.3	1112.5	1090.8	28.4
Cooling	03:29:02 PM	1095.9	250.4	143.8	1096.6	113.5	28.6

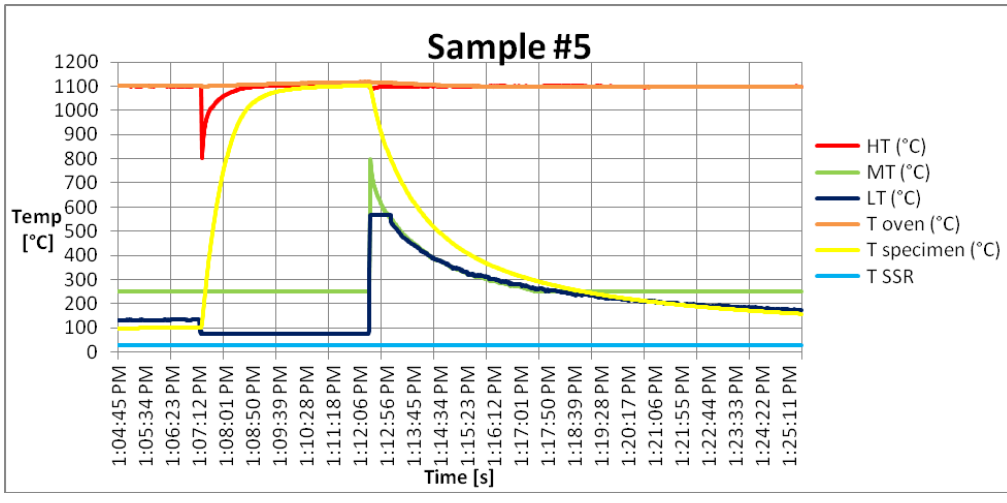

Fig. 4 – Thermal shock test of Sample #5 at 1100°C

Table 4. Temperatures recorded during thermal shock test of Sample #5

Sample #5	Time	HT (°C)	MT (°C)	LT (°C)	T_{oven} (°C)	$T_{specimen}$ (°C)	T SSR (°C)
Sample introduction into the oven	1:07:16 PM	1100	250.4	76.5	1100.9	101.8	28.2
The sample reaches the oven temperature	1:11:27 PM	1105.1	250.4	74.9	1115.2	1099	28.1
Sample removal from the oven	1:12:26 PM	1092.6	609	567.3	1116.8	1099.7	28.1
Cooling	2:06:10 PM	1094.9	250.2	140.7	1099.4	107.7	28.1

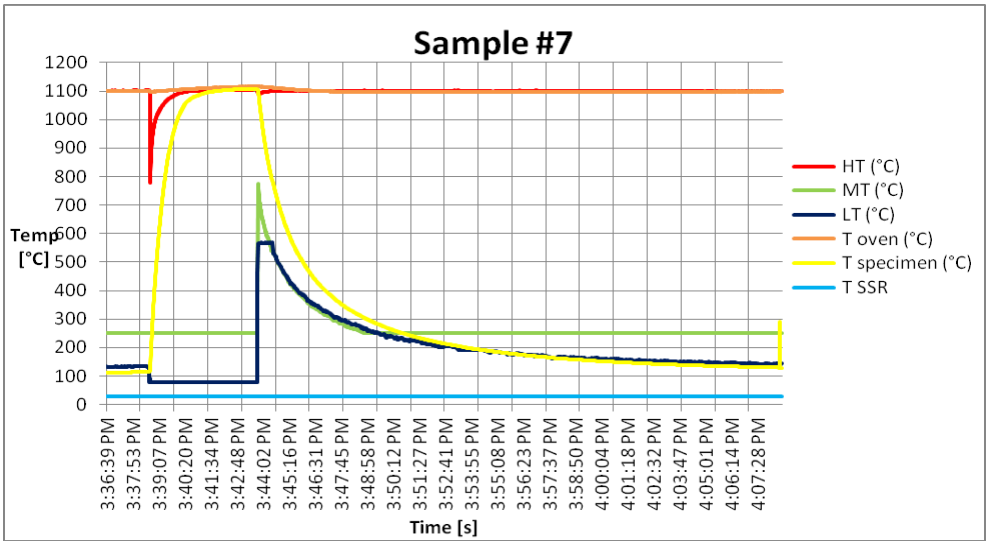

Fig. 5 – Thermal shock test of Sample #7 at 1100°C

Table 5. Temperatures recorded during thermal shock test of Sample #7

Sample #7	Time	HT (°C)	MT (°C)	LT (°C)	T_{oven} (°C)	$T_{specimen}$ (°C)	T SSR (°C)
Sample introduction into the oven	3:38:41PM	1101.2	250.4	78.1	1099.6	114.5	28.7
The sample reaches the oven temperature	3:41:51PM	1103	250.3	77.8	1111.5	1100	28.6
Sample removal from the oven	3:43:50PM	1091.7	775.8	567.5	1116.4	1098.3	28.6
Cooling	4:07:52PM	1100.6	250.7	144.7	1098.7	130.5	28.9

Thermally, all samples behaved in the same manner, there were no major deviations in terms of their thermal response. There were some minor differences concerning the time in which the samples based on a specific adhesive reached the testing temperature. The graphite adhesive (CERAMABOND 669) based samples reached testing temperature the fastest, in an average of 152 seconds, while Zirconia adhesive (CERAMABOND 835) based samples reached the testing temperature in an average of 227 seconds.

All samples withstood successfully the thermal shock test at 1100°C, the thermocouple was kept at its initial position at the interface steadily, the adhesive material kept its adhesion properties, the CMC C/C-SiC part did not present any visible damage, whereas the ablative material edges are visibly burned and rounded because of it's consumption during extreme temperature testing. The ablative material loss is confirmed also by the gravimetric analysis.

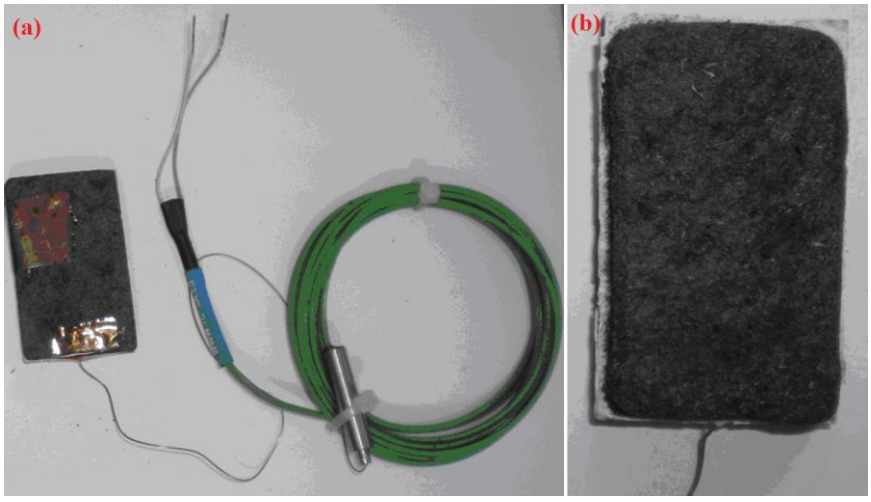

Fig. 6 – Sample#4 (CALCARB/CERAMABOND835/CMC-C/C-SIC) before (a) & after (b) testing at 1100°C

3.2 CALCARB/adhesive/SICARBON series

The set contained 9 samples, divided into 3 subsets according to adhesive type. The samples components were CALCARB as ablative material and SiCarbon as CMC layer. There were 3 samples based on AREMCO 669 (graphite based) adhesive (CAL_SiC_Graph_L_hf_1, 2, 3), 3 samples based on AREMCO 835 adhesive (ZrO2-ZrSiO4based) (CAL_SiC_Zr_H_hf_1, 2, 3), and 3 samples based on AREMCO 670 (Al2O3 based) adhesive (CAL_SiC_ALU_L_hf_1, 2, 3).

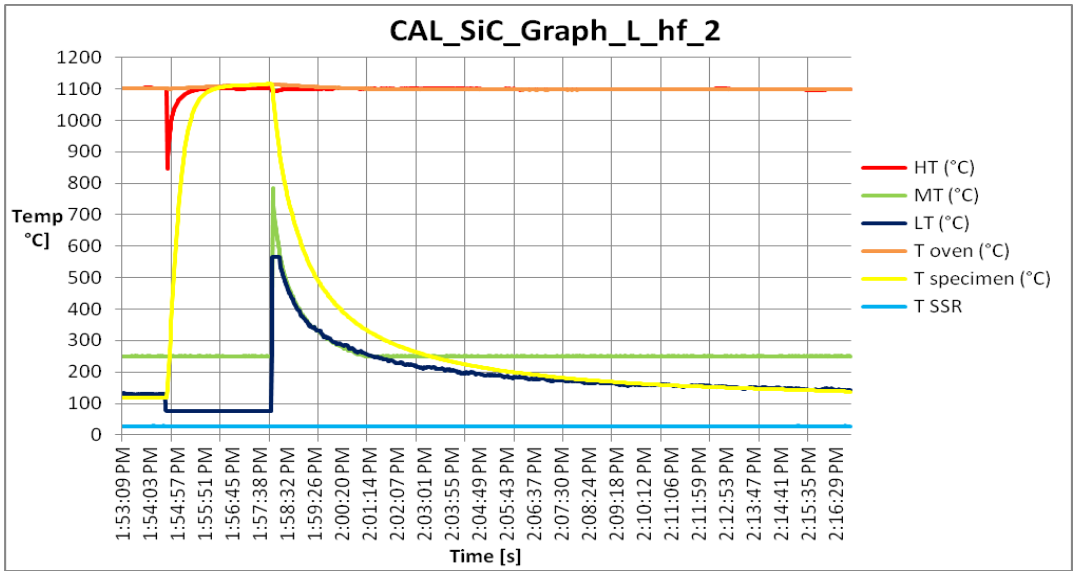

Fig. 7 – Thermal shock test of CAL_SiC_Graph_L_hf_2 at 1100°C

Table 6. Temperatures recorded during thermal shock test of CAL_SiC_Graph_L_hf_2

CAL_SiC_ Graph_L_hf_2	Time	HT (°C)	MT (°C)	LT (°C)	T_{oven} (°C)	$T_{specimen}$ (°C)	T SSR (°C)
Sample introduction into the oven	1:54:35 PM	1101.7	250.4	77.6	1101	118	28.5
The sample reaches the oven temperature	1:56:11 PM	1100.9	250.5	76.3	1108.1	1100.2	28.4
Sample removal from the oven	1:58:04 PM	1092.8	785.7	567.3	1113.8	1095.5	28.3
Cooling	2:16:58PM	1098.1	250.4	144	1099.6	137.7	28.5

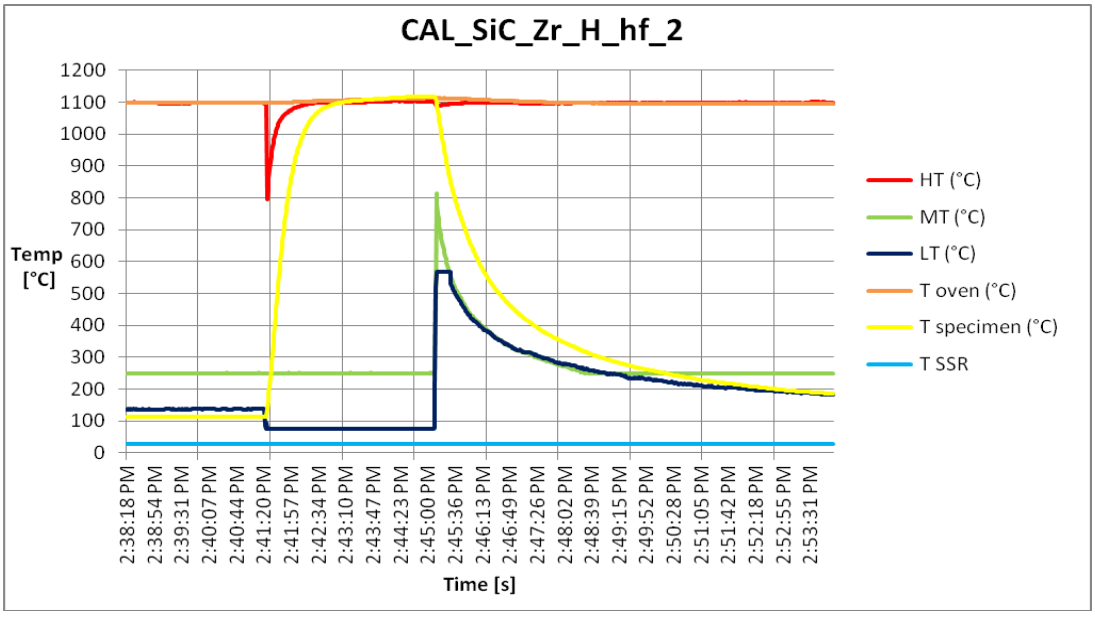

Fig. 8 – Thermal shock test of CAL_SiC_Zr_H_hf_2 at 1100°C

Table 7. Temperatures recorded during thermal shock test of CAL_SiC_Zr_H_hf_2

CAL_SiC_Zr_H_hf_ 2	Time	HT (°C)	MT (°C)	LT (°C)	T_{oven} (°C)	$T_{specimen}$ (°C)	T SSR (°C)
Sample introduction into the oven	2:41:24 PM	1096.6	250.3	76.2	1098.9	114.9	28.3
The sample reaches the oven temperature	2:43:08 PM	1099.4	250.4	75.7	1106	1100.2	28.4
Sample removal from the oven	2:45:12 PM	1090.5	813.2	567.2	1113.4	1101.5	28.4
Cooling	2:54:03PM	1096.8	250.4	183.8	1096.7	185.2	28.5

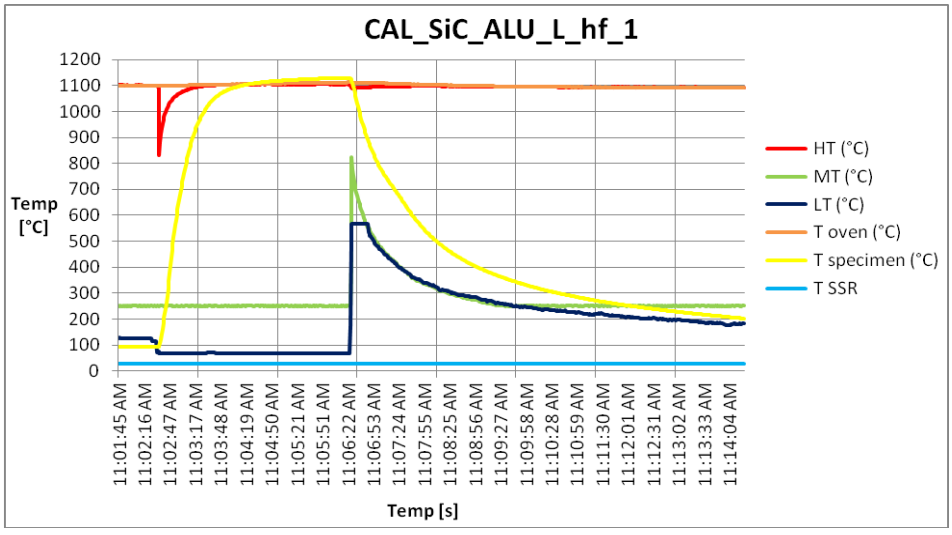

Fig. 9 – Thermal shock test of CAL_SiC_ALU_L_hf_1 at 1100°C

Table 8. Temperatures recorded during thermal shock test of CAL_SiC_ALU_L_hf_1

CAL_SiC_ALU_L_hf_1	Time	HT (°C)	MT (°C)	LT (°C)	T_{oven} (°C)	$T_{specimen}$ (°C)	T SSR (°C)
Sample introduction into the oven	11:02:35AM	883.7	250.6	68.1	1098.8	108.4	28
The sample reaches the oven temperature	11:04:15 AM	1103.9	250.6	68.1	1105.1	1100.3	27.9
Sample removal from the oven	11:06:29 AM	1088.9	749.9	567.4	1111	1097	28
Cooling	11:14:21 AM	1092.6	250.6	182.1	1092.4	202.4	28.2

In terms of thermal behaviour and thermal resistance, this set of samples did not present any differences compared to the other one.

There were some minor differences concerning the time in which the samples based on a specific adhesive reached the testing temperature, Zirconia adhesive (AREMCO 835) based samples reached 1100°C the fastest, in an average of less than 90 seconds, while Alumina adhesive (AREMCO 670) based samples reached the testing temperature in an average of 229 seconds.

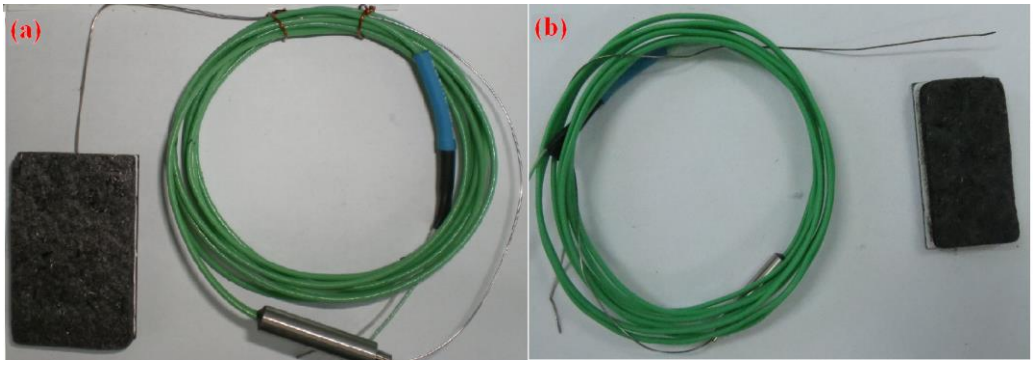

Fig. 10 – CALCARB/adhesive/SiCarbon (CAL_SiC_ALU_L_hf_2) before (a) and after (b) testing at 1100 °C

3.3 Gravimetric analysis

The gravimetric analysis performed on the samples consisted in weighting each specimen before and after it was subjected to thermal shock test, in order to evaluate the ablative material loss during the 2 minutes submission at extreme temperature.

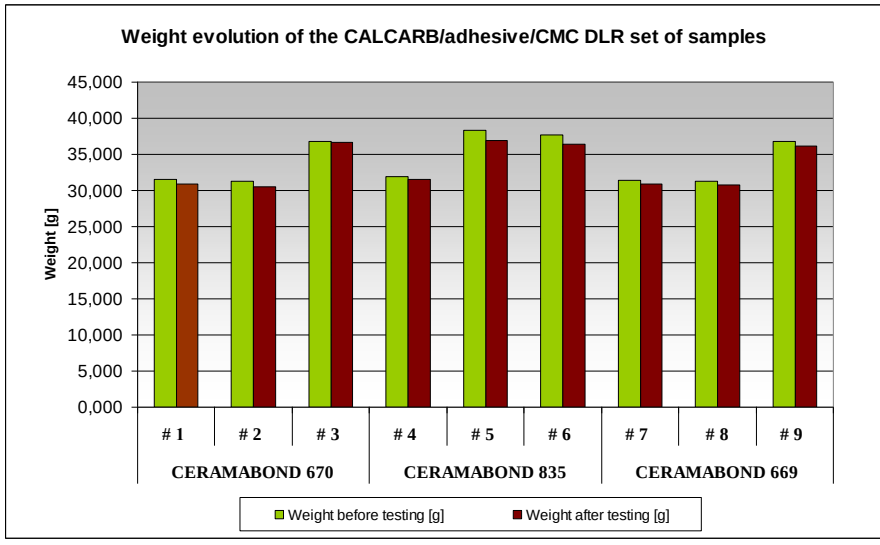

Fig. 11 − Gravimetric analysis of the CALCARB/adhesive/CMC C/C-SIC set of samples

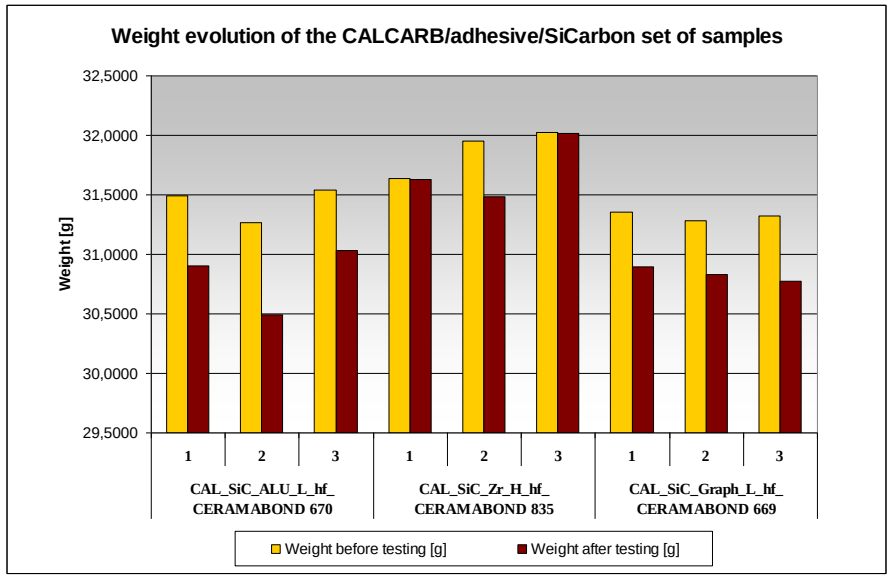

Fig. 12 − Gravimetric analysis of the CALCARB/adhesive/SICARBON set of samples

The average weigh loss was calculated for all the samples from one set, without differentiating the adhesive used as the weight loss is due to the ablative material consumption that is the same in all the samples. The ablative material weight loss was on average 0.72g representing approximately 2% of the initial weight for the CALCARB/adhesive/CMC-C/C-SiC set of samples, and 0.42g representing approximately 1.3% of the initial weight for the CALCARB/ adhesive/SICARBON set.

3.4 Microstructural investigation

The cross sections of the tested samples were microstructurally investigated using SEM.
Fig. 13 depicts the cross section from the specimen with ZrO_2-$ZrSiO_4$ based adhesive. The adhesion at the interface is very good presenting no voids. In the adhesive zone EDX analysis reveals a relatively high concentration of Al and Si element in the yellow marked area (grey areas) which indicates the presence of alumino silicate whereas the red marked areas (white area) are rich in Si and Zr (see Table 9) from the zirconium oxide and zirconium silicate.

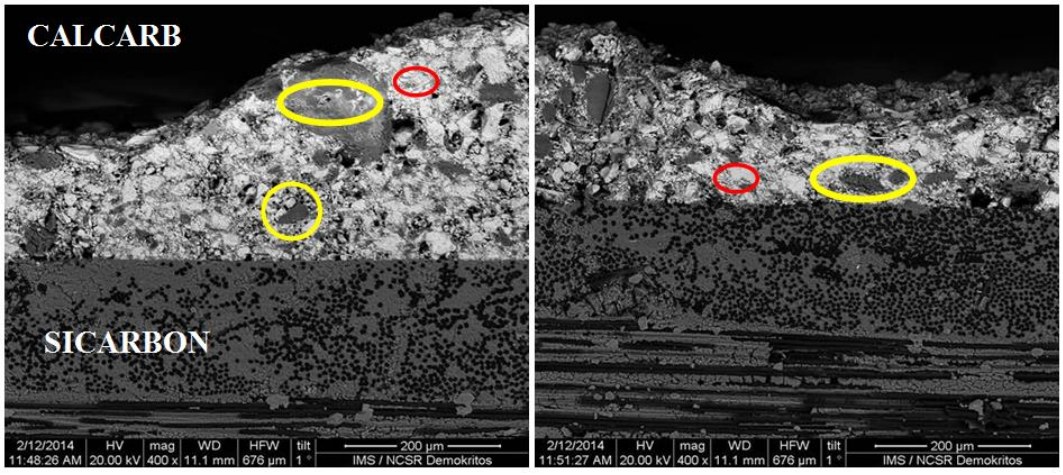

Fig. 13 − SEM backscattered electrons micrograph of CALCARB/SICARBON using ZrO_2-$ZrSiO_4$ based adhesive

Table 9. EDX analysis of the adhesive zone in the CALCARB/SICARBON sample using ZrO_2-$ZrSiO_4$ based adhesive

% at	O	Al	Si	Zr	K	Main phases
grey area, adhesive	52-59	20-23	20-24	-	≤1	alumino silicate
white area, adhesive	58	≤3	22-23	13-19	≤3	zirconium oxide, zirconium silicate

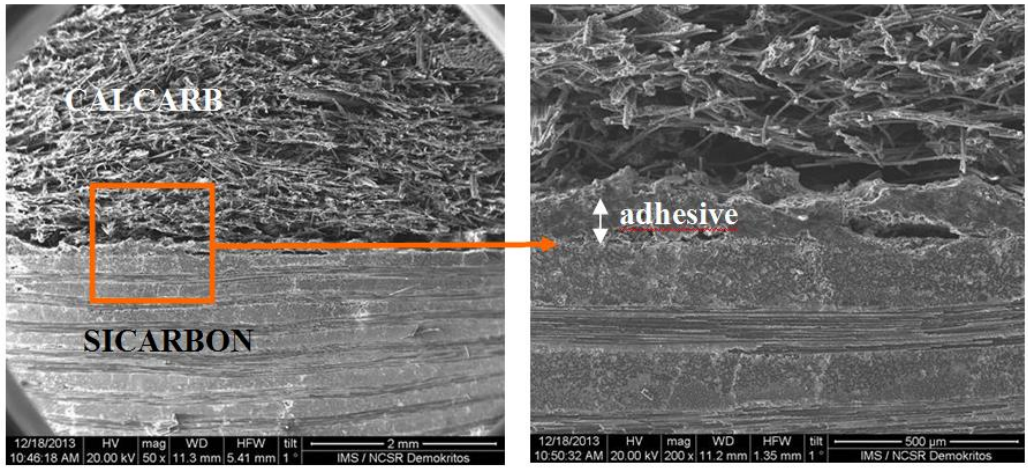

Fig. 14 − Cross section micrograph of CALCARB/SICARBON sample using graphite based adhesive

In the samples with the graphite based adhesive some gaps at the interface of the adhesive with the CALCARB. In general there is a good bonding with SICARBON, apart from some voids, small in number. In the other samples some cracks were observed at the adhesive/SICARBON interface (Fig. 14). The EDX analysis of the CALCARB and adhesive zone are presented in Table 10.

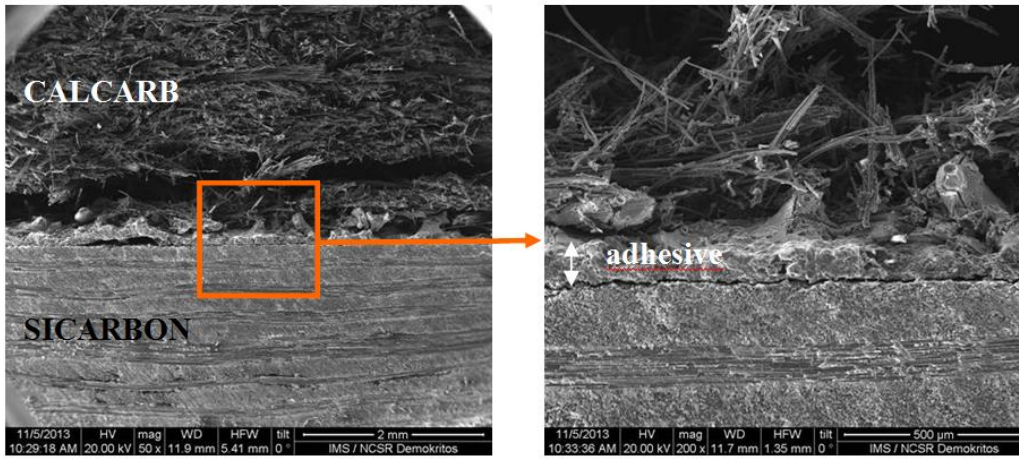

Fig. 15 − Cross section micrograph of CALCARB/SICARBON sample using graphite based adhesive

Table 10. EDX analysis of the CALCARB/SICARBON sample using graphite based based adhesive

% at	C	O	Si	K	Al
CALCARB away from the interface	88	10	<1	<2	-
adhesive zone	70	16	8	5	<1

In general the thermal shock tests have not changed the microstructure of the joints; similar features were observed in the as-fabricated samples.

In the samples where alumina based adhesive was used after the thermal shock tests exerting small force the two parts were separated and the failure was at the interface of the adhesive with CALCARB.

4. CONCLUSIONS

- Two sets of ablator/CMC samples were subject to thermal shock tests at 1100°C: in one set C/C-SiC material was used and in the other Cf/SiC material; the two parts of the samples were bonded using 3 different adhesives supplied by AREMCO based on Al_2O_3, ZrO2- ZrSiO4 and graphite.
- Thermally, both sets of samples behaved similarly, but there were some minor differences concerning the time in which the samples based on a specific adhesive reached the testing temperature: graphite samples reached 1100°C in 152 seconds for Tecnalia set and 103 seconds for NCSRD set, zirconia based samples reached 1100°C in 227 sec for Tecnalia set and 87 for NCSRD set, while alumina based samples reached this temperature in 197 sec in Tecnalia samples and 229 sec in NCSRD set.
- In general, all samples survived the thermal shock tests and in addition the microstructure at the interface of the adhesive with the base materials was not modified. In the set with Cf/SiC material using Al_2O_3 based adhesive there was a debonding of the CALCARB material from the adhesive.

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