DOI: 10.13009/EUCASS2017-504

STABILIZATION OF C/C BASED SHELL STRUCTURES FOR HIGH TEMPERATURE RE-ENTRY

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Abstract

The use of laminated composite shells in many engineering applications has been expanding rapidly in the past five decades due to their higher strength and stiffness to weight ratios when compared to most metallic materials. There are multiple options for dealing with the severe thermal environments encountered during hypersonic flight. Passive, semi-passive, and actively cooled approaches can be utilized.
The aim of this paper is to study a shell structure for space applications such as leading edges of a re-entry vehicle. The structure has to be reusable, lightweight and thin.
The use of Carbon/Carbon composites for the design of shells allows structures to withstand temperatures over 1600°C. The main features of these composites are the high resistance, high elongation modulus, high mechanical properties at high temperature and very low CTE. The key factor for using this kind of material in re-entry applications is the high stability at high temperature, preserving its mechanical properties.
A 3-D shell prototype manufactured via CVI will undergo to the stabilization process. The manufacturing process will be controlled via testing control samples which follows the prototype during its production cycle. The samples will be tested in order to analyze the morphological and thermo-mechanical characteristics.

1. Introduction

In the last decades, the research on composite materials have been acquiring importance due to the possibility of increasing the material mechanical performances while contemporary decreasing both mass and volume of the structures.
The employment of composites within the space environment may result in different detrimental effects via modification of their chemical, electrical, thermal, optical and mechanical properties, as well as surface erosion. The major degradation effects in composites are generally due to exposure to atomic oxygen, vacuum ultraviolet, thermal cycling and combined effects during orbit period, as well as to the harsh environment induced by plasma, which affects the external surfaces of the vehicles during re-entry phase.
Carbon-Carbon (C/C) composites are engineered materials that are principally composed by carbon fibers and carbon matrix, sometimes enriched with other components in particulate or fibrous form. C/C composites offer a wide range of properties that can be tailored by the selection of constituent materials, fiber orientations, and details of fabrication. Typically, C/C material and components are designed simultaneously so that the composite properties can be addressed to enhance specific component performances. The characteristics of interest are strength and stiffness, fracture toughness, frictional properties, thermal conductivity and resistance to oxidation at high temperatures.
In order to obtain more stable characteristics of these composites high temperature stabilization cycles are performed usually.
In this paper the selection of raw materials, both C/C and C-SiC Foam, has been studied with the aim to manufacturing high thickness C/C prototypes for employment in re-entry systems. The C/C densification has been achieved by means of a customized CVI treatment: then the realized items have been tested and analyzed in order to assess and validate the whole manufacturing process. Moreover, an enhanced Thermal Treatment has been carried out in order to stabilize the C/C, at a temperature of 400°C, activating pyrolysis processes [1] that can improve the matrix microstructural geometry and thus the thermos-mechanical characteristics of the previously densified materials.

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In order to demonstrate this approach a test campaign has been performed: a morphological analysis has been carried out in order to analyze the chemical-physical properties of materials treated and not treated. Mechanical Compression Tests and CTE tests have been carried out in order to study the thermo-mechanical properties of stabilized C/C;

2. Materials and method

2.1 Carbon/Carbon composites manufacturing method

The C/C shell was manufactured on the basis of the experience obtained by previous studies [2]. A 6K twill textile produced by Microtex was used in order to constitute the 3D preform. The preform was then infiltrated with the Isothermal Chemical Vapour Deposition (CVD) method. In the C/C production by CVI the carbon fiber preform is the substrate, while the carbon matrix is obtained from the decomposition of hydrocarbon-based precursor. Although CH_4 requires a temperature above 550°C to initiate the carbon deposition, it is widely available and has excellent diffusion properties so that it is widely used in the CVD/CVI process. Diffusion can be further intensified by dilution with H_2, He, N_2 or Ar to increase the CH4 mean free path, that is the average distance that a gas molecule covers between two successive collisions. The forced flow of the precursor gases, the laminar flow diffusion, and the adsorption of reactants on the substrate surface to give solid products constitute the key stages of the densification. A porous substrate infiltration is required so as to secure a suitable balance between diffusion rate and surface reaction kinetic, since a high rate of deposition tends to block the pores thus preventing the preform filling. Such a blocking mechanism inevitably occurs during the process, thus it becomes necessary to machine the surface to re-open the pores for subsequent infiltration; consequently, the CVI process may require protracted processing times to gain successful densification.
The precursor used in the CVI process for the infiltration of the shell is the methane CH_4.
The preform were uniformly heated and some infiltration cycles were applied on the sample in order to densify it.
The shell was then refined by grinding operation from Aldebaran sample before performing the post treatment stabilization process. In order to evaluate the post treatment with more neutrality some control samples have been grinded from Antares preform also.
In the following table the main physical parameters are reported.

ITEM	Fiber yarn & D-stitch	Thickness (mm)	Density (g/cm3)
ANTARES	12 K / 3D	30-36	1.52
ALDEBARAN	12 K /4D	30-36	1.46

Table 1. Main characteristics of the five manufactured preforms.

Figure 1 : C/C Shell before the stabilization cycle.

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2.2 Carbon Carbon Stabilization Cycle

The graphitization process, that thermally transform non-graphitic carbon materials into graphite, is well known in the Carbon matrix composites. The rate and completeness of transformation of a starting carbon material into graphite depends on many factors: process temperature and time, nature of the raw materials used, composition and content of impurities, gas atmosphere and applied pressure [3]. CVI process has been selected as it allows to manufacture high thermal conductivity and the process may results in a very pure and graphitizable carbon matrix. [4].
The weak feature of the graphitization process are the high temperatures of activation of about 2000-3000°C. These temperatures imply high costs of processing. Thus the approach proposed in the present work is to perform a "low temperature cycle" of 400°C, temperature at which pyrolysis process is activated, in order to remove impurities and complete the carbonization process with partial re-ordering of the matrix. This will increase the mechanical properties and stabilize the thermal properties of the final product.
The leading edge prototype and a series of samples for the thermo-mechanical characterization have been prepared in the furnace. The abovementioned series is made of 10 samples for compression, of 25x25x25 mm size (5 for Aldebaran, 5 for Antares), nr. 4 (nr. 2 for Aldebaran, nr. 2 for Antares) for CTE, 4 Raman specimens and the Leading Edge.
The cycle was performed at 400°C for a period of 90 minutes in an argon saturated environment in order to avoid oxidation of the composites. A low vacuum system was activated during the cycle. In the diagram below is reported the temperature of the overall stabilization cycle.

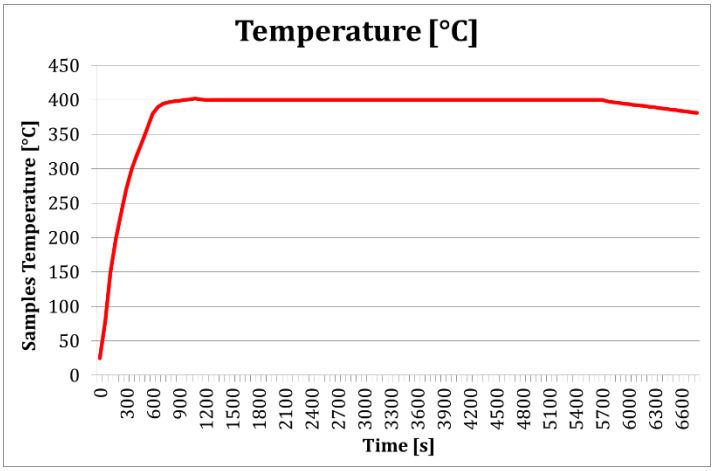

Figure 2 : Temperature vs. time during the stabilization cycle

2.3 Thermal Analysis

Thermal analysis has been performed by the use of a LINSEIS push rod dilatometer, L75H. All the test follows the ASTM E228 because it refers to the determination of the linear thermal expansion of rigid solid materials using push-rod dilatometers. Samples have been preconditioned in a humidity controlled environment before the tests. Control tests performed on alumina samples were performed in order to understand the measure error which is less than 0.2×10^{-6}/K.

2.4 Mechanical analysis

Mechanical analysis has been performed by the use of a Schenck Trebel Tester. The mechanical testing device is equipped by two parallel plates in order to compress the samples. The testing machine is equipped with an U2B (classe 00) 20 kN force transducer with a nominal sensitivity at 2mV/V and with a METIOR TRZ200 2 kN with a nominal sensitivity at 2mV/V.

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2.5 Morphological analysis

Morphological analysis has been carried out by the means of a B-1000 Optika optical microscope [5]. Moreover, the density has been evaluated by the use of a Mettler-Toledo XP26DR balance with a sensitivity of 2µg located in a ISO 8 clean room.
The principle of the confocal microscope is to illuminate only one spot on the sample at a time through a pinhole. The light is reflected by the objective back to the pinhole. By scanning the spot or the sample in a raster pattern a complete image can be formed.
Density is a very important parameter which allows to evaluate the volatile part of the matrix. Specimens were weighed before and after the stabilization cycle. In the table below weights are reported and the total mass loss is reported in terms of percentages.
The mean value of the total mass loss is 0.157. This underlines how the matrix is well structured around the fibers and that there was a low content of volatile components, thus proving the high stability of the material.
This suggests that the improvement in the thermal and mechanical characteristics is due to a re-arrangement of the matrix morphology.

Table 1 : Material Samples weight

ITEM	**Weight before cycle (g)**	**Weight after cycle (g)**	**Total Mass Loss %**
ANTARES			
Compression 1	37.30	37.25	0.13
Compression 2	36.51	36.44	0.19
Compression 3	36.70	36.65	0.14
Compression 4	37.56	37.51	0.13
ALDEBARAN			
Compression 1	35.00	34.94	0.17
Compression 2	26.45	26.40	0.19
Compression 3	34.65	34.61	0.12
Compression 4	38.67	38.60	0.18

From the Optical Microscope images, it appears quite clear the improvement that the 400°cycle induced on the material samples. In fact, in figure a and b it is possible to see, with a magnification of 500x on the side surface, that the Carbon matrix results much more attached to the Carbon fibers than in the pre-cycle material sample (b). It appears to be confirmed by fig c and d, at a magnification of 100x: although some vacuum zones remain, the interface appears more continuous. In figures e and f, upper surface has been investigated: the morphology of C/C composite appears more neat in the post-cycle sample.
All these results can be explained with the possible creation of further matrix aggregates, thanks to residual graphite powder inside the material samples. A part of this powder has been blown out of the sample during the vacuum pre-conditioning phase (see par.2), but a residual part remained and possibly aggregated.

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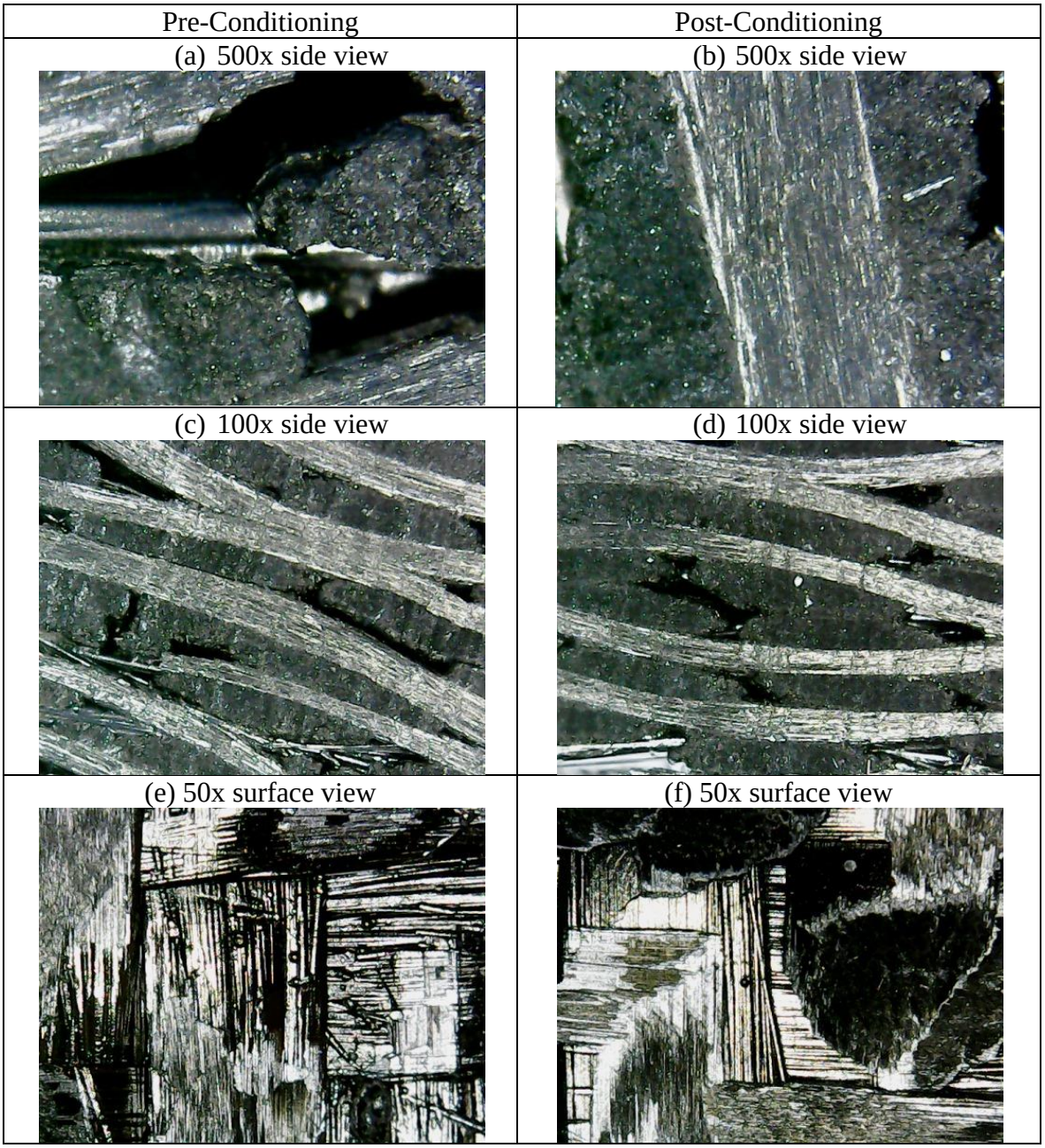

Figure 3 : Optical images of the samples

3. Thermal behavior analysis

Dilatometric analysis have been performed on both samples only infiltrated by CVI as well as on samples which underwent the stabilization process.

The table below reports the average values of the thermal expansion coefficients of the pre-treatment samples and post treatment samples.

As it is possible to see the mean difference is of 9.3% and 0.17×10^{-6}/K, standing within the measure error of 0.2×10^{-6}/K and it demonstrates that the thermal properties of the composites remain stable with the increase of the temperature. The plots also show a great stability on over 1000°C regardless of performing the stabilization cycle (Figure 3).

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Table 2 : CTE for CC samples

Temperature (°C)	Average value of pre-treatment (10^{-6}/K)	Average value of post treatment (10^{-6}/K)	Difference (10^{-6}/K)	Difference (%)
400	1.60	1.60	0	0
500	1.60	1.60	0	0
600	1.60	1.70	-0.10	6.25
700	1.60	1.70	-0.10	6.25
800	1.70	1.80	-0.10	5.88
900	1.70	1.90	-0.20	11.76
1000	1.70	2.00	-0.30	17.65
1100	1.80	2.00	-0.20	11.11
1200	1.90	2.10	-0.20	10.53
1300	1.90	2.10	-0.20	10.53
1400	1.90	2.20	-0.30	15.79
1500	1.90	2.20	-0.30	15.79

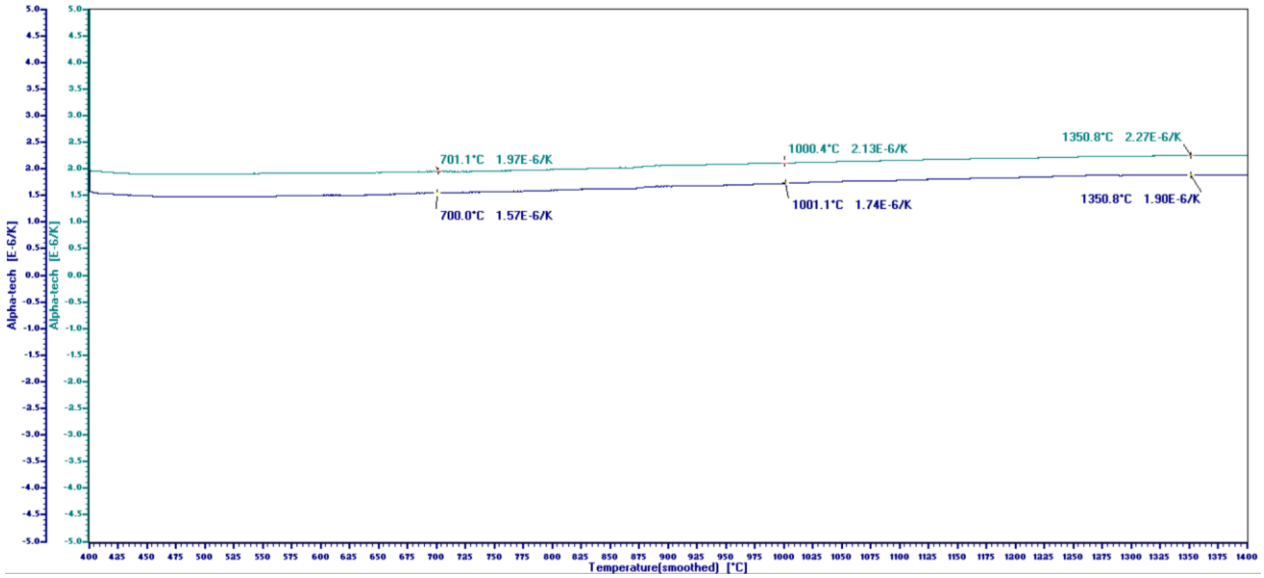

Figure 4 : Thermal expansion coefficient of pre (blue) and post (light blue) treatment of C/C

4. Mechanical behavior analysis

Mechanical tests allowed to assess the break load of the composite. In the diagrams of Figure 5 and Figure 6 the break load values are reported for the tested samples. The tested samples have the fibers oriented in the radial direction with respect of the load direction. The highest values refer to the different position of the fibers. In these latest cases the fibers are perpendicular with the respect to the load direction.

All the samples show an increase of the compression strength, the mean improvement for Aldebaran is of about 200%, the mean improvement for Antares is of 40%.

The difference between the two preforms could be due to the matrix morphology. In fact, the morphological analysis demonstrates an improvement of the matrix bonding to the fibers.

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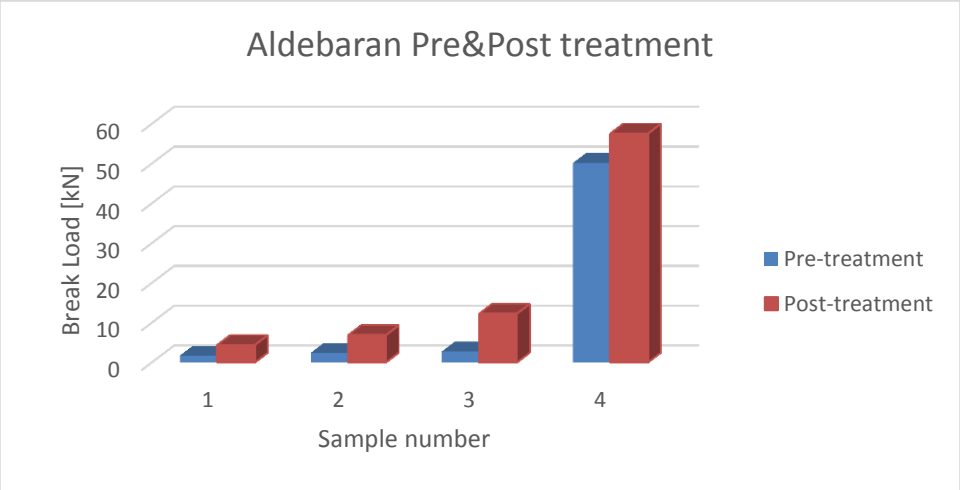

Figure 5 : Aldebaran pre and post treatment samples compression strength

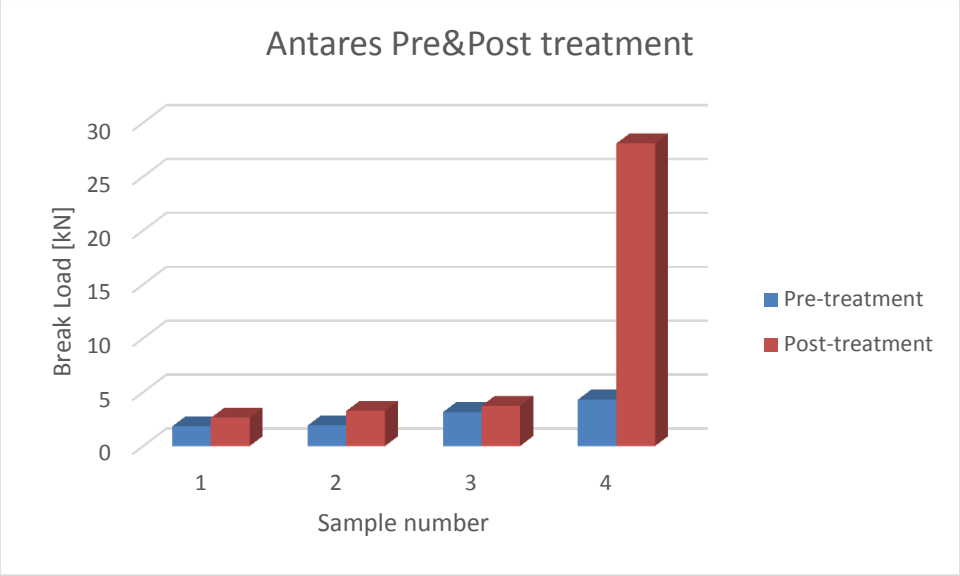

Figure 6 : Aldebaran pre and post treatment samples compression strength

5. Conclusions

In this work a stabilization process at low temperatures was analyzed in order to increase the thermo-mechanical properties of materials with the objective of providing a more cost effective solution compared to expensive graphitization process.
The proposed process, performed only for two hours at 400°C, showed a slight increase of the mechanical properties, thanks to the increase of the matrix bonding to the fibers whereas the thermal properties remained stable before and after the stabilization cycle.
Further morphological analysis to perform with Raman spectroscopy, SEM and EDS analysis will allow to confirm the positive impact of the process on the composite.

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Acronyms

CVI Chemical Vapour Infiltration
CTE Coefficient of Thermal Expansion

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