EFFECT OF THE ATMOSPHERE IN THE ABLATION OF CARBON-PHENOLIC COMPOSITES USED IN THERMAL PROTECTION SYSTEMS

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Abstract

Ablatives composite materials are vastly employed in rocket nozzle components and as thermal protection shields in aerospace industry. In this work, an experimental study on the influence of atmospheric pressure on the ablation of carbon-phenolic composites is performed. The composite is produced by wrapping process and used in the manufacture of thermal re-entry protections. Samples were tested in the following thermal fluxes: 0.626; 0.903; 1,376 and 1,725 MW/m^2 in the 30, 50, 70 and 90 sec exposure times in a plasma tunnel simulating the pressure of 400 Pa and compared to the results obtained in the same thermal fluxes and exposure times at atmospheric pressure. Results were also compared with a computational simulation and a simple and reliable model is proposed to express the influence of environment pressure, presenting good agreement and physical coherence. The specific mass loss rate at rarefied pressure was lower than obtained at dense atmospheric pressure but this difference decreases with the increase of the exposure time due to the process of densification of the carbonized layer. The low concentration of oxygen existing in the rarefied air pressure contributes to slow pyrolysis reaction during the ablation process

Keywords: ablation, carbon-phenolic composites, thermal protection.

1. INTRODUCTION

The launching and sounding vehicles are important devices for research and to practical and commercial use of space. They represent the transport system by which satellites, human beings and inhabited stations are placed into Earth orbit. Additionally, microgravity

experiments are conducted inside and outside the Earth's atmosphere and missions to space exploration [1].

Many components and integrated systems of launching vehicles are manufactured in composites in order to meet two basic design requirements for space vehicles that are stiffness and mechanical strength combined with low weight and heat resistance. Besides, mass reduction for components such as fairing, fins and motor cases is critical since they represents an increased in payload [2].

Some of these items made of composites for launching vehicles are exposed during a certain period of time under extreme temperature excursions (above 1000°C) and to high speed gas flow (Mach 3), as is the case of the thermal protections of fairings and of the reentry capsules when they return from their missions. Usually, these parts are exposed to temperatures which the working service limit and even the melting point of conventional alloys [3].

The heat absorbed by the composite structure (carbon fiber/phenolic resin) causes endothermic processes because the area in contact with the gas flow undergoing a pyrolisis process. This phenomenon is given the name of ablation [2].

The composites used as thermal protection systems have to present high heat capacity to dissipate heat per unit mass [2]. Among the composites that meet these requirements carbon fiber/phenolic resin composites plays their role. The choice of phenolic resin as matrix structure is because it has high carbon yield content when subjected to pyrolysis. The porous carbon residue structure obtained during the ablation process is a result of absorbed heat and protects the structural elements [3]

Ablation is a process involving phase change and chemical reactions suffered by the material, where the heat produced by the conversion of kinetic energy is eliminated by mass loss. Among the several factors that affect the physical phenomena during ablation of a composite, is the presence of the surrounding atmosphere and its composition. Since various chemical reactions are involved during the pyrolysis of the virgin material, resulting in the exit of the gases through the porous carbonized layer formed on the outer surface. Thus, it is necessary to evaluate the influence of the surrounding medium on the ablative properties of the material, so that it can be dimensioned accurately.

In the reentry phase, the vehicle starts from 120 km altitude with a speed of 7.6 km/s and decelerates by atmospheric friction to values of 2.0 km/s to 30 km altitude. Much of the kinetic energy of the vehicle is dissipated by braking in the atmosphere, generating thermal flows in the order of five to ten MW/m^2 and, consequently, heating at high temperatures, between 2000 K and 6000 K, due to the interaction of the gas with the surface of the vehicle characterizing this plasma of reentry as a thermal plasma.

Under these conditions, the gas is partially ionized consisting of neutral molecules, atomic and molecular radicals, electrons, positive ions, negative ions and photons. This ablative reentry environment [4][5] can be simulated in part by the use of thermal plasma torches, which are essential tools to reproduce the intense thermal flows in steady state (2 MW/m^2), to which these specimens were submitted.

In this work, a plasma tunnel consisting of a vacuum chamber with a volume of $3m^3$, which generates Mach 5 plasma jets, with a diameter of around 25 centimeters was used. The specific enthalpy levels reach 10 MJ/kg and plasma jet temperatures of the order of 3000 K.

The erosion rate of the samples was studied by varying their mass before and after the plasma torch ablation test. The experimental results allow to evaluate the properties and behavior of the ablative carbon-phenolic composites produced by wrapping process and also check the accuracy of these with the theoretical results obtained by computer simulation using a numerical method previously validated.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The specimens were extracted from a carbon-phenolic preform made by biased tape wrapping process. The carbon fiber cloth used is T22R-ECHO with thickness 0.45 mm, weave pattern 2x2 Twill, areal weight 350 g/m^2 ± 35 g/m^2 and density 1.55 g/cm^3. A phenolic resin resol type matrix with viscosity of 1000 cPs at 20°C (manufactured by Plastiflow) has been used. The prepreg process was carried out on the Plastflow facilities. After wetting, the volume of fiber reached 55-60%.

These pre-pregs were cut in tapes with 110 mm width and wound on reels mounted on a winding machine. In this machine, a metal mandrel adapted with a support was set up to obtain the wrapping angle of 20° relative to the main axis of the winding mandrel direction. This process consists of compacting the pre-impregnated tape by means of a roller which compresses it against the surface of the mandrel. This roller shall exert a force resulting in a surface compression at the roller/tape contact area of approximately 7 MPa. Immediately before reaching the mandrel/roller contact point, where the compression occurs, the tape is heated with a heating turbine at a temperature of 80°C so that the resin becomes more fluid and the prepreg more malleable. The process then develops continuously throughout the mandrel as shown in Figure 1.

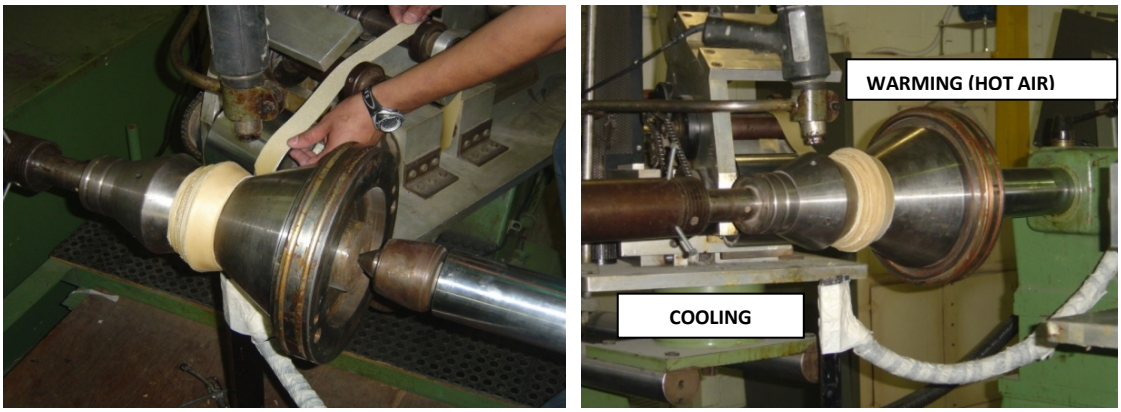


Figure 1: Biased tape wrapping process

After wrapping process, the workpiece was polymerized in a hydroclave following a cycle of 1h at 100°C and 3 hours at 165°C at a pressure of 7.0 MPa, with vacuum applied throughout the process to extract the volatiles from the phenolic reaction. After the curing cycle, the blank is demolded and undergoes a machining process to provide regular surface finish.

A cup saw was used to remove small cylinders with a diameter of 12.5 mm in the position indicated in Figure 2a. After cutting, the samples were machined with a diameter of 10.0 ± 0.3 mm with a length of 8 mm. these were identified and weighed on a precision scale (± 0.0001g). A new weighing of the specimens was also done after exposure to the thermal flow, to determine the rate of mass removed per unit area and time of exposure to the plasma jet (kg/m^{2}s), known as specific mass loss rate.

Sixteen (16) carbon/phenolic test specimens were machined and weighed, as shown in Figure 2b. Quartz/phenolic rings were machined and adjusted to the specimens in order to serve as a thermal insulation and in the sample holder assembly.

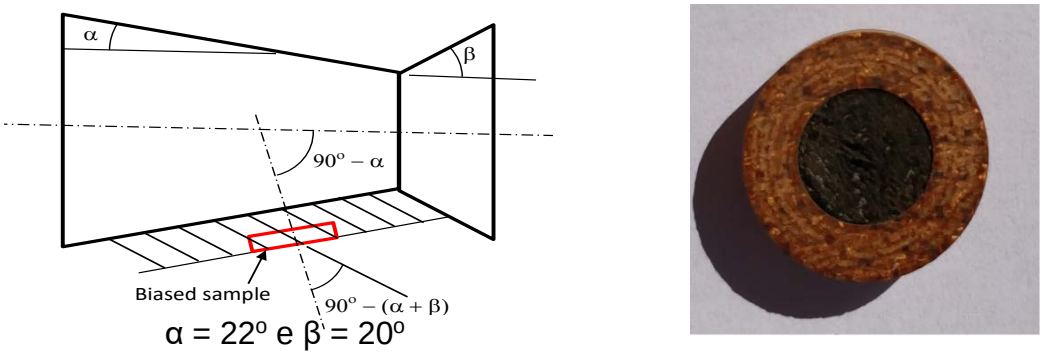


Figure 2:(a) Extraction position of the specimen in the blank; (b) Sample ready to tests

2.2 Ablation tests

The ablation tests were performed in the plasma wind tunnel of the Center of Science and Technology of Plasmas and Materials (Figure 3a), which contains an arc-jet plasma torch, according to Figure 3b. The plasma torch used in this work is a linear type with self-stabilized non-transferred electric arc. The supersonic nozzle in which the torch is coupled is known as Laval nozzle, used to accelerate the plasma jet, increasing the enthalpy of the torch. The assembly is coupled to the vacuum chamber (tunnel) by adaptation in one of the inspection windows of the rear chamber door [6].

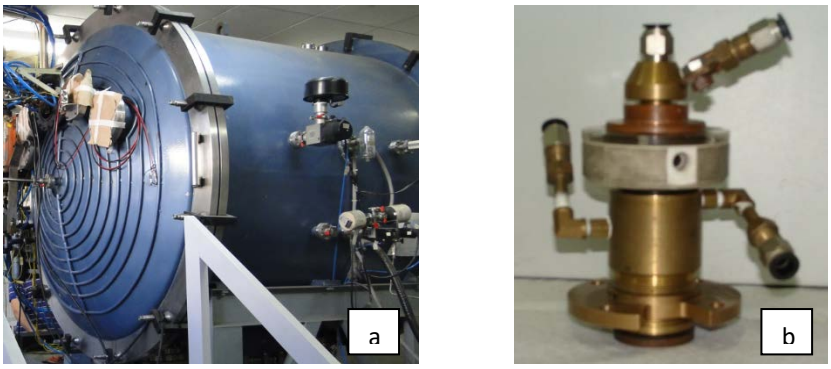


Figure 3: (a) Arc plasma facility; (b) Plasma torch

This vacuum chamber has a 3.2 m³ volume, built in stainless steel. It has a cylindrical shape of 1.5 m diameter and 1.8 m length and two doors with inspection windows. The side of the tunnel has flanges for insertion of accessories such as thermocouples, water hoses and electrical cables. There is a rotating structure, internal to the vacuum chamber, which has eight arms that supports the samples (sample holders), according to Figure 4a. These arms are cooled with water throughout the test, as are the torch and nozzle, and the sample is mounted at the tip of the arm to receive the plasma torch in the test, as shown in Figure 4b. The arms can be rotated and exposed to the plasma by the axis shown in Figure 4a, which pass through a hole to the external side of the chamber, and can be manipuled by a kind of steering wheel that guarantees the sample position.

a b

Figure 4: (a) Sample holder set ; (b) Sample holder 3D design

The test conditions were defined by relating the best enthalpy increase with the best thermal efficiency, obtaining an inlet gas flow value of 190 L/min.

The heat flux was measured along the axial line of the jet at several distances measured from the nozzle, to determine a relation between the thermal flux and the distance from the nozzle. It's used a copper disk calorimeter connected to a thermocouple at 3 mm from the exposed end of the calorimeter. The thermal flux curve was obtained as a function of the distance from the nozzle as shown in Figure 5. From this curve, the distances were calculated to perform the tests in varied determined heat flows.

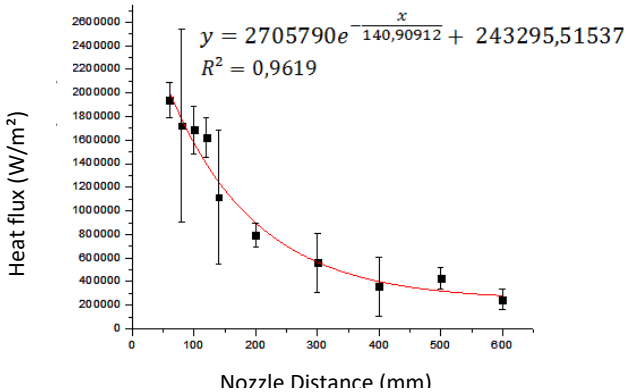


Figure 5: Thermal flux curve

Eight (8) sample holders containing the samples are first mounted on the rotating structure internally connected to the tunnel. They are positioned at the calculated distances for the desired heat flux and connected to the refrigeration system. Subsequently, the thermocouples are connected and the sample holders are aligned to the plasma jet axis using a laser system. The thermocouples collect the temperature of the unexposed surface of the sample, while exposed surface temperature is collected by an optical pyrometer connected to a computer.

The samples were exposed to the plasma jet heat fluxes: 0.636, 0.903 and 1.376 MW/m² at 30, 50, 70 and 90 sec.

2.3 Numerical Simulation

The mathematic model developed by Machado [7] was used for comparison between the experimental data and the simulation. The selected parameter was the specific mass loss rate, evaluated instantaneously by the model from the integration in each step of time. Also, the temperatures and the interfaces evolution were calculated and compared to the measured ones. The model used properties taken from literature, in Table 1.

Table 1 – Carbon/phenolic properties used on the mathematical model [8] [9] [10] [11]

Material	Property	Value
Virgin Material	Specific heat	1197 J/kg°C

	Thermal conductivity	0.867 W/m°C
	Specific mass	1398 kg/m^3
	Pyrolisis heat	1.40 MJ/kg
	Pyrolisis temperature	450 °C
	Emissivity	0.78
Char	Specific heat	1587 J/kg°C
	Thermal conductivity	1.58 W/m°C
	Specific mass	1135 kg/m^3
	Sublimation temperature	1666 °C
	Ablation heat (char)	26.48 MJ/kg
	Emissivity	0.70

The discrepancy between the experimental results for the tests performed at atmospheric pressure and low pressure must be explained by one or more physical phenomena. Due to the dependence of atmospheric pressure, these physical phenomena must occur on the external surface of the specimens. Thus, the mathematical model used must be modified taking account this effect.

One of the possibilities analyzed was the consideration of the convection between the external surface of the specimens and the environment air. A source term based on Newton's cooling law was added to the external contour condition, where the convective coefficient was estimated by empirical correlations where the environment pressure was inserted. No significant change was obtained in relation to the results obtained from the original model, which did not consider the effect of the pressure.

The gases resulting from the pyrolysis that percolate through the carbonized layer, degrade with temperature through complex reactions [12]. The modeling of these reactions goes beyond the scope of this work. However, it is possible to propose a simplified model based on the degradation and oxidation of these gases to account for their effect on surface heat flux, as a function of the environment pressure.

Assuming that the degradation reactions are approximately represented by a single carbon combustion reaction on the outer surface:

$$C + O_2 \rightarrow CO_2 + q_g$$

q_{CO20} – Combustion heat of CO_2, 8.95 MJ/kg for the resulting product at 300 K [13].
Cp_{CO2} – Specific heat of CO_2, 871 J/kgK at 300 K [13].

In this case, the surface heat flux in W/m^2 will be given by :

$$\dot{q_g} = q_g \dot{m_g} \quad (1)$$

Where: $\dot{m_g}$ is the rate of product formation of the reaction per unit area of the surface, in kg/m^{2}s . Assuming that the degradation reactions due to oxygen of the environment air occur according to the Arrhenius model, the reaction rate will be given by:

$$\frac{\partial \dot{C_{CO_2}}}{\partial t} = K e^{-Ea/RT} C_C C_{O2} \quad (2)$$

Where: C is the concentration of reactants and product. The parameters K, Ea e R are respectively the reaction constant, the activation energy and the CO_2 constant. To construct an empirical model, the previous equation will be related term to term with the rate of formation of the product.

The concentration of the reactant carbon is linked to the gases formed by the pyrolysis. Thus, it is assumed that it is proportional to the rate of pyrolysis, that is, to the velocity of recession of the pyrolysis front:

$$C_C \propto V_p$$

The concentration of O_2 on the surface depends on the partial pressure thereof. As the percentage of O_2 in environment air is constant, it must be directly proportional to the environment pressure from the ideal gas equation (Amagat model):

$$C_{O2} \propto \frac{P}{RT}$$

Where: *R* is the air constant, 287 J/kgK.

Finally, the rate of formation of the products will be considered proportional to the rate of change of the CO_2 concentration generated by the reactions:

$$\dot{m_g} \propto \frac{\partial \dot{c_{CO_2}}}{\partial t}$$

Combining the three proportions with the Arrhenius formulation, we can consider:

$$\dot{m_g} \propto \frac{P}{RT} V_p = C_g \frac{P}{RT} V_p$$

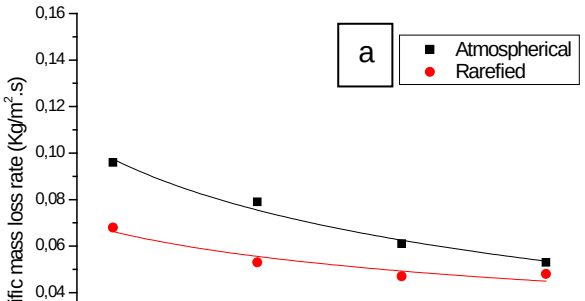
Where: *Cg* is a dimensionless proportionality constant unknown a priori, which must be evaluated empirically, from experimental results. Thus, the term source to be added to the heat flux imposed on the external surface will be:

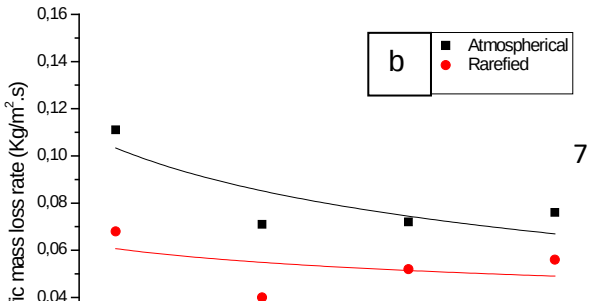
$$\dot{q_g} = [q_{CO20} + Cp_{CO2}(T - 300)] C_g \frac{P}{RT} V_p \qquad (3)$$

This empirical equation correlates the effects of pressure, temperature and pyrolisis rate with the generation of an additional heat flux on the external surface where the ablation of the carbonized layer occurs, related to the degradation of percolated gases from the decomposition of the polymer resin.

3. RESULTS AND DISCUSSION

Figures 6a, 6b, 6c and 6d show the mass loss rate graphs obtained in dense atmospheric environment, taken from Silva [3], together with the rates obtained in this work. It is observed that the rates are lower for the tests performed in rarefied atmosphere, but the differences in these rates decrease according as the exposure time increases. This behavior is explained by the low pressure of the rarefied environment and its lower concentration of oxygen, which generates lower rates of chemical reactions and consequently less heat addition to the system, leading to a reduction of the pyrolisis process speed and consequent *char* formation. This tendency of convergence between the curves according as the exposure time increases can be attributed to the phenomenon of cracking, which is the reduction of gases from pyrolisis to others of lower molecular mass. In this phenomenon occurs the pyrolitic deposition of carbon in the pore contours in the carbonized region generating densification of the carbonized structure and the consequent improvement in the thermal protection characteristics. At low pressure, this densification, although slower, with increasing exposure time has a tendency to equilibrate with the densification of the structure at atmospheric pressure, equating thermophysical properties and their effects.





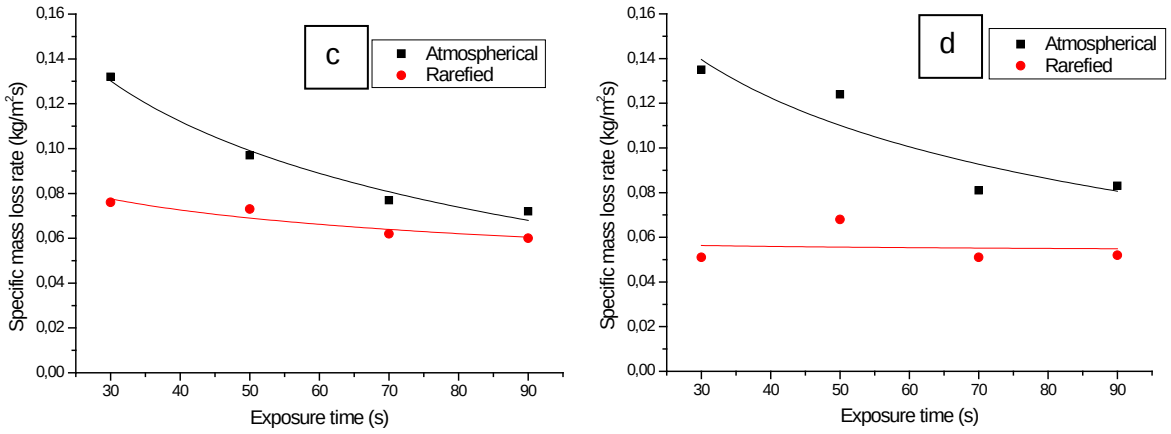


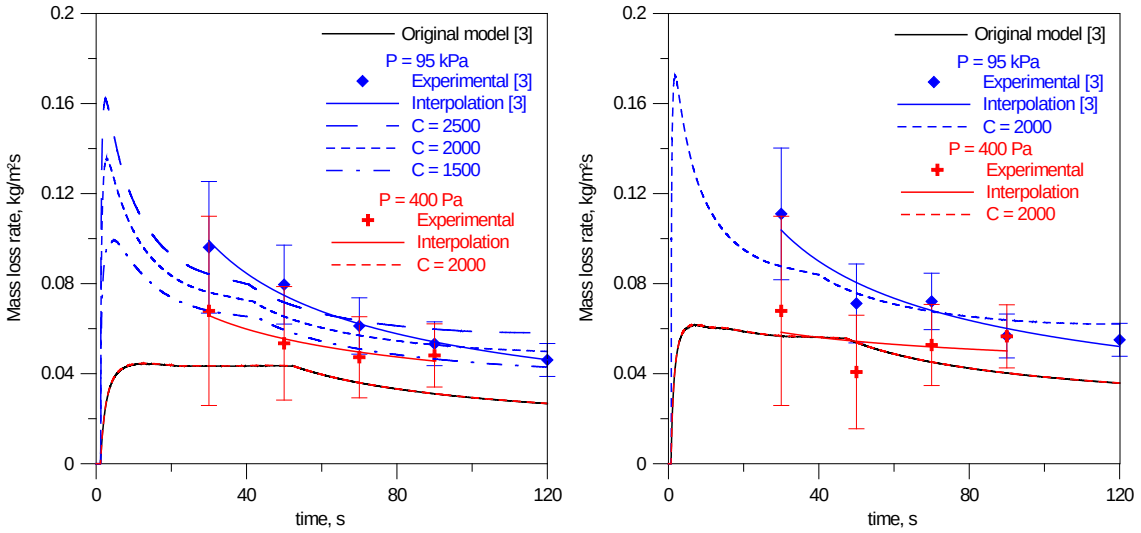
Figure 6: Mass loss rate versus exposure time to the fluxes:(a) 0.626 MW/m^2;(b) 0.903 MW/m^2;(c)1.376 MW/m^2;(d)1.725 MW/m^2

A computational model was used to simulate a one-dimensional process of ablation. This model has now been corrected considering the influence of the atmospheric pressure and its results compared with the data obtained experimentally. For this model, the data used in the simulation were presented in Table 1.

Figures 7a and 7b, 8a and 8b show the mass loss rate curves as a function of the exposure time for the analyzed thermal flows. Due to several processes occurring on the external surface exposed to the plasma torch, it was not possible to reproduce the temperatures measured in the experiments. However, this is not a parameter of interest for the model but rather the internal surface temperatures and the rate of mass loss, which effectively report on the performance of the material as thermal protection.

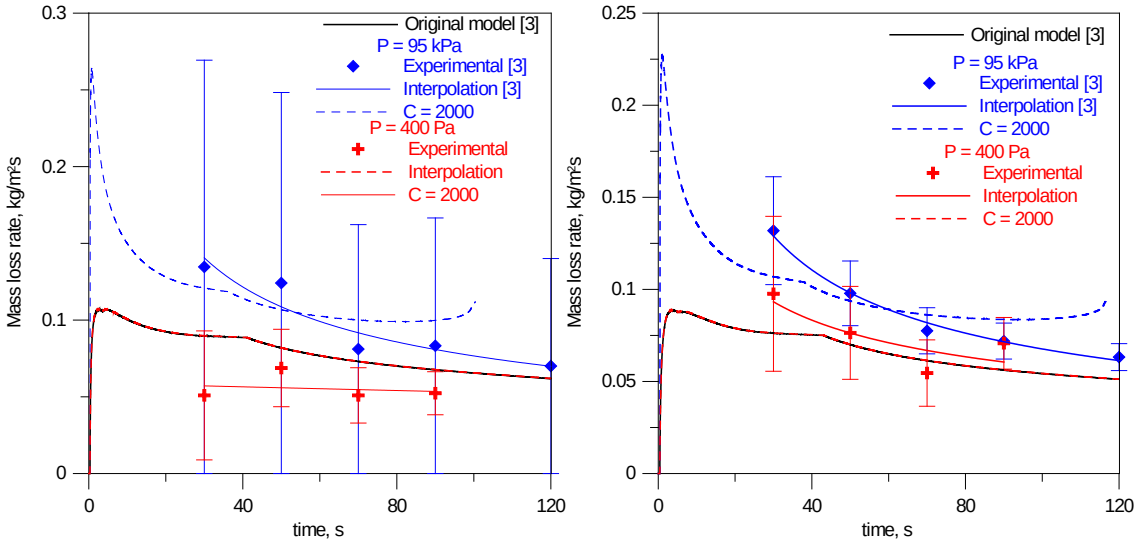
Initially, the experimental data obtained from Silva [3] were plotted considering the average atmospheric pressure of the city of São José dos Campos, 95 kPa identified in blue in the graphs. The constant C was obtained by trial and error in case of lower heat flux. A minimum, average and maximum value of 1500, 2000 and 2500, respectively, were tested. According to Figure 8a, where the results for the mass loss rate are presented, the best result was obtained for the mean value of 2000 because its curve is consistent with the corrected physical values within the error bar, which is then assumed for the other cases, shown in Figure 7b, 8a and 8b. The experimental data, in rarefied environment, are identified in red. It is observed that the curve corrected for this pressure of 400 Pa also involves the experimental points within the respective error bars. It is possible to observe the physical coherence of the modified model, which although it does not obtain a perfect agreement, reproduces the

behavior of the experimental data. It should be considered that the properties used in the simulation were extracted from literature sources for generic carbon-phenolic composites and not measured from the composite used in the experiments.



(a) (b)

Figure 7: (a) Curves of mass loss rate with time between simulations and experimental data, q= 0.626 MW/m^2; (b) Curves of the mass loss rate with time between the simulations and experimental data, q= 0.903 MW/m^2.



(a) (b)

Figure 8: (a) Mass loss rate curves with time between simulations and experimental data, q = 1.376 MW/m^2, (b) Mass loss rate curve with time between simulations and experimental data , q = 1.725 MW/m^2.

4. CONCLUSIONS

- The rates of mass loss as a function of the exposure time obtained in this study are lower than atmospheric pressure but the differences in these rates decrease according as the exposure time increases. This behavior is explained by the low pressure of the rarefied environment and its lower oxygen concentration. According to the

qualitative correction proposed for the physical model, the reactions between the gases resulting from the pyrolisis and the oxygen of the atmosphere generate an increase in the heat flux imposed on the external surface. The lower oxygen concentration implies lower reaction rates and consequently less heat addition to the system, causing a reduction of the pyrolysis process velocity and consequent char formation. The reduction of the difference between the rates of mass loss according as the exposure time increases can be attributed to the cracking phenomenon, which is the reduction of gases from the pyrolysis in others of lower molecular mass. In this phenomenon occurs the pyrolytic deposition of carbon in the pore contours in the carbonized region generating densification of the carbonized structure and the consequent improvement in the thermal protection characteristics. At low pressure, this densification, although slower, with increasing exposure time has a tendency to equilibrate with the densification of the structure at atmospheric pressure, equating the thermophysical properties and their effects.

- The ablation of carbon-phenolic composite used in thermal protection systems was studied experimentally and numerically. A plasma torch was used to produce ablation in the samples at two different pressures, and the mass loss rates was measured. The results were compared with the numerical data obtained from a modified form of a previous model to account the effect of pressure.
- The numerical computational simulation was validated with respect its modification considering the low test pressure when used in carbon/phenolic composites. To simulate the mass loss rate, the results were close to those obtained experimentally, so that the results of the error bars cross the simulation curve. The pyrolysis and ablation profiles show a great proximity to the profiles obtained experimentally.
- The difference between the numerical and experimental results shows coherence with respect to the order of magnitude and evolutionary behavior of the investigated parameters, considering the limits of the proposed theoretical model, due to the simplification of the physical and chemical processes involved in the ablation process.

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