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ANALYSIS OF MULLITE ABLATIVE PROPERTIES SIMULATED IN HYPERSONIC PLASMA WIND TUNNEL

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abstract
Mullite is a ceramic composed of silicon oxide and aluminum used in various technological applications due to its physical and chemical properties, such as: Low thermal expansion, high thermal stability, low density, low thermal conductivity, good mechanical resistance and creep resistance, good stability in severe chemical environments, among other properties. The supersonic plasma wind tunnel was optimized to investigate the ablative properties of the ceramic composite coating – Mullite $(3Al_2O_3.2SiO_2)$ *deposited by the spray plasma process on Carbon-Carbon substrate (C/C). The tests were performed at low pressure in a reactive air plasma using a DC non-transferred arc plasma torch with enthalpies of 7.2MJ/kg at 18.5MJ/kg and heat fluxes of 0.52 MW/m^2 to 2.2 MW/m^2. The specific mass loss rate of the coated Mullite on the (C/C) was evaluated as a function of the exposure time and of the heat flow. Microstructural and chemical analysis of the (C/C) substrate of the coated mullite before and after the ablation process through SEM/EDS were also performed. The analysis of the results showed that the adhesion of the mullite is directly related to the exposure time of the substrate (C/C) in the spray plasma process, in the formation of the coating as a protective layer.*

Keywords: *Plasma Wind Tunnel, Ceramic Composite Coating, Mullite, Hypersonic Flow, Hypersonic Plasma Torch*

1. INTRODUCTION

Overcoming the supersonic (hypersonic) speed barrier will be one of the biggest technological challenges in the area of manned and unmanned space or intercontinental flights. In order to be able to carry passengers or loads at high speeds it will be necessary to use materials capable of withstanding a high aerothermodynamic load when it is subjected to atmospheric re-entry. aircraft, which causes accelerated ablative degradation in the material. In this situation the application of a Thermal Protection System (TPS) is of fundamental importance to avoid damage to the loads and astronauts inside these vehicles. The performance of TPS materials depends on the conditions of use and we must analyze the material used and its thermal, mechanical and geometric properties among others. Also analyze the behavior of these materials when subjected to high heat flux intensity, chemical characteristics of the atmosphere and the boundary conditions, among other aspects to which these materials will be subjected (Riccio et al., 2017; Hu et al., 2012).

These TPS systems are based on the principle that the energy transmitted by the heat flux through the boundary layer must be absorbed or rejected (re-irradiated). One of the most common systems used in TPS space vehicles is that made from ablative materials. Ablation is a process that involves surface radiation, phase shifting and chemical reactions. Part of the heat input stream is blocked by the flow of hot gases resulting from material degradation. The ablative system is generally used on vehicles designed for one mission only (Riccio et al., 2017; Hu et al., 2012; Bittencourt et al., 2018). The degradation of an ablative material should be an endothermic reaction such as fusion, sublimation and carbonization, based on the principle of thermal energy absorption, generating a reasonable amount of gases, resulting in thermal insulation and progressively occurring material consumption. Carbonization ablators are the most commonly used thermal protection systems and are mainly produced with phenolic, epoxy or silicon resins using short fibers, silica, glass or organic spheres as reinforcement (Pesci et al., 2018; Machado, 2012). Carbon fiber reinforced (C/C) carbon arrays have fundamental properties for this type of application, such as: high strength and exceptional fracture toughness combined with their refractory properties, low density, high erosion, corrosion and wear resistance make this material ideal for applications in structural components subjected to high temperatures such as turbines and atmospheric reentry vehicles. These matrices are one of the most common types of reinforcement used in TPS systems because in carbonization ablation their main feature is the formation of a porous skeleton where gases can flow while the degradation reaction evolves, absorbing energy and blocking heat flow. when injected into the boundary layer (Machado, 2013; Pesci et al., 2018; Bittencourt et al., 2018).

Therefore, carbon fiber reinforced (C/C) carbon arrays are used in materials in the aerospace industry due to their desirable characteristics such as high ablation and mechanical resistance, heat resistance, dimensional stability, high solvent resistance, acids and water, flame resistance, low smoke emission when material is incinerated, excellent ablative properties and low cost. They absorb energy as they degrade and serve as a binder for the other components (Miranda et al., 2017; Zhongliu et al., 2015; Machado, 2012). However, under re-entry conditions at high temperature oxidizing atmospheres, carbon fiber composites undergo intense thermal degradation due to the high catalytic reactions between carbon and oxygen, and in some situations make their use in aerospace devices difficult. This problem can be overcome by coating this matrix surface (C/C) by gradually depositing (graded) SiO_2 oxide coatings. The formation of this oxide acts as a TPS barrier when subjected to aerothermodynamic effects to protect the C / C composite against oxidation, mass loss and consequently preserving its mechanical properties. There are several techniques used to deposit and / or coat a material according to its application, namely chemical vapor deposition, package cementation, hydrothermal electrophoretic deposition, mud methods and plasma spraying (Miranda et al., 2017; Zhongliu et al., 2015; Aparicio et al., 2000).

Mullite-coated carbon-carbon (C/C) composites $(3Al_2O_3.2SiO_2)$ were used to investigate the behavior of these materials in simulated reentry environments. C / C and Mullite composites were chosen due to their large number of applications, mainly in the aerospace sector. Mullite has attractive physical and chemical properties such as: low thermal expansion, high thermal stability, low density, low thermal conductivity, good mechanical strength and creep resistance, good stability in harsh chemical environments (Miranda et al., 2017, Moreira et al., 2011).

Therefore, the aim of this paper is to investigate the behavior of materials used as a thermal protection system for aerospace vehicles subjected to hypersonic turbulent flow conditions (Mach 5). The plasma wind tunnel located at the Plasma and Process Laboratory - LPP-ITA was used to investigate the ablative properties of the ceramic composite. Ablation tests performed on Mulita coated matrices (C/C). The coatings were performed at the Plasma and Process Laboratory (LPP-ITA) using the plasma spray technique as this technique offers flexibility in processing various types of materials, few geometric restrictions on substrate shape and high deposition rates. Solution Plasma Spraying (SPS) uses liquid precursors containing the final coating composition or its major elements that react with the substrate, plasma gas or the surrounding atmosphere. SPS allows you to create materials with nanoscale grain sizes, correlating with lower defect rates, higher strain tolerances and better porosity distributions, which reduce thermal conductivity and modulus of elasticity, particularly in ceramic materials (Miranda et al., 2017; Liu et al., 2014). Microstructural and chemical analyzes performed on the substrate (C / C) with the coated mullite before and after the SEM / EDS ablation process were also performed. The analysis of the results showed that the adhesion of the mullite is directly related to the substrate exposure time (C / C) in the plasma spraying process, in the coating formation as a protective layer.

2. MATERIALS AND METHODS

2.1. preparation of C / C composites and Mullite coatings by plasma spray

Carbon / carbon composites (C / C) are widely used in structural components, particularly in the aerospace and aeronautical sectors. However, the application of C / C composites is limited by the low oxidation resistance at high temperatures. To overcome this problem, Mullite graduated coatings $(3Al_2O_3.2SiO_2)$ were deposited in C / C compounds by a High-Speed Plasma Spray (HVSPS) process. Graduated coatings were formed by reactions between the liquid precursor sprayed with $Al2O_3$ and SiO_2 on a C / C substrate; these reactions were promoted by the high temperature of the plasma torch. The morphologies, microstructures and chemical compositions of the coatings were investigated by energy scattering electron microscopy. By changing the deposition time, the coating thickness was controlled, thus demonstrating the formation of $(3Al_2O_3.2SiO_2)$. Deposits were performed by HVSPS on a composite substrate C / C developed by the materials group of the Institute of Aeronautics and Space (IAE / DCTA). The C / C composites were obtained from carbon fiber prepregs and phenolic resins with a density of approximately 1.78 g / cm^3, cut into blocks of 20 × 15 × 4 mm, sanded at the edges to remove irregularities and clean. The experimental system developed for the HVSPS described in detail by Miranda et al. (Miranda et al., 2017, Moreira et al., 2011) originally comprised a supersonic plasma torch with axial injection, powder injection system, cooling subsystems, electric power source and gas supply. However, for the processing of the liquid precursor, certain adaptations were made to the transport line; a pressurized 0.001 m^3 capacity vessel was added as well as a needle valve and flow meter connected to a nozzle atomizer coupled directly to the plasma torch. To distinguish the two systems, the former is referred to as HVSPS. A dynamic support of samples with three-dimensional (3D) position and rotation control with capacity to process eight samples simultaneously was used (Miranda et al., 2017, Cividanes et al., 2010, Li et al., 2016).

2.2. Plasma Wind Tunnel

The experimental apparatus, Figure 1 is composed by a stainless-steel vacuum chamber (3 m^3); vacuum system with two stage rotary pumps (160 m^3/h) connected to a booster roots (500 m^3/h); pressure sensors and gas lines (oxygen, nitrogen, argon, hydrogen) with mass flow. Through a programmable controller connected to a valve it is possible to automatically adjust the pumping speed, keeping the constant pressure 216 Pa inside of the vacuum chamber, for small variations in the injected gas flow.

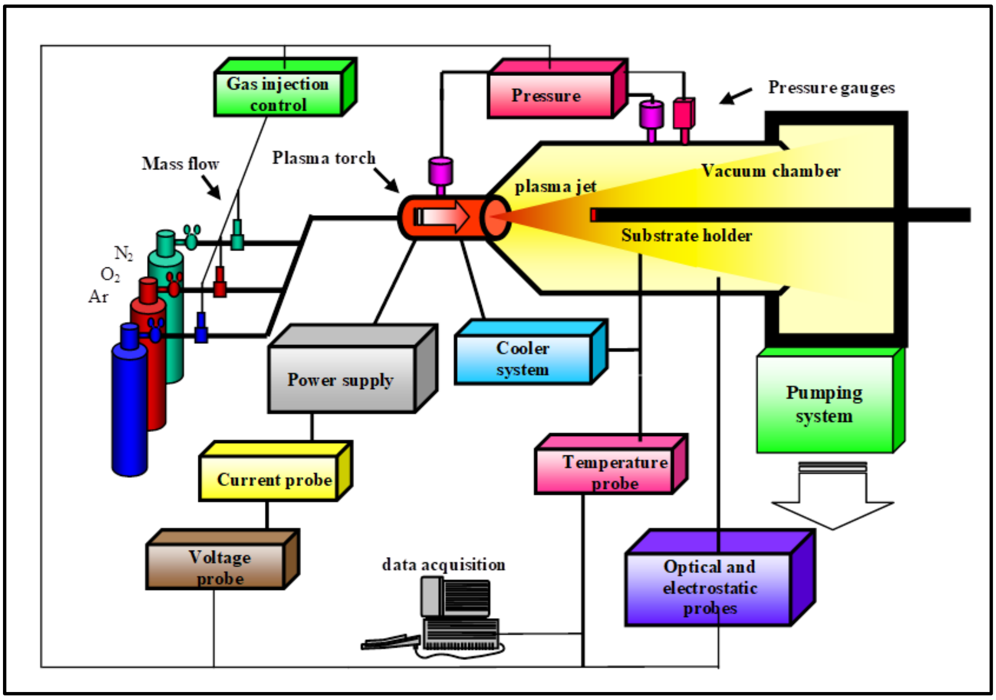


Figure 1. Schematic diagram of the experimental apparatus.

The system has a non-transferred arc plasma torch, which operates with direct current (DC), cooled internally through the forced water circulation. A divergent-convergent nozzle is coupled to the plasma torch, which allows the operation with hypersonic plasma jet (Mach 5). Figure 2 shows the schematic drawing of the plasma torch and sample holder arrangement with a max capacity of 8 samples. The sample holder has freedom rotation (360º), allowing changing the sample for execution of 8 sequential tests.

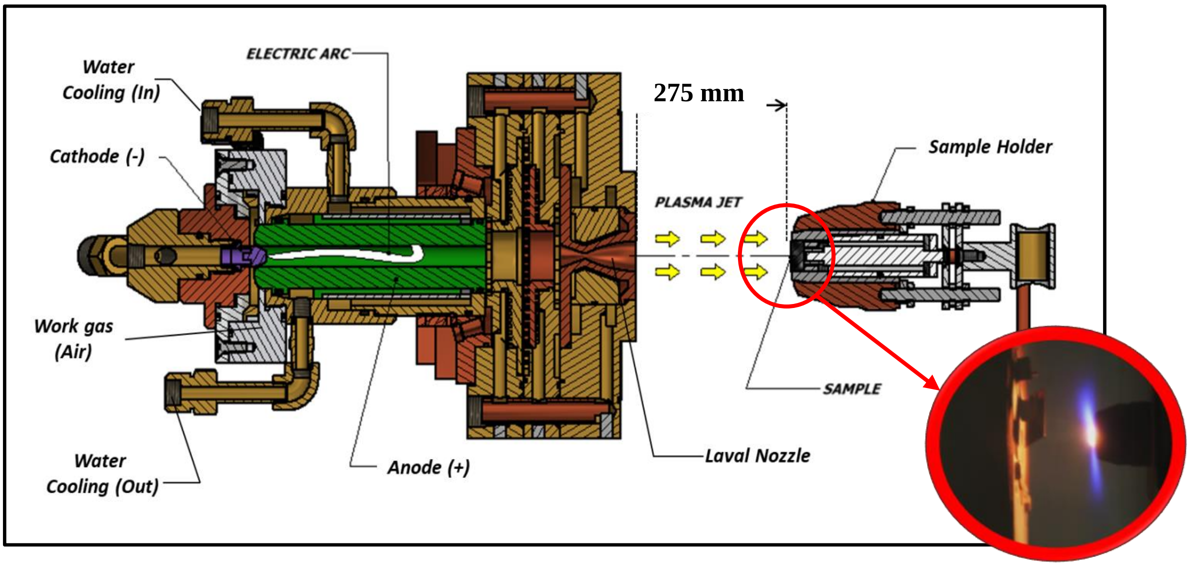


Figure 2. Schematic drawing of the plasma torch and sample holder arrangement

Considering the low capacity of the vacuum exhaust system in the plasma wind tunnel, in this case we would be very restricted by the variety of jet operating parameters that interconnect through the characteristics of the plasma heater. Therefore, without any special solution, we could not correctly simulate the effects of thermal flow of the plasma jet in the ablative processes. To solve this problem and obtain maximum independent control of the main parameters of the generated hypersonic plasma jet, adjusted the characteristics of the projected supersonic plasma heater and the vacuum system by means of the pre-nozzle inserted between the plasma torch outlet and the inlet Hypersonic nozzle.

2.3. Ablation tests

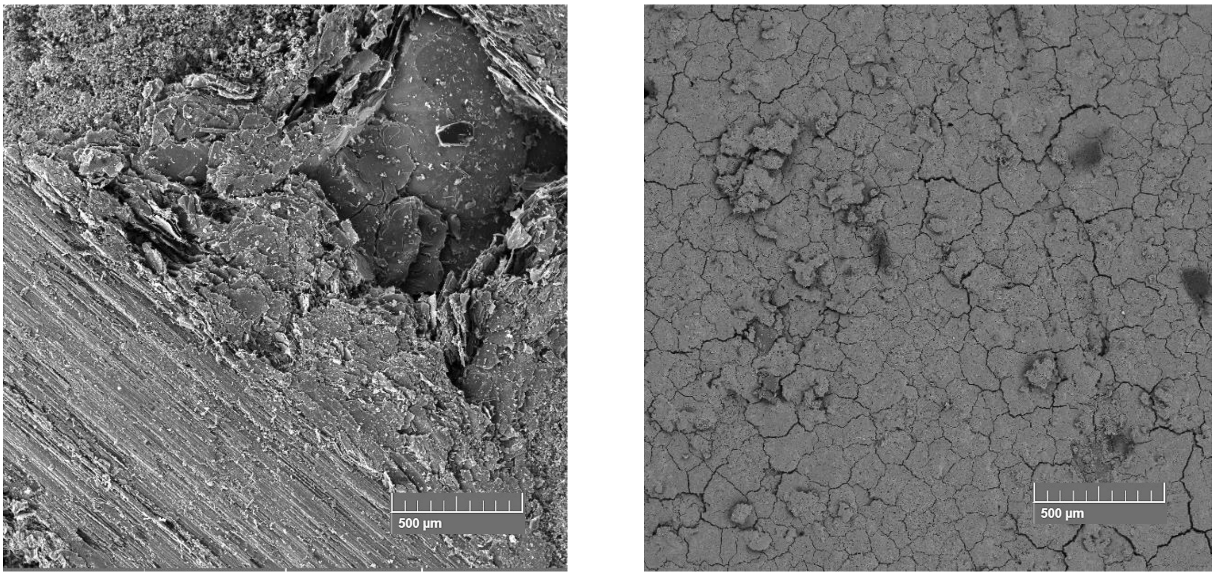
The ablation tests were performed in the Plasma Wind Tunnel using a non-transferred DC arc plasma torch powered with low pressure reactive air environment of P = 75 Pa and the air working gas flow rate of 20 l/min. The plasma torch operating at a power of 35 kW coupled to Hypersonic nozzle Mach 5 under a thermal flow of 0.65 MW / m^2 and average enthalpy of 7.2 MJ / kg. For these conditions the measured temperature of 950 °C, The specific mass loss rate of coated mullite on (C / C) samples was evaluated at function of exposure time for t = 5s, 10s, 20s, maintained at the fixed stand-off distance of 275 mm and constant thermal flow for the operating regime. Microstructural and chemical analyzes of the substrate of (C / C) and the coated mullite before and after the MEV / EDS ablation process were also performed to analyze the microstructure behavior and the chemical composition behavior of the Mullite coating on o (C / C). Measurements of temperatures on sample surfaces were performed using an infrared pyrometer, Pyrofiber Lab. The mass and thickness of each sample were measured before and after the ablation test.

3. RESULTS AND DISCUSSIONS

3.1. Microstructural and morphological analysis

The analysis of the results showed that the adherence of the mullite was practically constant when related to the time of exposure to the plasma jet inside the plasma wind tunnel, ie, the longer the exposure time of the mullite coated surface, the lower the effect. degradation of the coated surface when subjected to the same heat flux. To understand the behavior of the mullite coating on the (C / C) matrix when subjected to the ablation process, micrographs are presented before and after the ablation process.

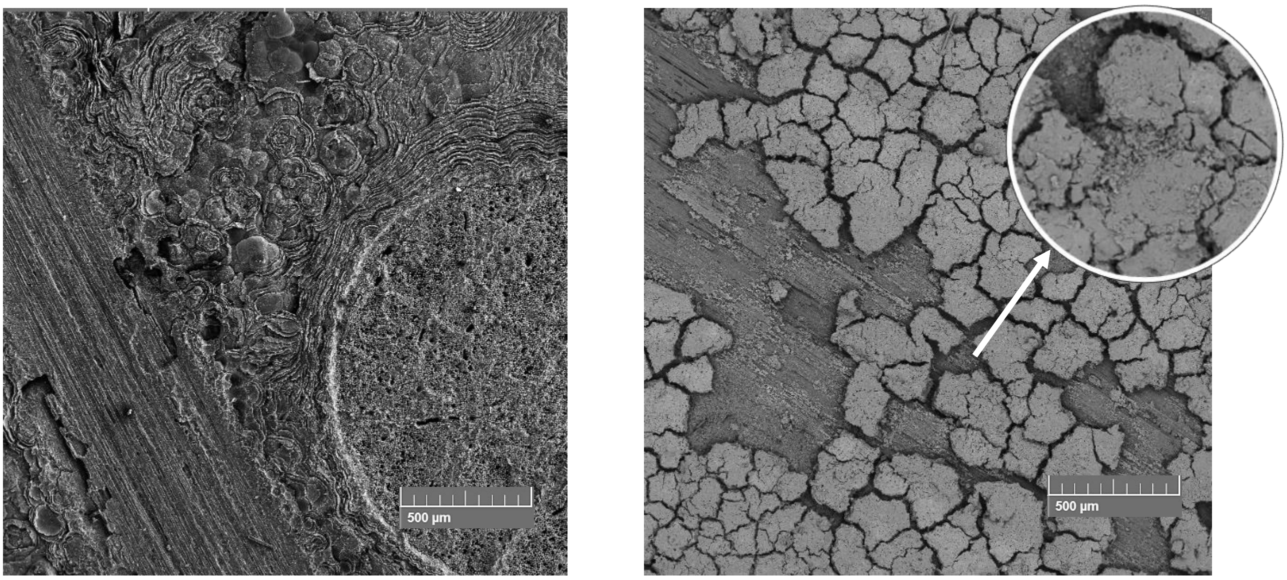
In Figure 1 (a) the carbon fiber reinforced (C / C) matrix as received from the IAE and Figure 1 (b) shows the mullite coating on the surface of the (C / C) matrix obtained by HVSPS before undergoing the ablation process. It can be seen from Figure 1 (b) that the (C / C) matrix was completely coated with mullite, and that this coating had some cracks in this process.



(a) **(b)**

Figure 1 (a) Matrix of (C / C) before ablation. (b) HVSPS mullite-coated matrix (C / C) before to ablation. Magnification of 500 μm, 100x.

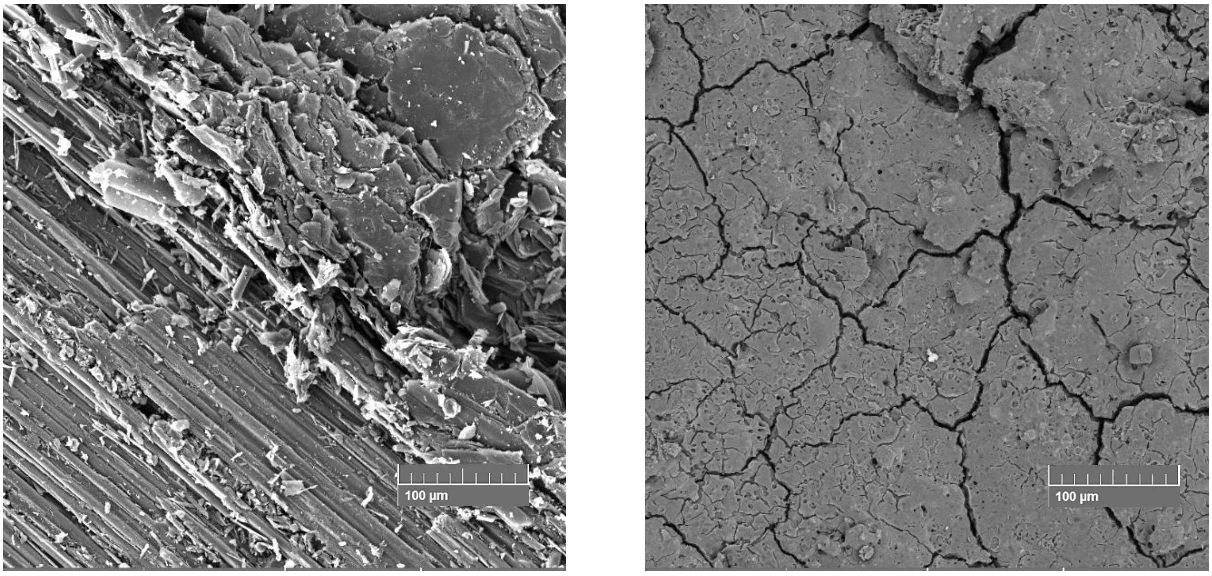
In the ablation assays, the samples were subjected to a 0.6 MW / m^2 continuous flow plasma torch and a fixed distance of 275 mm. The variable element in the process was the exposure time, in this case the exposure period equal to 5 s. Figure 1 (c) the matrix sample (C / C) after the ablation test, where the formation of spongy material is observed when subjected to the effects of intense thermal flux, showing that the material under intense thermal aggression, not resisting to the effect of thermal flow. In Figure 1 (d) shows that for the same test conditions, the Mulita coating protects the material surface, even if exposed to intense thermal flux, it is possible to observe that the fiber reinforced (C / C) matrix sample carbon remains virtually intact. Thus, preserving its physical and chemical properties. In this case part of the coating was removed, but it was enough to protect the material and reaching its initial proposal of its use as TPS.



(c) **(d)**

Figure 1 (c) Matrix of (C / C) after ablation. (d) HVSPS mullite-coated Matrix (C / C) after ablation. Exposure period t = 5 s. Magnification of 500 μm, 100x.

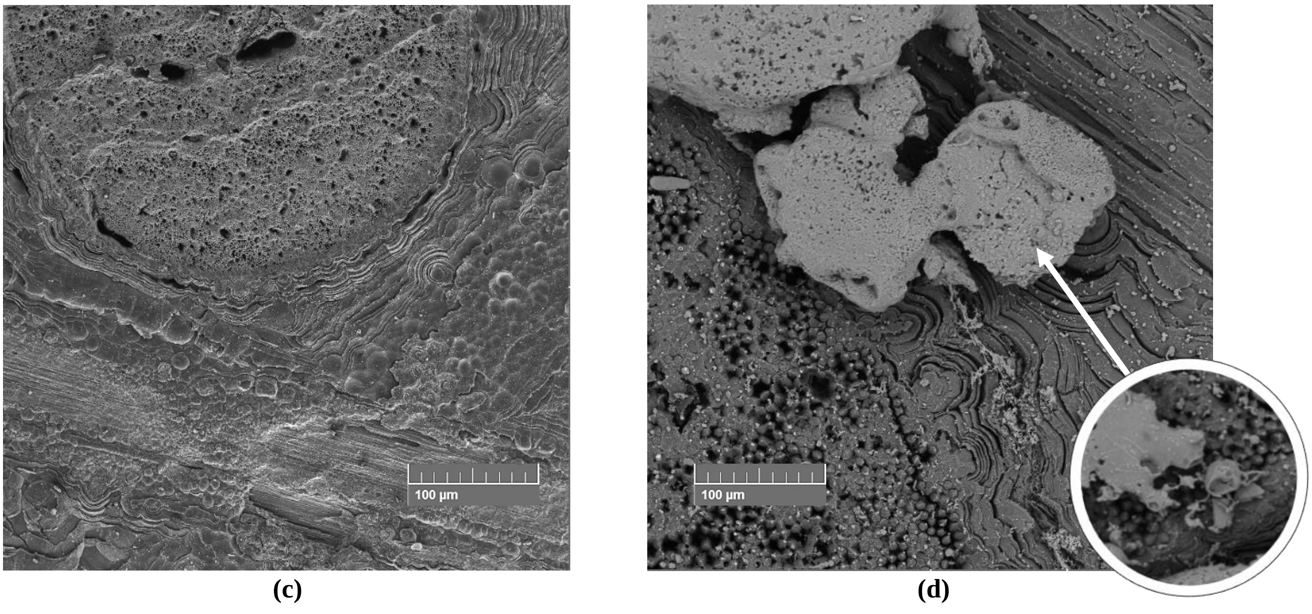
In the micrographs of Figures 2 (a) and 2 (b), the same initial preparation conditions of the samples were repeated as the ablative test conditions. Indicating that in Figure 2 (a) the natural state received by the IAE supplier and Figure 2 (b) shows the Mulita coating on the surface of the (C / C) matrix obtained by HVSPS, where both cases before submitting to ablation process.



(a) **(b)**

Figure 2 (a) Matrix of (C / C) before ablation. (b) HVSPS mullite-coated matrix (C / C) before to ablation. Magnification of 100 µm, 500x.

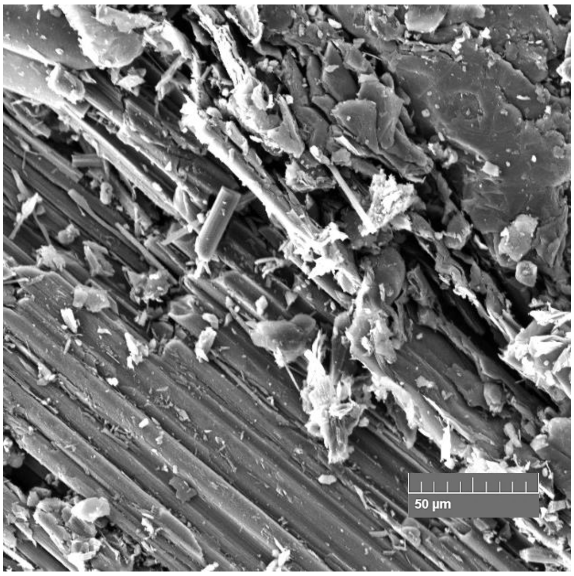
Figure 2 (c) shows the behavior of the reinforced matrix (C / C) when subjected to the thermal effects of the plasma jet again indicating changes in its surface. Figure 2 (d) shows the same behavior as described above for the 5 s exposure time, except in this case the 10 s exposure time. Shows the efficiency of the mullite coating again protecting the matrix surface from (C / C) that can be observed in the micrograph plane.



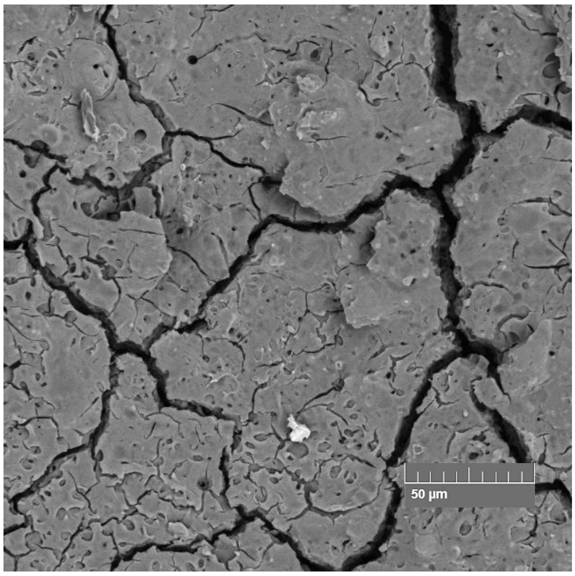
(c) **(d)**

Figure 2 (c) Matrix of (C / C) after ablation. (d) HVSPS mullite-coated matrix (C / C) after ablation. Exposure period t = 10 s. 100 µm magnification, 100x

The same behavior is observed for the tests of Figure 3 (a) matrix (C / C) in nature and Figure (b) after coating of mullite. The behavior of the samples for exposure time t = 20 s is consistent with the behavior described in the previous cases, once again showing the efficiency of the carbon-reinforced matrix surface coating (C / C).



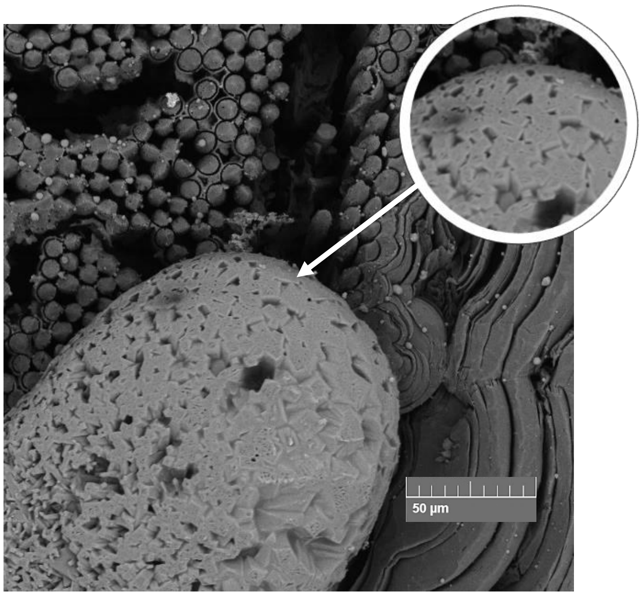
(a)



(b)

Figure 3 (a) Matrix of (C / C) before ablation. (b) HVSPS mullite-coated matrix (C / C) before to ablation. Magnification of 50 µm, 1000x.

(a)



(b)

Figure 3 (c) Matrix of (C / C) after ablation. (d) HVSPS mullite-coated matrix (C / C) after ablation. Exposure period t = 20 s. Magnification of 50 µm, 500x.

The EDS map of Figure 4 indicates the formation of the mullite components on the carbon-reinforced matrix surface (C / C). For the map of the presence of all the components of the mullite as in the coating shown there is the presence of Al and O indicating the formation of oxide (Al_2O_3) and also the presence of Si and O indicating the presence of oxide (SiO_2). the presence of the TPS system on the surface of the samples.

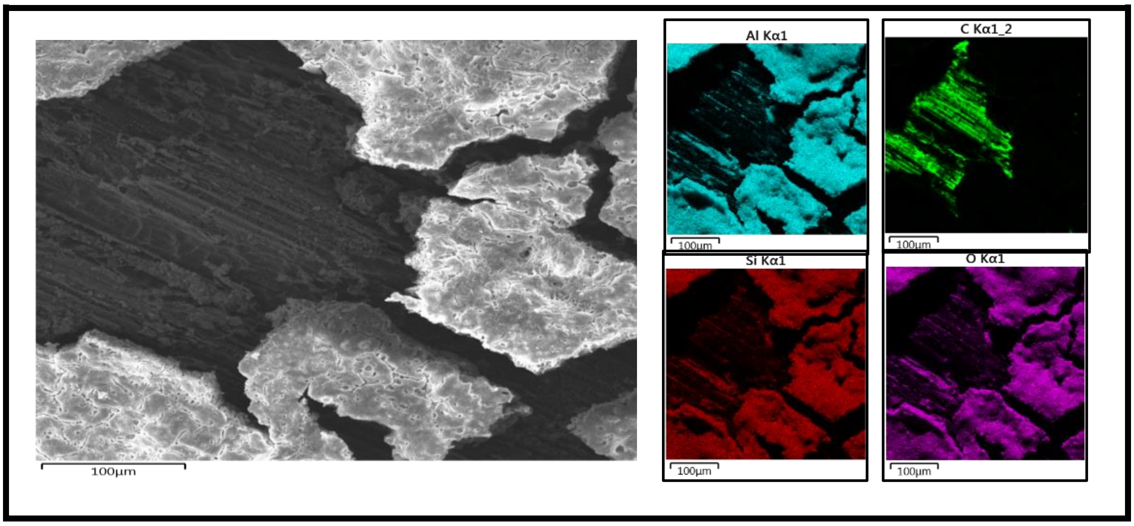


Figure 4. SEM surface ablation process of (C / C) – Mullite and EDS map

In Figure 5 it is observed that in the ablation process comparing ablation rates for samples only as the (C / C) matrix with ablation rates with mullite coated samples indicate that the effects of ablation process on materials which has the coatings obtained by HVSPS are efficient in the proposed application in this article. Because the longer the exposure time shown in Figure 5, the lower the ablation rate for the mullite coated material relative to the matrix (C / C) when subjected to the same proposed test conditions.

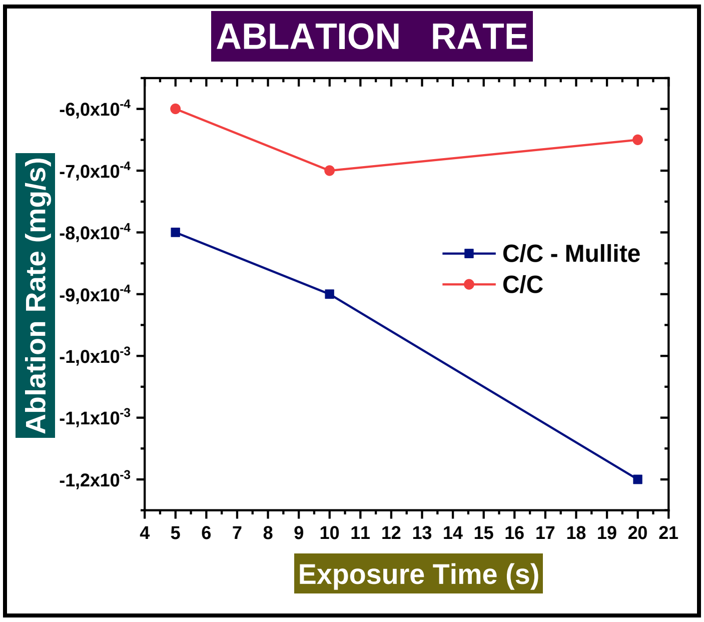


Figure 5. Ablation rate of C/C substrate and Coated C/C

4. CONCLUSION

When comparing the SEM results for the uncoated and Mullite coated (C / C) samples before (b) and after (d) the ablation process, there is a high thermal corrosion region as the samples are tested inside the plasma wind tunnel and subjected to high thermal flow.

When comparing the SEM results for the mullite coating samples (C / C) before (b) and after (d) the ablation process for all time intervals considered, it is observed that the mullite coating layer promoted thermal protection of samples (C / C) when subjected to the same exposure time and under ablation process simulation conditions.

By analyzing the SEM micrograph and the ESD map of Figure 4, it is shown that the (C / C) sample was preserved as shown by the EDS map for the carbon element - (C), and we observed that the mullite coating suffered thermal corrosion and even wear and tear and fulfilled its function with thermal protection system.

Figure 5 shows that the rate of mullite lining ablation in (C / C) samples is lower for longer time values compared to uncoated (C / C) samples.

5. ACKNOWLEDGMENT

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7. RESPONSIBILITY NOTICE

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