Materials Research Express

PAPER

Microstructural and ablative properties of graphite nozzles with SiC coating deposited by CVD technique

Oswaldo B Loureda1,2, Felipe Rocha Caliari1, Inácio Regiani1, Felipe de Souza Miranda1, Roberson José da Silva1 and Gilberto Petraconi Filho1

1 Instituto Tecnológico de Aeronáutica—ITA, Pça Eduardo Gomes, 50 Campus DCTA 12228-900—São José dos Campos—SP, Brasil
2 Acrux Aerospace Technologies, Pça Eduardo Gomes, 50, Incubaero, Campus DCTA 12228-615—São José dos Campos—SP, Brasil
E-mail: mirannda.fs@gmail.com

Keywords: rocket engines, ablation test, SiC coating, plasma torch

Abstract

The development of efficient, reliable and affordable propulsion units is one of the main objectives in the development of aerospace technology. Typically the final cost of the vehicle is deeply affected by this subsystem. In this study, a hybrid combination of the ablative chamber is presented where graphite nozzles coated with chemical vapor deposited Silicon Carbide (CVD-SiC) is submitted to the ablative environment, generated by a DC plasma torch operating at a power of 35 kW and homogeneous heat flow of 0.75 MW m$^{-2}$. The ablative properties of the samples were evaluated by measuring the weight loss as a function of the exposure time, weight loss of 0.11% after 70 s of exposition due to the formation of SiO gas was observed. The microstructure characteristics of SiC coating before and after ablation tests were carried out by SEM and XRD showing that it goes to scale oxidation to forming of SiO$_2$ ($\beta$-quartz) and SiC ($\beta$ to $\alpha$) phase transformation. Whereas the ablation mechanism showed to be dependent on the initial coating thickness and exposure time.

1. Introduction

The use of modern, efficient and reliable thrusters is a primary requirement for the development and operation of any aerospace system, from satellites to launch vehicles and orbital stations. The development of new materials provides alternative options for the construction of rocket engines, aiming at low cost and higher efficiency gains. Several thruster technologies, however, possess a very similar characteristic considering the thermal, mechanical and chemical loads [1]. Focusing on smaller engines, typically applied in upper stages of launch vehicles [2], sounding rockets, satellites and space platforms, it is possible to use the Liquid Rocket Engines (LRE) and Plasma thrusters, where the main loads are due to the thermal and chemical energy. In this context, the use of ablative materials based on graphite shows a feasible solution to increase reliability and reduce costs. Regarding ablative materials for chambers, the work of Kim, Conger and Fisher [3–5] are very similar, referring to materials and technologies already employed in 1968 during the development of the propulsion unit of North American manned lunar landing module. Essentially, that technology was based on an internal layer of silica fibers with phenolic resin and an overwrapped outer layer of carbon fiber and epoxy resin [5]. A more recent solution is based on the Chemical Vapor Infiltration (CVI) technique, where the formation of SiC among carbon fiber fabric was promoted [6]. Ceramic Matrix Composite (CMC) has demonstrated wide applicability, however with considerably higher cost and manufacturing complexity than the technique presented in this research [7].

The technique herein proposed is based on the modular construction of the chamber using techniques already dominated to sections of lower thermal and chemical load, with the use of phenolic resin and high purity silica fibers. These materials exhibit excessive and irregular wear, especially on the sections of the throat of the rocket engine chamber, however, it exhibits excellent resistance in the cylindrical regions of the chambers and regions away from the throat [8]. The use of materials with higher wear-resistant in the throat, it is possible to build most of the chamber with less exotic materials, lower cost and improved handling materials [9].
In this work, in order to provide an alternative solution to this most loaded region in the motor, pure graphite nozzles were coated with Silicon Carbide (SiC) and tested on the thermal plasma environment, in order to verify its capability to be used in the throat of the rocket. The results of exposure of the samples to the thermal plasma show that it is possible to simulate the severe thermal stress achieved in rocket engines.

2. Experimental

2.1. Graphite substrate and CVD coating process
The nozzles were manufactured by fine grain, high density (1.85 g cm\(^{-3}\)) graphite showing a hexagonal-2H crystal structure. CVD depositions were performed inside a hot wall tubular ceramic furnace to allow the entry and exit of gases and vacuum. Depositions were performed on the largest surface of the nozzles, which was kept transversal to the gas flow. SiC films were deposited under the following conditions: 1 Torr of pressure, at the temperature of 1100 °C, and 0.5 l min\(^{-1}\) of 99.9% pure H\(_2\). Hydrogen was bubbled into a methyltrichlorosilane (MTS) reservoir before entering the reactor. Coatings of 20 μm thickness took 36 h of deposition.

2.2. Simulation and experimental set-up for ablation tests
One of the main purposes of this study is to assess the ablative resistance of the graphite nozzle coated with CVD-SiC. The resistance at the throat is particularly important since the strongest heat fluxes are found in this region, as represented in figure 1. The total thermal flux profile is estimated from an analytical thermal analysis based on a Russian methodology [10–12] combined with Bartz correlation, that shows a maximum thermal load of 0.75 MW m\(^{-2}\) is obtained in the throat region of a 5 kN chamber [13].

2.3. Experimental set-up with plasma torch
Preliminary studies realized by Petraconi et al [14] using the same experimental setup determined the ideal point of positioning samples in order to simulate the thermal flux (0.75 MW m\(^{-2}\)), which has been calculated. Figure 2 shows the plasma torch used in the ablation experiments and the sample holder, along with the relationship between thermal flux and axial distance.

For the purpose of testing the protection efficiency of SiC coating in graphite nozzle, ablative tests were performed using a 35 kW DC plasma torch operating with air as the working gas at 3 g s\(^{-1}\) and thermal efficiency of approximately 75%.

Table 1 records the ablation tests performed over pure graphite and the CVD-SiC coated nozzles, whereas coatings with 10 μm and 20 μm were evaluated. All nozzles were submitted to the ablative tests at the axial distance of 80 mm, having the exposure time and thickness of SiC coatings the main initial parameters.

After the tests, the nozzles were sectioned (figure 3) in order to enable further analysis using SEM and XRD. After the tests, the nozzles were measured using calipers, coordinate-measuring machine and the weight loss was measured using an analytical balance.
2.4. Materials characterization

The characterization of graphite-based nozzle and SiC coatings were performed before and after ablation tests using an x-ray diffractometer model X’Pert Powder model from Panalytical, 2θ range from 5° to 100°, with step size of 0.02° at 40 kV and 50 mA, working with a Cu Kα radiation at 40 mA and 40 kV. Additionally, a scanning electron microscopy (SEM) model Vega 3 XMU from Tescan was used to study the substrate and coating morphology.

Table 1. Main parameters of SiC coatings and ablation tests.

| Graphite nozzle (n°) | CVD-SiC film thickness (μm) | Time exposure (s) |
|---------------------|-----------------------------|------------------|
| 3n                  | 0                           | 10               |
| 12n                 | 0                           | 20               |
| 6n                  | 0                           | 70               |
| 4a                  | 10                          | 10               |
| 11a                 | 10                          | 20               |
| 5a                  | 10                          | 70               |
| 8b                  | 20                          | 10               |
| 10b                 | 20                          | 20               |

Figure 2. Plasma torch and curve of Thermal Flux versus axial distance [15].

Figure 3. Nozzles prepared to analysis in SEM and XRD respectively.
3. Results and discussion

3.1. Ablation tests

Figure 4 shows the weight loss of graphite-based nozzle without SiC coating exposed to the plasma jet during 10, 20 and 70 s. Within 10 s of exposure, samples showed a weight loss of 0.21% and no increase in throat diameter. The first 20 s of the ablation process follows a linear behaviour until 0.6% of the weight is lost, and an increase of 0.45 mm was observed. When the time of exposition is extended to 70 s almost 10% of the weight is lost, followed by an increase of 12 mm in throat diameter. This exponential increase in weight loss and roughness can be attributed to the erosion, which contributes to the increase of heat transfer \[16\].

The ablation in pure graphite occurs due to oxidation and erosion, whereas the arc plasma jet contributes majorly with high surface temperatures, how were observed by Petraconi et al\[14\]. In fact, the momentum of plasma jet and therefore the pressure exerted at the stagnation point is lower than in a supersonic combustion gas-flow \[17, 18\], despite this limitation, the employment of plasma torch is a valid and useful methodology to develop materials and manufacturing technologies on liquid and solid rocket engines.

The successful protection of the graphite nozzle using a CVD-SiC coating is evident. Firstly, none of the coated samples showed an increase in throat diameter, when comparing the results presented in figures 4 and 5. A substantial reduction in weight loss is observed. According to figure 5, the ablation behaviour of SiC coating with either 10 \( \mu \)m or 20 \( \mu \)m thickness has a linear dependence until 20 s, as well as similar weight loss. Sample 5a, having a SiC coating with 10 \( \mu \)m experiences a reduction of weight loss between 20 s and 70 s.

3.2. Substrate and coating characterizations

3.2.1. As-deposited CVD-SiC coating

According to the XRD pattern of the as-deposited silicon carbide coating (figure 6), the \( \beta \) phase (cubic-3C) was crystallized. The XRD suggests that SiC coating is highly oriented to the plane (111).

The SEM surface image of the as-deposited CVD-SiC coating (figure 7(a)) shows a uniform granular structure of round grain-sized in the range of 2–8 \( \mu \)m, where the grain size presents a multimodal distribution with averages at 3.2 \( \mu \)m, 6.2 \( \mu \)m and 7.5 \( \mu \)m (figure 7(b)). This morphology is representative of SiC coatings with 10 \( \mu \)m and 20 \( \mu \)m thickness.

3.2.2. Substrate and CVD-SiC coatings after ablations tests

SEM image of pure graphite after 20 s ablation test exhibit a highly eroded surface in figure 8. This degradation pattern is consistent for all internal sections of the nozzle, and it is coherent with the proposed oxidation-erosion degradation mechanism proposed Petraconi et al\[14\].

The ablation mechanism for the nozzle with 10 \( \mu \)m SiC coating and exposed for 20 s to the plasma jet can be clearly denoted in XRD of sample 11a, where the formation of glassy SiO\(_2\) and quartz (Hexagonal SiO\(_2\)) were detected, (figure 9). Hence, the heat transfer was intense enough to promote the complete oxidation of \( \beta \)-SiC,
which is coherent with the mass increase observed in figure 5. The drag force imposed by the plasma jet was not sufficiently high to remove the glassy layer of SiO$_2$, considering the 20 s of plasma exposure.

The nozzle 11a shows a great change in the coating structure, as can be seen in figure 10. At this test condition, the grains have increased, showing an average size of 35 $\mu$m. SEM images show no delamination or naked areas, which means that the SiO$_2$ film protects the graphite for this small period of time test.

The detection of graphite-2H as well as $\beta$-quartz (hexagonal SiO$_2$) phases in the XRD of nozzle 5a, in figure 11, indicates that SiC coating has suffered an intensive degradation process in long ablation test. Hexagonal SiO$_2$ detected on sample 5a was crystalized due to the stagnation pressure of the arc plasma jet, around 40 MPa, over the SiC surface and to the high temperature at the nozzle internal wall [19, 20]. Besides, the shape of the background also indicates that some amorphous phase is present, which probably is glassy SiO$_2$.

According to Boulos et al [21], the main species presented in air arc plasma jet at atmospheric pressure and 4000 °C are N$_2$, O, NO, O$_2$, Ar and NO$^+$ . Despite the abundant plasma-chemical composition, the main oxidant species are assumed to be O$_2$ and O. High temperature from plasma jet and the presence of plasma-oxidant species leads to accelerated oxidation of graphite nozzle. The ablation mechanism of the SiC coating, however, follows an intermediate dependent-step where SiC oxidation can be either passive or active [22, 23]. The detection of SiO$_2$ (figures 9 and 11) indicates that the oxidation mechanism on sample 5 followed the oxidation of SiC to SiO$_2$ according to reaction 1. Whereas this degradation reaction is based on the passive oxidation
Figure 7. Surface SEM image of the as-deposited SiC coating and (b) grain size distribution.

Figure 8. SEM images from the graphite nozzle (sample 12n), (a) convergent, (b) throat and (c) divergent sections.
mechanism [24]. Therefore, the active degradation is triggered, mainly by the temperature effect at the SiC/SiO₂ interface as in reactions 2 and 3. The good wettability between SiO₂ and graphite initially provides a good shield against oxidation, but both the vaporization of SiO₂ (Reaction 2) and reaction between SiC and SiO₂ (Reaction 3) occur as a result of the elevated heat flux and a consequent increase of the internal wall temperature [18, 20, 25].

\[
\begin{align*}
\text{SiC(s)} + 3 \text{O}_2(g) &\rightarrow 2 \text{SiO}_2(\text{g}) + 2 \text{CO}(\text{g}) \quad (1) \\
\text{SiC(s)} + \text{O}_2(g) &\rightarrow \text{SiO}(\text{g}) + \text{CO}(\text{g}) \quad (2) \\
\text{SiC(s)} + 2\text{SiO}_2(\text{g}) &\rightarrow 3\text{SiO}(\text{g}) + \text{CO}_2(\text{g}) \quad (3)
\end{align*}
\]

The active oxidation mechanism denoted by equations (2) and (3) is expected at low oxygen partial pressures, which seems not to be the case of experimental conditions in this research since plenty of oxygen molecules and radical species are available at the plasma gas and from the surrounding atmosphere. Therefore, it is assumed that the weight loss dominant mechanism in sample 5a is based on equation (3).

Figure 12 represents the surface of convergent, throat and divergent sections of sample 5a after ablation tests, where scale oxidation of SiC is observed along with the increase of grain size distribution to 30–130 μm (figure 12(e)), the formation of cracks and delamination of the coating. The grain deformation observed in figures 12(b) and (c) is due to the high-temperature viscoplastic behaviour of glassy SiO₂. Figure 12(d) presents a detailed microstructured sample 5a throat section after the ablation test, in which the grains assume a flat-like shape resulted from intense oxidation started at the grain boundary.

Therefore, for SiC coatings of 10 μm thick, it was found a sequence of transformation. First, in a short period of time (20 s), the SiC coating reacts with oxygen and forms glassy SiO₂ coating and some hexagonal SiO₂ (quartz), regions. The SiO₂ glassy and quartz coating transformations mark the evolution of the process.

The x-ray diffraction pattern of sample 10b (figure 13) demonstrates that SiC coating has undergone to both oxidation and phase transformation during ablation tests. Overall, sample 10b with 20 μm of SiC coating showed different transformation paths and intense exothermic oxidation of SiC to SiO₂, followed by the active oxidation mechanism (equation (3)).

As an ablation-product, the SiC phase transformation (equation (4)) shall be highlighted. This \( \beta \rightarrow \alpha \) phase transition represents the change of SiC from zincblende to a hexagonal crystal structure, where the motion of partial dislocations plays a major rule in the modification of the stacking planes from ABCABC to ABAB [26].

\[
\beta - \text{SiC}(\beta - \text{cubic}) \rightarrow \alpha - \text{SiC}(\alpha - \text{hexagonal})
\]

Nevertheless, the driving force of this phase transformation can be due to either pressure or temperature, and according to Ryan et al [27], who studied the \( \beta \rightarrow \alpha \) phase transition at 0.1 MPa and 2000 °C.

No delaminations were observed on sample 10b as shown in figures 14(a) through (c). The SiC coating on sample 10b has also gone through a grain size growth on the convergent, throat and divergent sections. According to figure 14(d) a multimodal distribution among 30–145 μm is observed.

According to the XRD results, the 20 μm coating contains SiO₂ and SiC after the ablation test. It is possible to infer that SiO₂ is formed on the surface and mainly in grains boundaries of SiC grains. This region has more
defects and allows for more oxygen diffusion. The XRD identify SiO₂ and SiC because the depth of the analysis change during the XRD procedure, on the surface there is a SiO₂ layer, beneath it, there is a SiC layer.

According to these three results, it is possible to say that different reactions occur simultaneously on the SiC coating during the plasma jet exposure. First, there is a phase transformation reaction from $\beta$-SiC to $\alpha$-SiC. Meanwhile, an oxidation reaction transforms SiC into glassy SiO₂, and finally, after some period, the high temperature and pressure of the plasma jet trigger the active ablation mechanism, through the evaporation of SiO between 20–70 s.

4. Conclusions

The ablative environment inside a liquid rocket engine was successfully simulated using a plasma torch. The SiC-CVD coating has a 3C-cubic crystal structure and grain size distribution between 2–8 μm is capable to protect graphite nozzles from high-temperature ablative environment promoted by air plasma jet. After the 70 s of the ablation test, the sample with 10 μm coating thickness suffered a SiC oxidation to SiO₂ and weight loss due to the evaporation of SiO₂. The sample with 20 μm coating thickness undergoes a $\beta \rightarrow \alpha$ phase transformation of SiC, and the oxidation forms SiO₂ (glass and quartz structure). The growth of SiO₂ grains was observed on both samples after the ablation test, with a grain size distribution of 30–145 μm.

Figure 10. SEM images from the nozzle with 10 μm SiC coating (sample 11a), (a) convergent, (b) throat and (c) divergent, (d) grain size distribution.
The plasma torch testing indicated that the tested graphite nozzles coated with SiC have ablation resistance that allows its consideration as a prospective candidate for the manufacturing of rocket nozzles. Mainly in a scenario of low-cost engines applied on small launchers, boosters, and sounding rockets. The predictable behaviour of this combination of materials can be correctly matched on liquid rocket chambers, with pressure and mass flow adjustment in the function of diameter increase or mass loss of nozzle throat, keeping a higher efficiency of the engine, with a small fraction cost of a superalloy brazed chamber.

Figure 11. XRD pattern of sample 5a.

Figure 12. SEM images from the nozzle with 10 μm SiC coating (sample 5a), (a) convergent, (b) throat and (c) divergent, (d) detail of oxidized surface of sample 5a and (e) grain size distribution.
Figure 13. XRD pattern of sample 10b.

Figure 14. SEM/BSE images of sample 10b after ablation tests.
Acknowledgments

The authors acknowledge the financial support provided by the Coordination for the Improvement of Higher Education Personnel (CAPES) and the Technological Institute of Aeronautics (ITA), and Materials Laboratory of ITA, in the figure of Dr. Jorge Otubo and the Associate Laboratory of Sensors of INPE, in the figure of Dr. João Paulo Barros Machado.

ORCID iDs

Felipe de Souza Miranda  
https://orcid.org/0000-0002-2010-4478

References

[1] Sutton G P and Biblarz O 2016 Rocket Propulsion Elements (Hoboken, New Jersey: Wiley)
[2] Porte R 2004 Launch vehicle design features for minimum cost 40th AIAA/ASME/SAE/ASEE J. Propuls. Conf. Exhibit
[3] Kim P Y, Majumardi A, Papes R, Schneider D, Thomson M and Weinieck V D 2005 Design and development testing of the TR108—A 30 K杀thrust-class hydrogen peroxide/hydrocarbon pump-fed engine 41st AIAA/ASME/SAE/ASEE J. Propuls. Conf. Exhibit pp. 1–11
[4] Conger E R, Chakroborty S and Wertz J R 2002 ‘The scorpius’ expendable launch vehicle family and status of the sprite mini-lift 20th AIAA Int Commun. Satell. Syst. Conf. Exhibit pp. 1–9
[5] Fisher M F and Ise M R 1998 Low-cost propulsion technology at the Marshall space flight centerfastrac engine and the propulsion test article 34th AIAA/ASME/SAE/ASEE J. Propuls. Conf. Exhibit
[6] Wilson A, Bostwick C, Besnard E and Shinavski R J 2009 Ceramic matrix composite as liners for improved ablative chambers 45th AIAA/ASME/SAE/ASEE J. Propuls. Conf. Exhibit pp. 1–10
[7] Glass D E 2008 Ceramic matrix composite (CMC) thermal protection systems (TPS) and hot structures for hypersonic vehicles 15th AIAA Int. Sp. Planes Hypersonic Syst. Technol. Conf pp. 1–37
[8] Winter J, Peterson D, Shin A and Pavli A 1971 Development And Testing Of Ablative Rocket Engine With Selected 7.62 Centimeter (3.0 inches) Diameter Throat Inserts (Cleveland)
[9] de Almeida D S and de Moraes Pagnulo C M 2014 Development status of L75: a Brazilian liquid propellant rocket engine J. Aerosp. Technol. Manag. 6 475–84
[10] Kessae K 2008 Introduction to liquid rocket engine design Fundamental Course in Engine Design (Sao Jose dos Campos) I 1120
[11] Zintchuk I 2008 Introduction To Chamber Design Fundamental Course In Engine Design (Sao Jose dos Campos) I 1550
[12] Pizzarel I, Nasuti F and Onofri M 2013 Coupled wall heat conduction and coolant flow analysis for liquid rocket engines J. Propuls. Power 29 34–41
[13] Mota F A, da S, Hinckel J N, Rocco E M and Schlingloff H 2018 Modeling and analysis of a LOX/Ethanol liquid rocket engine J. Aerosp. Technol. Manag. 10 1–17
[14] Petracconi G, Essipchouch A M, Charakhovski I L, Otani C, Maciel H S, Pessoa R S, Gregori M L and Costa S F 2010 Degradation of carbon-based materials under ablative conditions produced by a high enthalpy plasma jet J. Aerosp. Technol. Manag. 2 33–40
[15] da Silva R J, Reis R I, Pardini L C, Sias D F and Filho G P 2019 Low-energy ablative and low thermal diffusivity of a CFRP composite modified by SiC J. Int. J. Thermophysics. 40 1–16
[16] KUO K K and KESWANI S T 1985 A comprehensive theoretical model for carbon-carbon composite nozzle recession Combust. Sci. Technol. 42 145–64
[17] Grad P R and Valentine P G 2017 Carbon-carbon nozzle extension development in support of in-space and upper-stage liquid rocket engines 53rd AIAA/SAE/ASEE J. Propuls. Conf. 2017
[18] Li B, Kang P, Gou H and Wu G 2014 Microstructure and ablation mechanism of graphite/SiC composites under oxy-acetylene flame Ceram. Int. 40 5497–505
[19] Kihara K 1990 An x-ray study of the temperature dependence of the quartz structure Eur. J. Mineral. 2 63–78
[20] Presser V and Nickel K G 2008 Silica on silicon carbide Crit. Rev. Solid State Mater. Sci. 33 1–99
[21] Boulos M J, Fauhafl P and Pender E 1994 Thermal Plasma Fundamentals and Applications (New York: Springer Science+Business Media, LLC)
[22] Silva R J, Maciel H S, Essipchouch A M and Petracconi G 2014 Comparison of the Ablation Mechanism of C/C-SiC Composite under atmospheric and low pressure Adv. Sci. Technol. 91 134–9
[23] Sakraker I and Asma C O 2013 Experimental investigation of passive/active oxidation behavior of SiC-based ceramic thermal protection materials exposed to high enthalpy plasma J. Eur. Ceram. Soc. 33 351–9
[24] Hald H 2003 Operational limits for reusable space transportation systems due to physical boundaries of C/SiC materials Aerosp. Sci. Technol. 7 551–9
[25] Bronson A and Chessa J 2008 An evaluation of vaporizing rates of SiO2 and TiO2 as protective coatings for ultrahigh temperature ceramic composites J. Am. Ceram. Soc. 91 1448–52
[26] Moberlykan W and De Jonghe I 1998 Controlling interface chemical and structure to process and toughen silicon carbide Acta Mater. —Acta Mater. 46 2471–7
[27] Ryan C E, Marshall R C, Hawley J L, Bernard I and Considine D P 1968 The conversion of cubic and hexagonal silicon carbide as a function of temperature and pressure b—anisotropy in single-crystal refractory compounds Proc. of an Int. Symp. on Anisotropy in Single-Crystal Refractory Compounds, held o ed FW Vahlidiek and S A Mersol (Boston, MA: Springer US) pp. 177–97