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Influence of the Porosity of SiC on its Optical Properties And Oxidation Kinetics

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Abstract. CEA laboratory has developed an additive manufacturing technique with SiC powders and the material obtained need to be characterized. Therefore, we studied the change of optical properties and oxidation kinetics of SiC samples for the last step of the elaboration process. In this investigation, the optical properties and the oxidation kinetics of two SiC materials of two different densities and post-treated at LCTS laboratory have been compared. Their room-temperature optical properties were measured and both materials were oxidized using solar facilities at PROMES laboratory. It was observed that a higher porosity would increase both the solar absorptivity α and total emissivity ε of the SiC. Nevertheless, the α/ε ratio is improved with the density, increasing from 1.04 to 1.22. The less dense SiC presents also a faster oxidation kinetics, the determined activation energy increasing from 110 to 270 kJ mol^{-1}.

INTRODUCTION

Silicon Carbide (SiC) is a well-suited ceramic materials for the conception of volumetric solar receivers[1], as it can resist to passive oxidation with the formation of a protective silica layer up to 2000 K in air. In this passive mode, the semi-parabolic oxidation kinetics is controlled by the diffusion of molecular oxygen through the oxide layer. However, there is an important discrepancy between the activation energies (which ranges from 85 to 670 kJ mol^{-1}) that can be found in the literature[2], which is caused by the difference in the materials used (especially the purity and density of the materials). On the other hand, the publications regarding the optical properties rarely mention the influence of the surface roughness on them[3].

In this paper, SiC materials produced by CEA laboratory with a new additive manufacturing technique have been studied. We have compared the optical properties and the oxidation kinetics of two SiC bulk materials post-treated at LCTS laboratory, with two different densities. The aim of this investigation is to define how the density may affect the performance of a material that could be used for volumetric solar receiver. The two most important characteristics we have measured are the radiative properties (high capacity to absorb the incoming solar flux, with the lowest possible infrared emissivity in order to minimize the radiative heat loss), and the resistance to oxidation in air (air coolant being the most convenient transfer medium for solar applications).

MATERIALS AND METHODS

Sample of 25 mm-diameter and 2 mm-thickness bulk SiC were produced at CEA. The samples further identified as *Rough* SiC were produced by 3D-printing of SiC powders and did not support any post-treatment, hence their name. Their density was measured around 40% of the theoretical one and they contain up to 3 wt.% of carbon due to the use of polycarbosilane (SMP-10 polymer) in the manufacturing process. Some samples were produced by 3D-

printing of SiC powders, then reinforced using Chemical Vapor Deposition (CVD) at LCTS: those are further identified as *CVD* SiC and their density was increased up to 90 %. Figure 1 presents these samples. Some of them have 2mm-diameter holes that were used to fix the samples for the CVD process, the other ones were fixed by two handles that were removed by polishing.

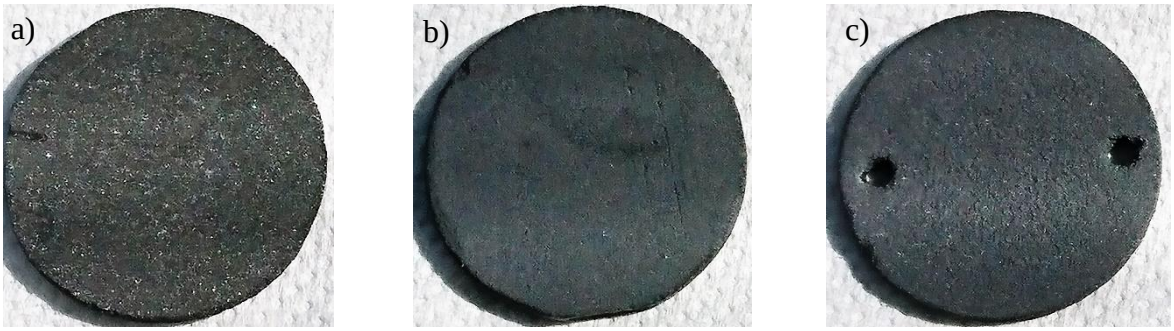


FIGURE 1. Pictures of the a) Rough, b) CVD (with removed handles) and c) CVD (with holes) SiC.

Figure 2 presents SEM images of the surface of both materials (performed using a Hitachi S-4500 apparatus). The surface of the Rough SiC presents grains of the initial powder that have agglomerated with an important porosity. The surface of the CVD SiC is cauliflower-like, which is typical of the CVD growth of SiC.

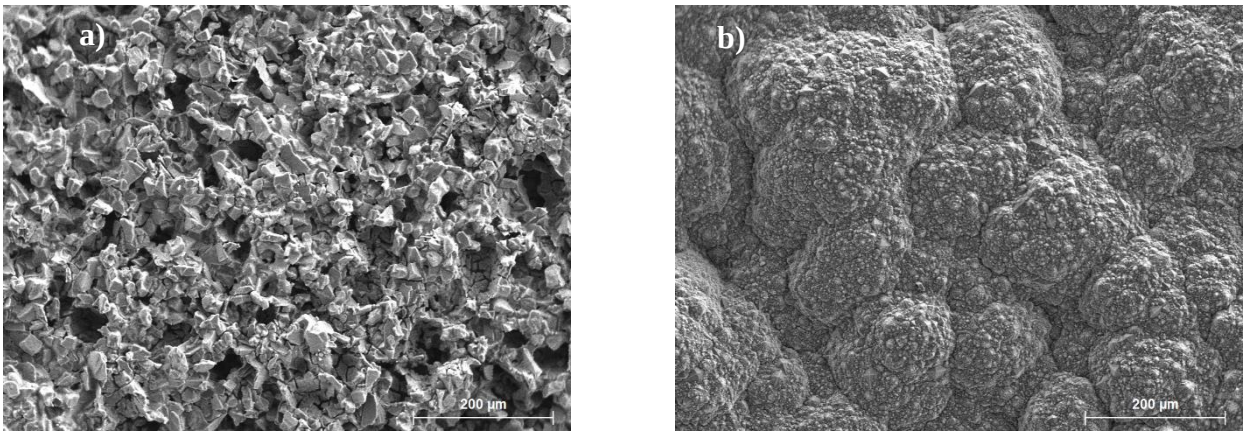


FIGURE 2. SEM images (Secondary electron mode) of a) Rough and b) CVD SiC

Reflectivity ρ and transmittivity τ were measured on Rough and CVD SiC at 300 K using the Perkin Elmer UV/VIS/NIR Lambda 900 apparatus (wavelength range from 0.25 to 2.5 µm) and the SOC-100 HDR (from 1.5 to 25 µm). From these measurements the spectral emissivity ε_λ was deduced. From these curves it was possible to calculate the total solar absorptivity α in the 0.25 – 2.5 µm range, and the total emissivity ε on the 0.25 – 25 µm range at 300 K by integration, using as shown in equation (1) and (2) the spectral emissivity, the values of solar irradiance I(λ) and the blackbody emittance $E^{bb}(\lambda, T)$ that can be calculated at 300 K using Planck's law.

$$\alpha = \frac{\int_{0.25}^{2.5} \varepsilon_\lambda \cdot I(\lambda) \mathrm{d}\lambda}{\int_{0.25}^{2.5} I(\lambda) \mathrm{d}\lambda} \quad (1)$$

$$\varepsilon = \frac{\int_{0.25}^{25} \varepsilon_\lambda \cdot E^{bb}(\lambda, \mathrm{T}) \mathrm{d}\lambda}{\int_{0.25}^{25} E^{bb}(\lambda, \mathrm{T}) \mathrm{d}\lambda} \quad (2)$$

The REHPTS (*REacteur Hautes Pression et Température Solaire* – High Temperature and Pressure Solar Reactor, Fig. 3a), implemented at the focus of a 6-kW solar furnace at PROMES-CNRS was used to oxidize the samples in open air at P = 87 kPa at temperatures of 1800 and 1900 K (as explained further, we have added a supplementary set of experiments at 1600 K for the CVD sample). We have tried to perform 4 cycles during which the temperature would have stayed constant during 20 minutes, nevertheless in some case the cycles had to be

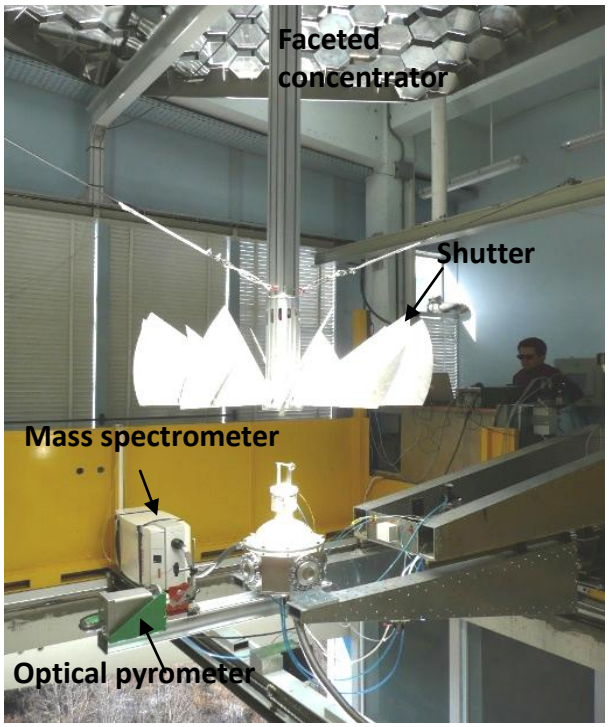
shorten due to the drop of the incoming concentrated solar flux (because of cloudy episodes) and therefore some supplementary cycles were added to keep a total oxidation time close to 80 minutes. Figure 3b shows the temperature variations during the 4 cycles performed on the Rough sample treated at 1900 K. The temperature was measured using an optical pyrometer at $\lambda = 5$ µm (so that the measurement is solar-blind). We can observe some fluctuations during the first temperature plateau, those are due to the fluctuations of the incoming solar flux because of the passages of slight cloudy veils. Playing on the opening of the shutter enabled us to maintain the temperature plateau despites these fluctuations. The samples were weighted before and after each cycles to follow mass change evolution, and the production of CO and consumption of O_2 were analyzed using a mass spectrometer (Pfeiffer Omnistar).

RESULTS AND DISCUSSION

Optical Properties

Figure 4 shows the optical properties for Rough and CVD SiC. We observe in figure 4 a) that the spectral emissivity of the Rough SiC is higher than the one of the CVD SiC, especially in two areas. The first one corresponds to the 0.25 to 1µm range, the second one to the reflectivity band around 10 µm that is deeper for the CVD SiC. Consequently, Rough SiC presents a higher solar absorptivity (0.90 vs. 0.88) and total emissivity (0.87 vs. 0.72) at 300 K than the CVD SiC, which can be explained by a higher surface porosity that increases the absorptivity and emissivity by multiple reflections. Nevertheless, the α/ε ratio is improved with the CVD reinforcement, increasing from 1.04 to 1.22.

a)



b)

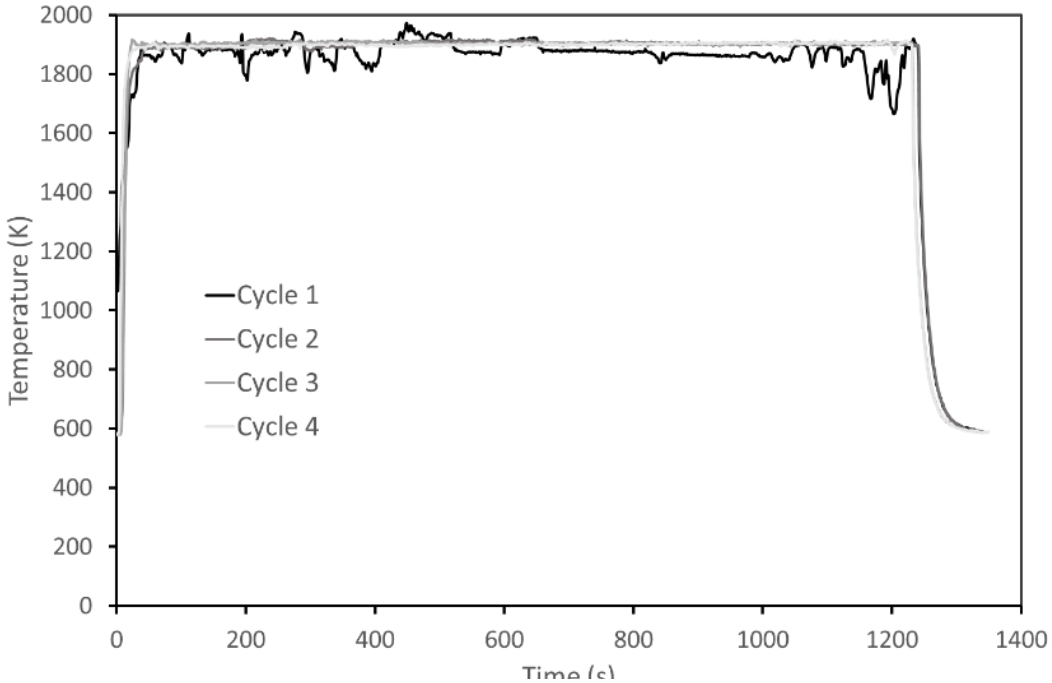


FIGURE 3. a) The REHPTS facility and b) The 4 temperature cycles that were applied on the Rough sample exposed at 1900 K.

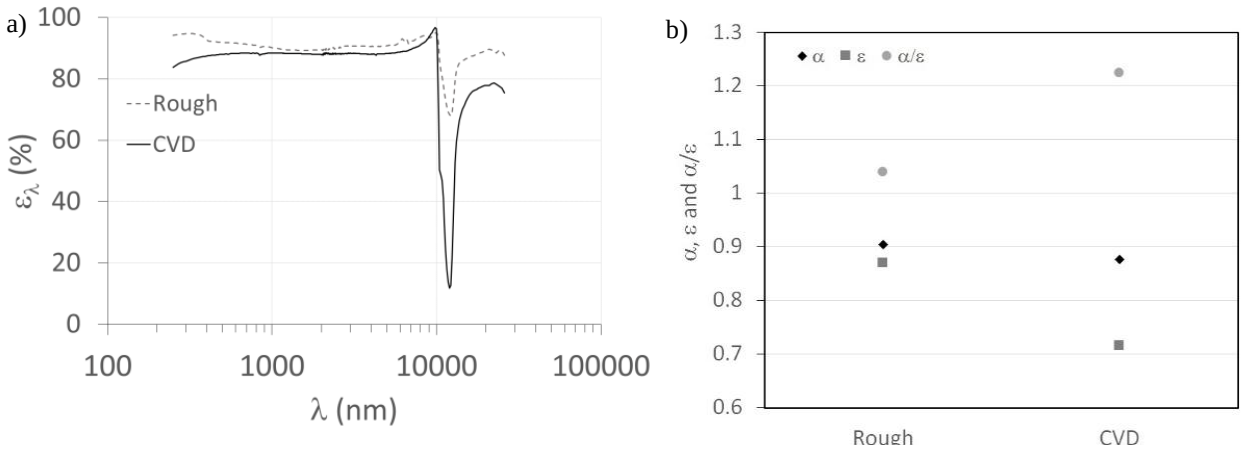


FIGURE 4. a) Evolution of the emissivity according to the wavelength (at 300 K) for Rough and CVD SiC; b) values of the solar absorptivity α, the total emissivity ε and the α/ε ratio for rough and CVD SiC, at 300 K.

Oxidation Kinetics

Figure 5 compares the mass variation (reported to the initial mass of the sample, m_0) during the oxidation of Rough and CVD samples at 1800 and 1900 K. After an initial mass loss probably due to the consumption of the free carbon, the rough samples gain weight continuously due to the production of SiO_2, heavier than the consumed SiC (60 g mol^{-1} vs 40 g mol^{-1}, respectively), unlike the CVD samples which lose continuously weight. We have added a supplementary set of experiments at 1600 K for the CVD samples to see if this unexpected trend occurred at lower temperatures, but the weight variations are not significant at this temperature.

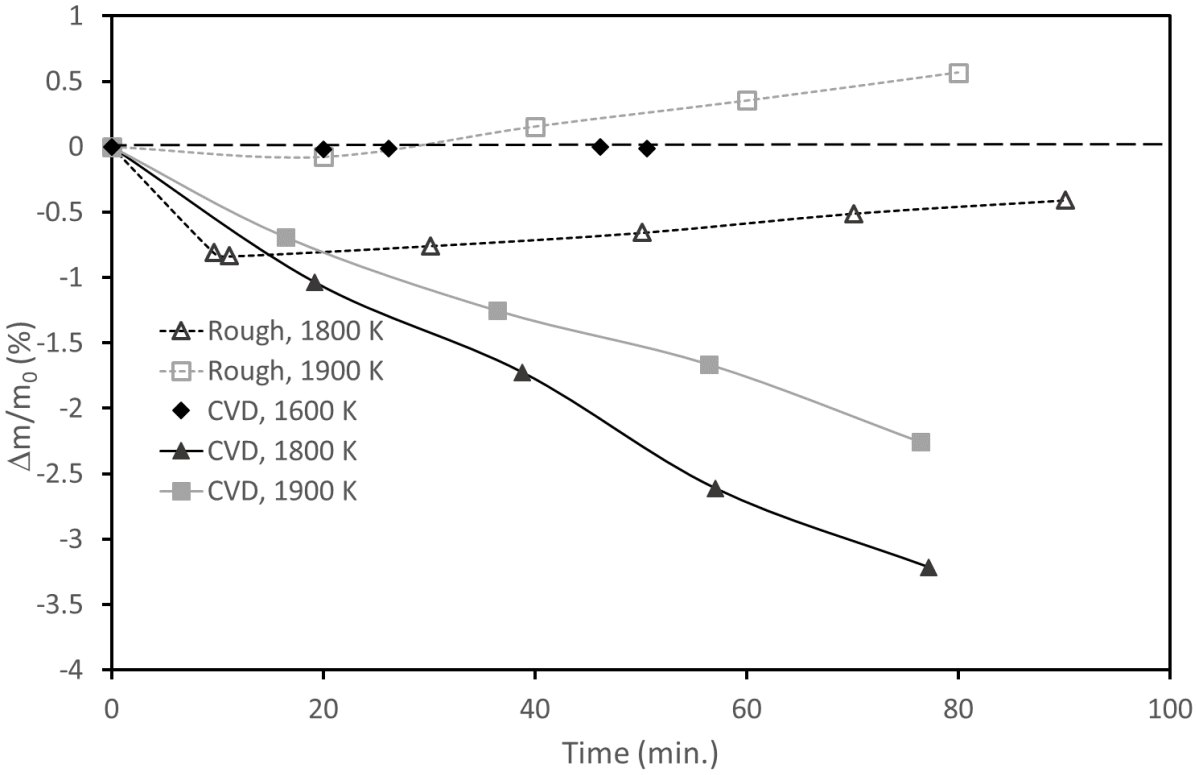


FIGURE 5. Evolution of the mass variation with time, according to various temperatures for Rough and CVD SiC samples.

Figure 6 presents the pictures of the samples according to different temperatures and time of exposure for Rough and CVD samples. The differences of color from the references (Fig. 1) and with the temperature and exposure time evidence the growth of a silica layer, looking brown or blue when it is thin (T = 1600 or 1800 K), darkening when it gets thicker (at T = 1900 K). We also observe cracks showing the oxide layer on the CVD samples peels during the heat treatment at 1800 and 1900 K, which explains the weight losses reported on figure 5. No peeling is observed on the CVD samples treated at 1600 K. Due to this important damaging during the oxidation experiments, the mass change is not an appropriate parameter to perform kinetic analysis.

The analysis of the CO production (as shown on Fig.7) looks therefore more accurate than the mass variation to follow the oxidation kinetics. We observe than after a faster oxidation during the first cycle, this production is depending on the square root of time (despite some fluctuations due to the measurement, the deviation from the square root law being below 5%), showing the kinetics is parabolic. The parabolic law, described by Equation (3) means that the molecular diffusion of oxygen through the oxide layer controls the oxidation rate[4]. The oxidation kinetics is faster at the beginning of the oxidation, when the oxide layer is thinner, and can increase if the oxide layer breaks or peels.

$$C^2 = kp.t \tag{3}$$

Table 1 summarizes the average values of the parabolic constant determined for each sample at various temperatures. The activation energy calculated from these values was determined around 270 $kJ.mol^{-1}$ for the Rough samples and 110 $kJ.mol^{-1}$ for the CVD samples. This difference can be explained by the higher porosity that favors a deeper oxidation of the sample. The parabolic kinetics and the determined activation energy are coherent with the results reviewed by Kovalcikova *et al.*[2] who reported the activation energy may vary from 85 kJ mol^{-1} for a dense SiC produced by CVD and can increase up to 670 kJ mol^{-1} for a sintered polycrystalline SiC, according to its density and the presence of additives or impurities (Al and Na cations can favor the oxygen diffusion). The SiC materials we investigated are extremely pure, so the activation energy is mainly affected by the density, and therefore the values we found are coherent towards the values reported by Kovalcikova *et al*[2].

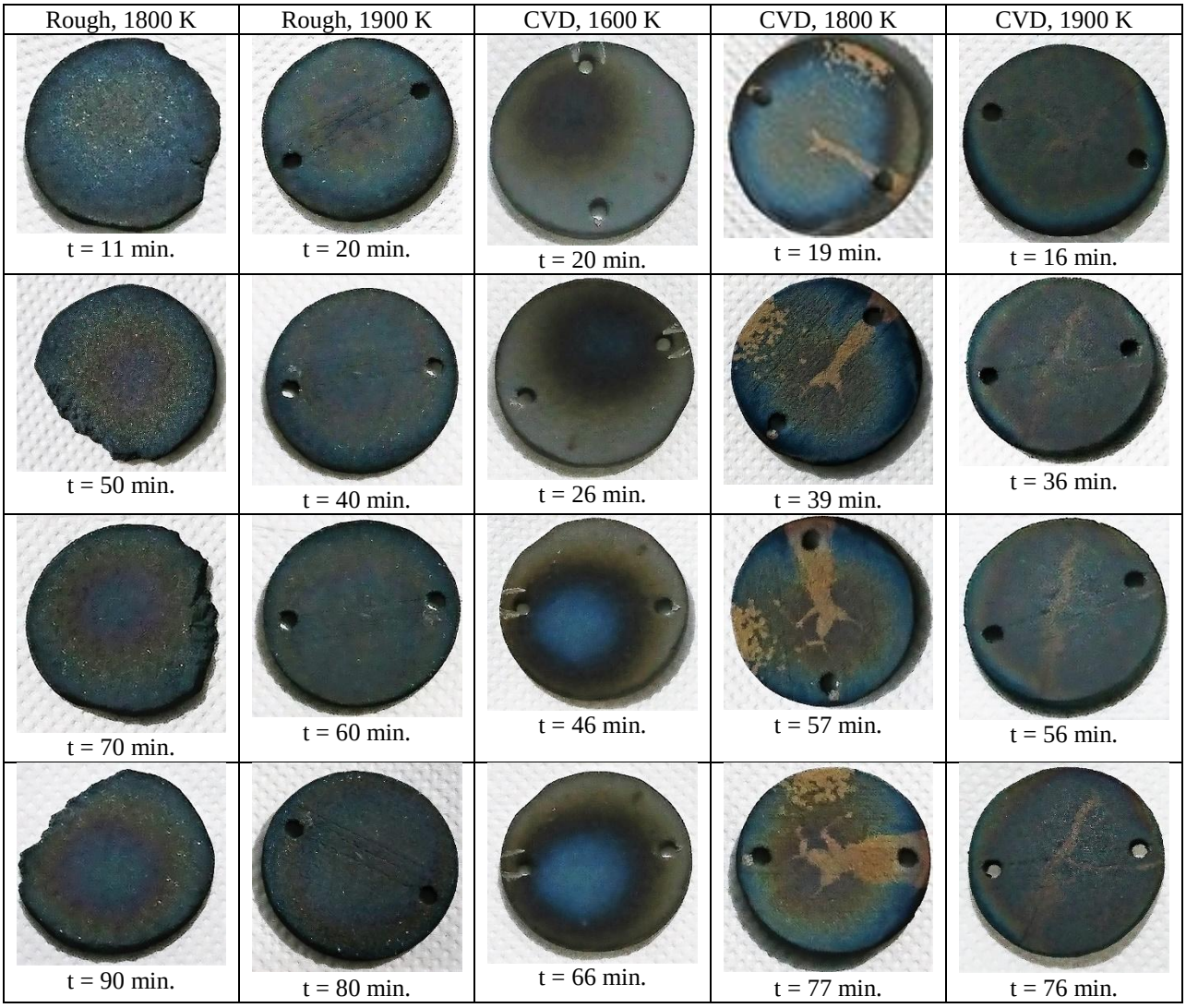


FIGURE 6. Pictures of the oxidized Rough and CVD SiC, at various times of oxidation.

TABLE 1. Values of the parabolic kinetic constant determined at different temperatures, and corresponding activation energy for Rough and CVD samples

Samples	**k_p, T =1600 K ($\%^2$ min^{-1})**	**k_p, T = 1800 K ($\%^2$ min^{-1})**	**k_p, T = 1900 K ($\%^2$ min^{-1})**	**E_a (kJ mol^{-1})**
Rough		0.035	0.090	270
CVD	0.018	0.036	0.078	110

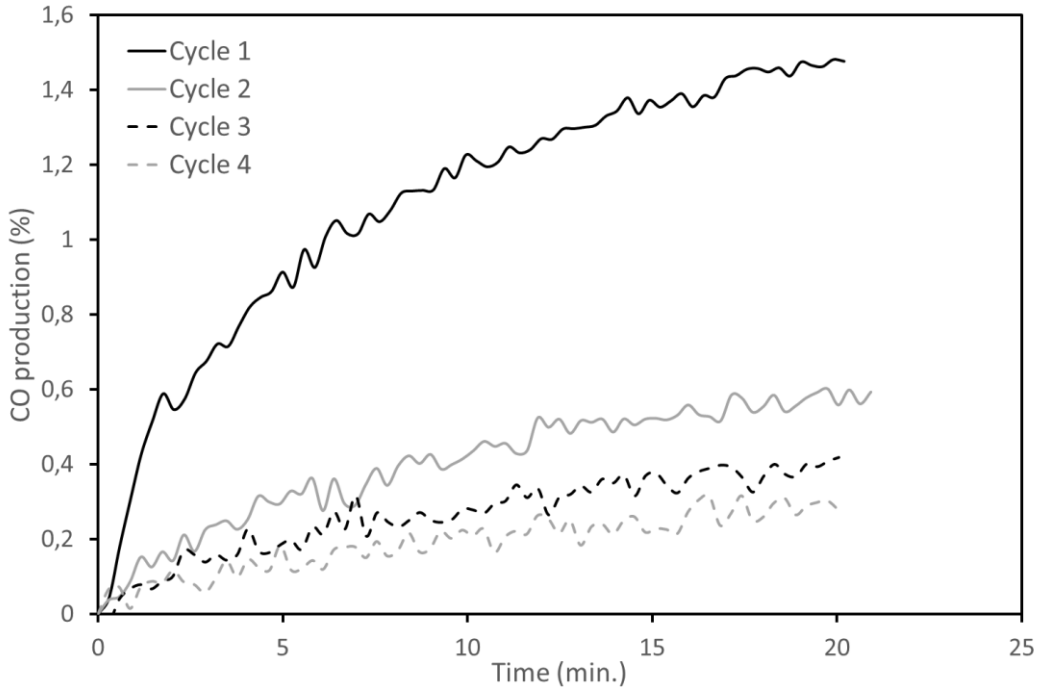


FIGURE 7. Variation of the production of CO with time during 4 cycles of oxidation of Rough SiC at 1900 K.

CONCLUSION

For the last elaboration steps of an additively manufactured SiC material, we have shown the influence of the porosity on the radiative properties and oxidation kinetics. We have observed a higher porosity would increase both the solar absorptivity and total emissivity of the SiC. Nevertheless, the α/ε ratio is improved with the CVD reinforcement, increasing from 1.04 to 1.22.

Due to higher porosity, the Rough SiC samples also present faster oxidation kinetics than the CVD reinforced one. We also observed the oxide layer at the surface of the CVD samples may peel due to thermal shocks at temperature above 1800 K. Following the CO production enabled to determine the activation energies of 110 kJ mol^{-1} for the CVD reinforced samples and 270 kJ mol^{-1} for the rough ones, which is coherent with the values reported in the literature[2] for very pure SiC, the activation energy being mainly affected by the density of the material.

In future work, the evolution of mechanical, physical and radiative properties with the temperature would be investigated.

ACKNOWLEDGEMENTS

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