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Effect of TiC incorporation on the optical properties and the oxidation resistance of SiC ceramics

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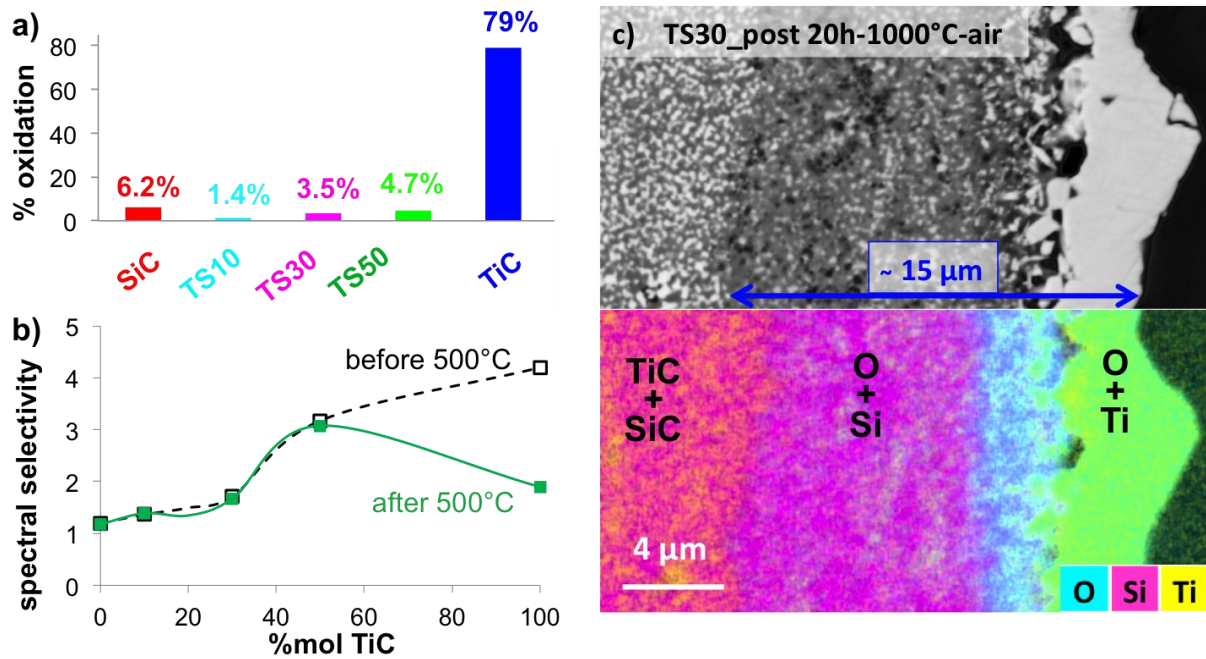
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Keywords: SiC, TiC, nano composite, oxidation resistance, optical properties, CSP, high temperature, ceramics, reflectance.

Abstract

In concentrating solar power (CSP) technologies, the absorber material should be spectrally selective under severe operating conditions, i.e. $\sim 1000^\circ\text{C}$ under air atmosphere. SiC-TiC nanocomposites could be good candidates for this application due to their spectral selectivity at room temperature, but their behavior under CSP operating conditions is unknown. Therefore, the spectral selectivity and oxidation resistance of TiC-SiC composites were studied up to 500°C , under air, for various compositions. During heating, the emittance increased with the temperature. After heating, the TiC grains at the surface were oxidized into TiO_2 , while SiC grains showed good behavior. However, despite little oxidation, the spectral selectivity of the nanocomposites remained interesting after heating. Specific oxidation tests up to 9 days at 1000°C under air showed an increase of the oxidation resistance with the amount of SiC. This result is the consequence of the formation of a protective layer of SiO_2 preventing the oxidation of the TiC grains. The composition 30 at% TiC – 70 at% SiC seems to be a good compromise between low oxidation and good selectivity.



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35

36 1. Introduction

37 Solar energy is a powerful source of renewable energy which can be efficiently exploited by
 38 Concentrating solar power technologies (CSP) [1, 2]. In this promising and sustainable systems,
 39 the sunlight is collected by several heliostats and concentrated towards the absorber. The
 40 absorber converts the solar radiation into heat and transfers it to a thermal fluid, which will
 41 drive a turbine in power block to generate electricity. However, when heated by sunlight, the
 42 absorber may behave as a blackbody and lose some energy by thermal emission. To maximize
 43 its efficiency, the ideal absorber should be spectrally selective, i.e., have a high absorptance in
 44 the sunlight region (0.25-2.5 μm) and a low infrared emittance in the blackbody region
 45 (typically 1.25-25 μm at 500 °C) [3-6]. The Carnot efficiency of the solar thermal power plants
 46 increases when increasing the working temperature [7, 8]. Therefore, the absorber must also be
 47 able to maintain good mechanical, physical and chemical properties under severe operating
 48 conditions (T ~ 1000 °C under air atmosphere).

49 Silicon carbide (SiC) is the material commonly used as the absorber because of its high
 50 resistance to oxidation and its good sunlight absorptance. The surface oxidation of SiC leads to
 51 the formation of an amorphous SiO₂ passivating layer. This SiO₂ layer protects the SiC
 52 underneath up to temperatures of 1400 °C [7]. However, SiC has a high thermal emittance
 53 leading to significant energy losses in the infrared region, especially when increasing the
 54 working temperatures [9, 10].

55 Thanks to their spectral selectivity, metal borides, nitrides or carbides could be good candidates
56 for solar absorber applications [11-24]. In addition, these materials have extremely high thermal
57 stability, good thermo-chemical and thermo-mechanical properties, high hardness, high
58 electrical and thermal conductivities [25-28]. Coulibaly *et al.* compared the optical properties
59 of several carbides and demonstrated that titanium carbide (TiC) is one of the best compound
60 in this group, due to its particularly low emittance [29]. However, the major limitation of this
61 material is its low resistance to oxidation [30-37].

62 To improve both the optical selectivity of SiC and the oxidation resistance of TiC, they can be
63 combined in a nanocomposite structure [29, 38]. Indeed, the association of SiC and TiC showed
64 better optical selectivity than pure SiC and better oxidation resistance than pure TiC. According
65 to Banu *et al.*, the oxidation of a TiC/SiC composite material produced TiO₂/SiC up to 750 °C,
66 and a TiO₂/SiO₂/SiC mixture at higher temperatures [39]. The addition of SiC increased the
67 oxidation resistance of ZrC [40], ZrB₂ and HfB₂ materials [26, 41].

68
69 In a previous paper [38], we have shown how the porous characteristics (density and surface
70 roughness) can change the selectivity of SiC 70% at. –TiC 30% at. nanocomposite at room
71 temperature. In this paper, we studied the mutual dependency between the TiC content, the
72 oxidation resistance and the spectral selectivity by reflectance measurements at various
73 temperatures up to 500 °C, and thorough material characterization. To go further on the
74 assessment of the oxidation resistance, the samples were also heated to 1000 °C under air during
75 20 h to 9 days to precise the nature of the oxide layers.

76

77 **2. Experimental**

78 The complete synthesis route, starting materials, sample preparation and characterization
79 techniques used are described in detail in Supplementary Information (SI 1) and in our previous
80 paper [38]. The main information are given below.

81 A “molecular route” involving hydrolysis and polycondensation of alkoxides as metal oxide
82 precursors, and sucrose and citric acid as carbon sources was used to synthesize the
83 nanocomposites [42]. Two heat treatments were used to transform the resulting oxide powders
84 into carbides; the decomposition of the organic part into carbon (800 °C – 4h – under Ar), and
85 then, the carbothermal reduction (1550 °C – 4h – under Ar). Composites with increasing Ti/Si
86 proportions were produced by this molecular synthesis route and commercial powders were
87 used for the pure TiC and SiC reference samples (Table 1). Dense materials were produced by

88 Spark Plasma Sintering (Syntex, Dr. Sinter 825, Japan), with sintering temperatures of 1700°C
 89 for TiC, 1950°C for SiC and 1750°C for the composites. The densified materials were mirror
 90 polished (Beta Buehler grinder-polisher), using SiC grinding papers and 1 μm diamond paste
 91 (Struers). The samples density and porosity was evaluated using Archimedes method, helium
 92 pycnometry and the proportions of Ti, Si, O and C determined by elemental analysis (C and O
 93 wt% - LECO CS230 and TCH600), and X-Ray Fluorescence (Spectro-Xepos).

Sample name	TS10	TS30	TS50	TiC	SiC
Origin	Sol-gel synthesis route			Commercial products	
Ti / Si (%at)	10 / 90	30 / 70	50 / 50	100 / 0	0 / 100
Ti / Si (%wt)	14.3 / 85.7	39 / 61	60 / 40	100 / 0	0 / 100
Tsintering (°C)	1750			1700	1950

95 *Table 1: Name, composition and sintering temperature for all samples. "TS" refers to TiC-SiC composite*
 96 *materials, the number across refers to the at% of TiC. For example, TS10 = 10 %at TiC – 90 %at SiC.*

97
 98 All samples were characterized in terms of: (i) roughness by optical interferometry (Fogale
 99 Nanotech), (ii) morphology and composition by Scanning Electron Microscopy (SEM - FEI
 100 Quanta 200 ESEM) coupled with Energy Dispersive X-ray Spectrometry (EDX - Bruker SDD
 101 5030 detector), (iii) structure by X-Ray Diffraction (XRD) and Grazing Incident X-Ray
 102 Diffraction (GI-XRD) with an incident angle of 0.4° (Bruker D8_10-90° (2θ)), and (iv) optical
 103 properties through the measurement of the reflectance in the 0.25 to 25 μm range of
 104 wavelengths (Perkin Elmer Lambda 950 with a 150 mm integrating sphere coated with
 105 Spectralon, and a SOC-100 HDR coated with gold and using a 700 °C (973 K) blackbody). A
 106 heating plate on the sample holder enabled measurements at different temperatures (from room
 107 temperature to 500 °C). The temperature of the sample was controlled by a surface
 108 thermocouple connected to PID (proportional–integral–derivative) regulation of the heating
 109 resistance. The complete description of the devices used for reflectance measurements is
 110 detailed in [43, 44]. The absorptance (α), *i. e.* the propensity of the material to absorb sunlight,
 111 was calculated in the range of wavelengths (λ) 0.25 to 4 μm, from the total spectral reflectance
 112 $R(\lambda, T_a)$ measured at room temperature (T_a), and the standard solar irradiance spectrum $G(\lambda)$,
 113 according to Equation 1. The directional emittance (ϵ_{θ}), *i. e.* the tendency of the material to
 114 emit thermal radiations, was calculated in the range of wavelengths 1.25 to 25 μm, from the
 115 total spectral reflectance $R(\lambda, T_a, \theta)$ measured at various temperatures (T), and the spectral
 116 exitance of a blackbody $P(\lambda, T)$ at the same temperatures, derived from Planck's law (Equation

117 2). Since all samples were completely opaque, the transmittance was not calculated and
 118 considered null. The total spectral reflectance was measured at various detection angles (θ from
 119 8 to 80°) to calculate the hemispherical emittance (ε_H) at room temperature (Equation 3).

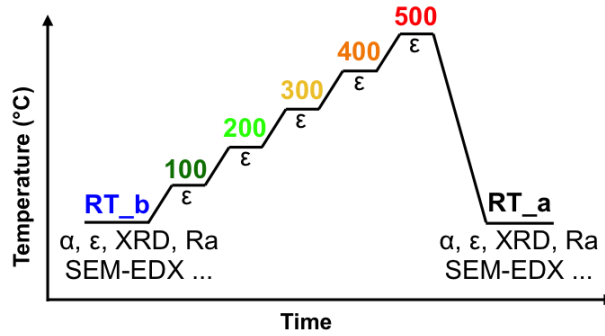
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$$121 \quad \alpha = \frac{\int_{0.25 \mu m}^{4 \mu m} [1-R_{8^\circ}(\lambda, T_a)] \cdot G(\lambda) \cdot d\lambda}{\int_{0.25 \mu m}^{4 \mu m} G(\lambda) \cdot d\lambda} \quad (1) \quad \varepsilon_\theta(\theta, T) = \frac{\int_{1.25 \mu m}^{25 \mu m} [1-R(\lambda, T, \theta)] \cdot P(\lambda, T) \cdot d\lambda}{\int_{1.25 \mu m}^{25 \mu m} P(\lambda, T) \cdot d\lambda} \quad (2)$$

$$122 \quad \varepsilon_H(T_a) = 2 \int_0^{\pi/2} \varepsilon_\theta(\theta, T_a) \cdot \sin \theta \cdot \cos \theta \cdot d\theta \quad (3)$$

123 To measure the near-normal spectral reflectance at various temperatures, the samples were
 124 heated up to 500°C (450°C for TS30) as described in Figure 1 [44]. The atmosphere was not
 125 controlled during heating therefore the samples were submitted to oxidation. The samples were
 126 thoroughly characterized at room temperature before and after heating, using various
 127 techniques (SEM, (GI)XRD, and interferometry) to evaluate the effects of heating.

128



129

130 *Figure 1: Heating procedure to measure the near-normal spectral reflectance at various temperatures.*

131

In the case of TS30, the maximum temperature was 450°C .

132

133 Finally, thermogravimetric analyses (TGA) were conducted (Setsys 1750Cs Evol Staram). The
 134 oxidation resistance of all samples was evaluated when exposed to 20 h dwell at 1000°C under
 135 air ($10^\circ\text{C}\cdot\text{min}^{-1}$ rise and $30^\circ\text{C}\cdot\text{min}^{-1}$ decrease).

136

137 3. Results

138 3.1. Materials characterization before heating

139 Physical shape

140 The composition and the characteristics of the sintered materials are reported in Table 2. All
 141 samples except pure SiC had a relative density higher than 90 % and a surface roughness lower

142 than or equal to 10 nm. Pure SiC sample presented a lower relative density (74 %) due to is
 143 high covalency of the Si-C bonds which induces low self-diffusion coefficient [45, 46]. The
 144 SiC sample presented 26 % of open porosity which resulted in surface holes partly accounted
 145 when measuring the surface roughness (24 nm). On the contrary, TiC sample was more easily
 146 densified due to the presence of Ti-Ti metallic bonds in the structure. The association of TiC
 147 with SiC in a composite made the sintering easier compared to pure SiC and lead to denser and
 148 denser materials as the proportion of TiC increased.

149 According to SEM-EDX and XRF analyses, the composites had the expected Ti/Si proportions,
 150 also a little enrichment in Ti was observed for TS10 and TS50 samples. The O content was
 151 high in sample TS30 (5.5 wt%), even though the C content was equal to the amount required
 152 for stoichiometric SiC-TiC materials. This result suggests an incomplete carbothermal
 153 reduction, possibly due to a lack of homogenization during the synthesis.

154
 155

Sample	Processing parameters	Composition						Sintered materials characteristics			
	T sintering (°C)	Ti / Si (at%)				C (wt%)	O (wt%)	Relative density (%)	Open porosity (%)	Closed porosity (%)	Surface roughness (nm)
		Theory	XRF	SEM-EDX	Average						
TS10	1750	10 / 90	12 / 88	14 / 86	13 / 87	29.78	0.79	92.8	4.2	3	4
TS30		30 / 70	35 / 65	28 / 72	32 / 68	25.99	5.5	95.8	1.2	3.1	10
TS50		50 / 50	55 / 45	53 / 47	54 / 46	22.6	1.89	99.7	0	0.3	3
TiC	1700	100 / 0				19.6	0.46	96	1.2	2.8	9
SiC	1950	0 / 100				30.38	0.2	73.9	26.1	0	24

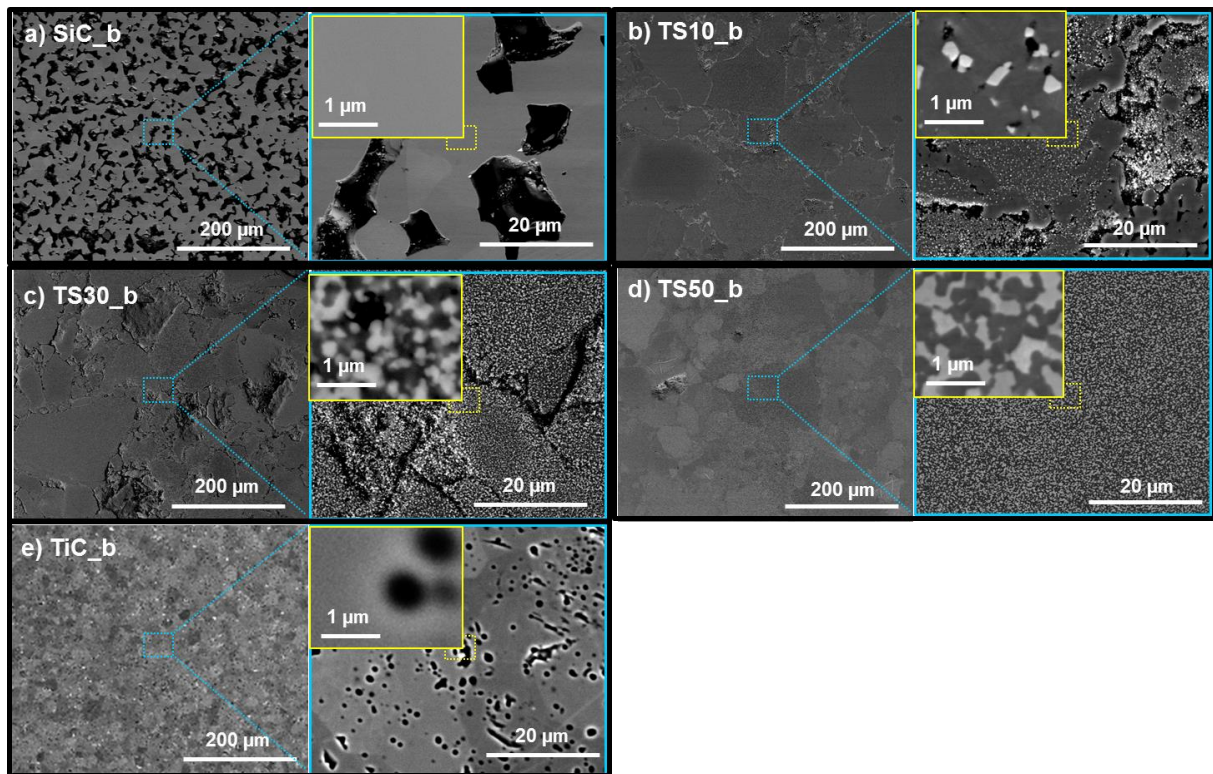
156 *Table 2: Characteristics of all samples after sintering. The theoretical wt% of C is 30 %, 29 %, 26 %, 24 % and*
 157 *20 % for pure SiC, TS10, TS30, TS50 and pure TiC, respectively. The standard errors are evaluated at 1 at% for*
 158 *Ti/Si proportion, 1 nm for surface roughness and 0.1 % for elemental analyses, relative density, and open and*
 159 *closed porosity.*

160

161 Morphology and structure

162 Scanning Electron Microscopy was used to characterize the composition and the morphology
 163 of the sintered materials (Figure 2). In back-scattering electron mode, the TiC grains appear
 164 white, while the SiC matrix is gray. The size of the TiC grains is similar in all composite
 165 samples (about 150 nm) and their repartition is homogenous at a short range. Nevertheless,

166 when the TiC proportion increases (TS10 to TS30), the space between two TiC grains decreases
167 and large TiC enriched domains are observed. In the TS50 sample, the TiC and SiC contents
168 form two distinct domains with adjacent grains gathered in aggregates. In addition, all
169 composites present large areas with variations in electronic contrast, which could be explained
170 by local changes in porosity or composition. Here again, a better homogeneization of the
171 precursors during the synthesis could improve the Ti – Si repartition; ongoing work is in
172 progress to improve the mixing. In the case of the pure TiC sample, the grains are very small
173 (< 100 nm) without any apparent porosity, while the pure SiC sample presents much bigger
174 grains (about $5 \mu\text{m}$) and the open porosity is evidenced by the presence of holes. The bigger
175 grain size for pure SiC could be due to its higher sintering temperature (1950°C vs 1750°C for
176 composites) and/or to the starting powders. Indeed, the composites were synthesized by the
177 molecular route while the pure TiC and SiC originated from commercial powders.



178
179 *Figure 2: SEM images of the surface of the samples a) pure SiC, b) TS10, c) TS30, d) TS50, e) pure TiC. The “_b”*
180 *stands for “before heating”. Based on SEM images, the grain size was measured on several grains and locations,*
181 *and a statistical average was considered.*

182 The structure of the sintered materials was analyzed by XRD and the cubic 3C SiC (F-43m
183 space group) and cubic TiC (Fm-3m space group) phases are identified (Figure 5 and SI 2). As
184 expected, when increasing the TiC content, the relative intensities of the SiC peaks decreases,
185 while those of the TiC peaks increases.

186 Optical properties

187 The optical properties of the samples were evaluated by the measurement of the total (specular
188 + diffuse) spectral reflectance in the 0.25 to 25 μm wavelength range. At room temperature
189 (Figure 3 blue curves, and SI 3), the reflectance of the SiC sample is much lower than that of
190 TiC with a typical reflectance peak (~60 %) around 12 μm . The reflectance curves of the TiC-
191 SiC composites are shaped like that of the SiC sample, with an increasing reflectance as the
192 amount of TiC increases (SI 3).

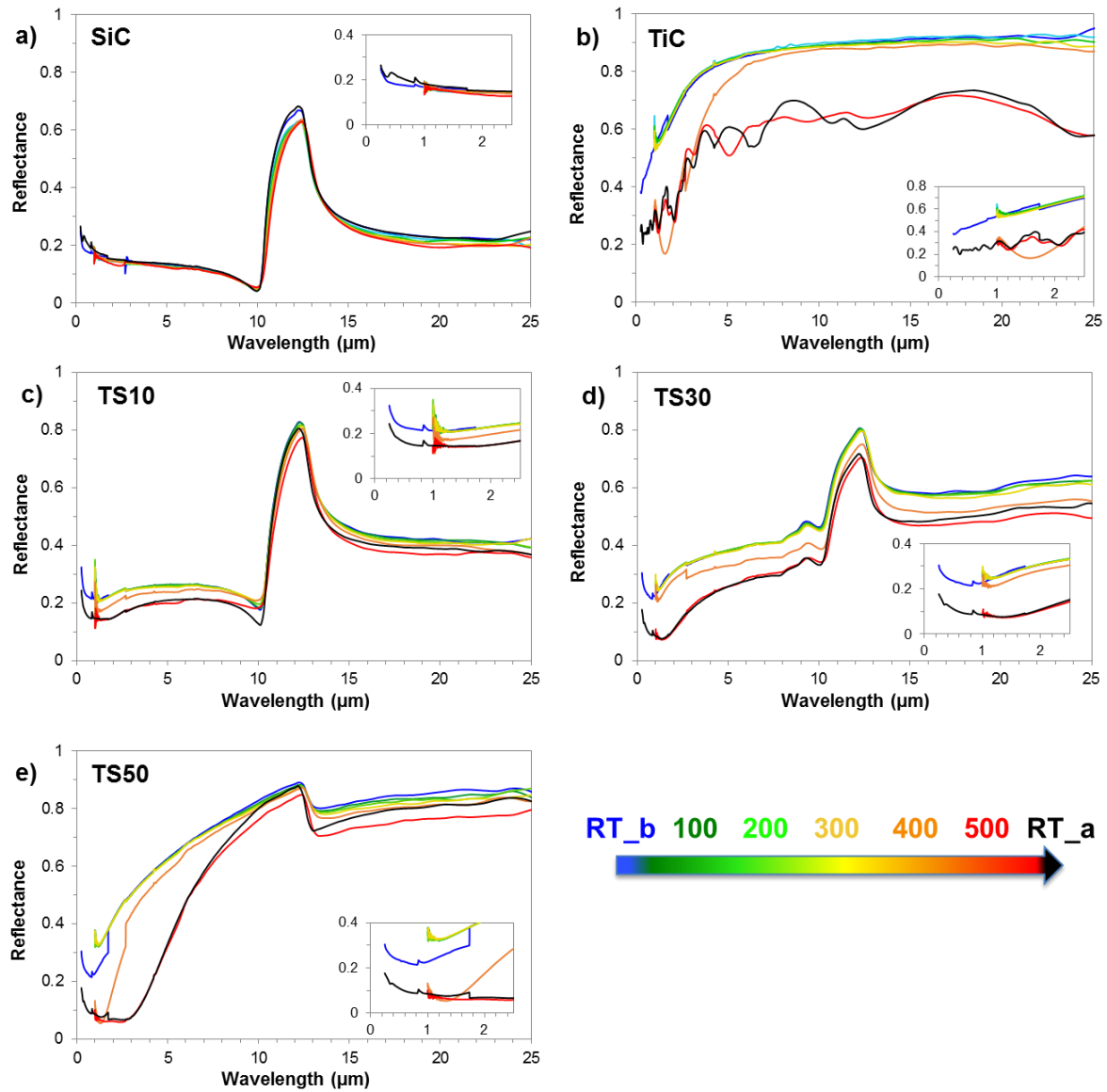
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194 **3.2. Materials characterization during and after heating**

195 Afterward, all samples were heated up to 500°C, to measure their total near normal spectral
196 reflectance (heating procedure described in Figure 1). The reflectance curves obtained at several
197 heating temperatures are reported in Figure 3, where (RT_b) and (RT_a) represent the room
198 temperature measurements recorded before, and after heating, respectively. For all samples,
199 and in the entire range of wavelengths, the reflectance decreases when increasing the
200 temperature. In the case of pure SiC, the reflectance curves before and after heating are almost
201 superimposable. On the contrary, for the TiC sample, the reflectance curve at 400 °C presents
202 a strong decrease in the wavelengths range below 10 μm . At 500 °C, this decrease in reflectance
203 goes on to the full range of wavelengths, and the reflectance curve presents oscillations. The
204 reflectance measured at room temperature after heating (RT_a) is very different from the one
205 measured before heating (RT_b), it is rather close to the one obtained at 500 °C, with even
206 stronger oscillations. In the case of TS10 and TS30 composites, heating induces a decrease in
207 reflectance but the shape of the curve is conserved. For the TS50 sample, the reflectance
208 strongly decreases, particularly in the 0.25 to 10 μm range of wavelengths.

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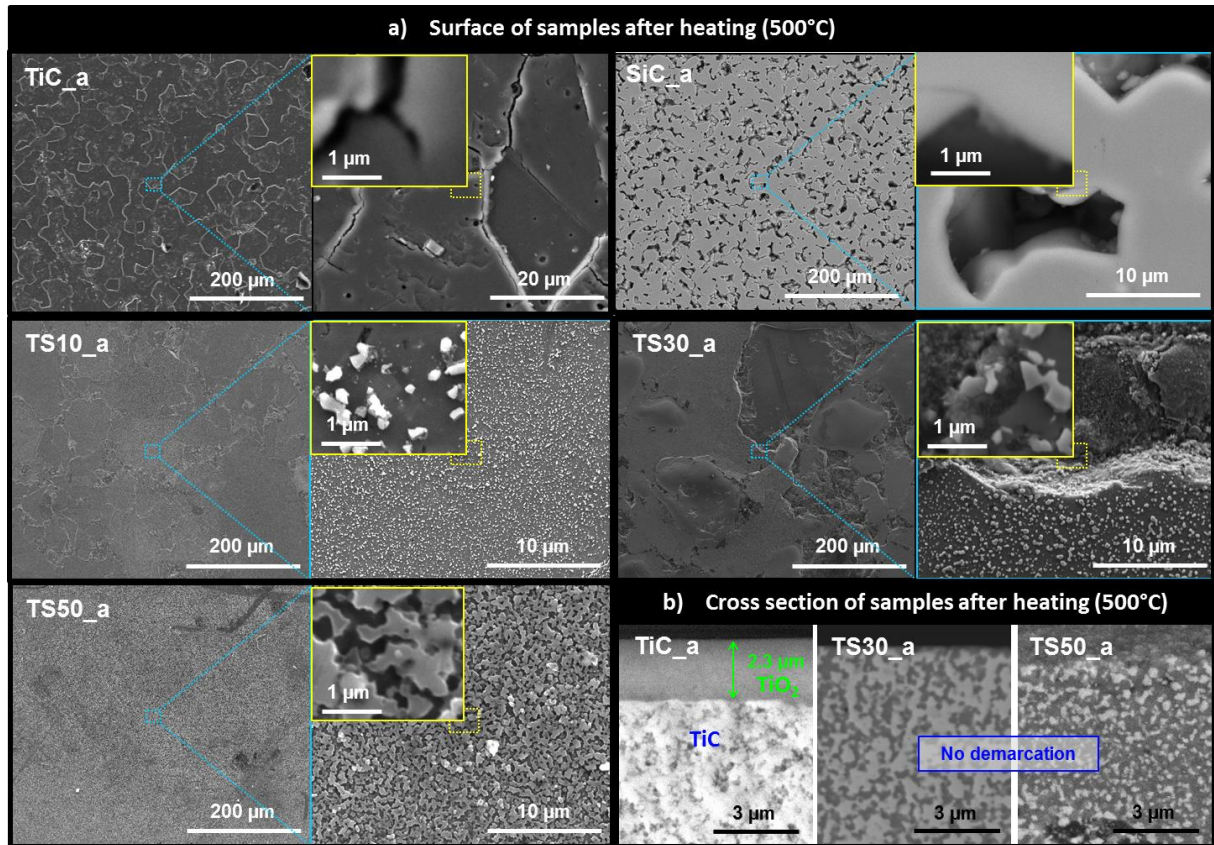


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 212 *Figure 3: Near normal spectral reflectance at various temperatures (°C) for a) pure SiC, b) pure TiC, c) TS10,*
 213 *d) TS30 and e) TS50.*

214
 215 Surface characterization after heating provided explanations for these evolutions. For all
 216 samples, the surface roughness has increased (from 4 to 38 for TS10, 10 to more than 550 nm
 217 for TS30, 3 to 47 nm for TS50, 24 to 40 nm for SiC and 8 to 47 nm for TiC), which is confirmed
 218 by SEM observations (Figure 4).

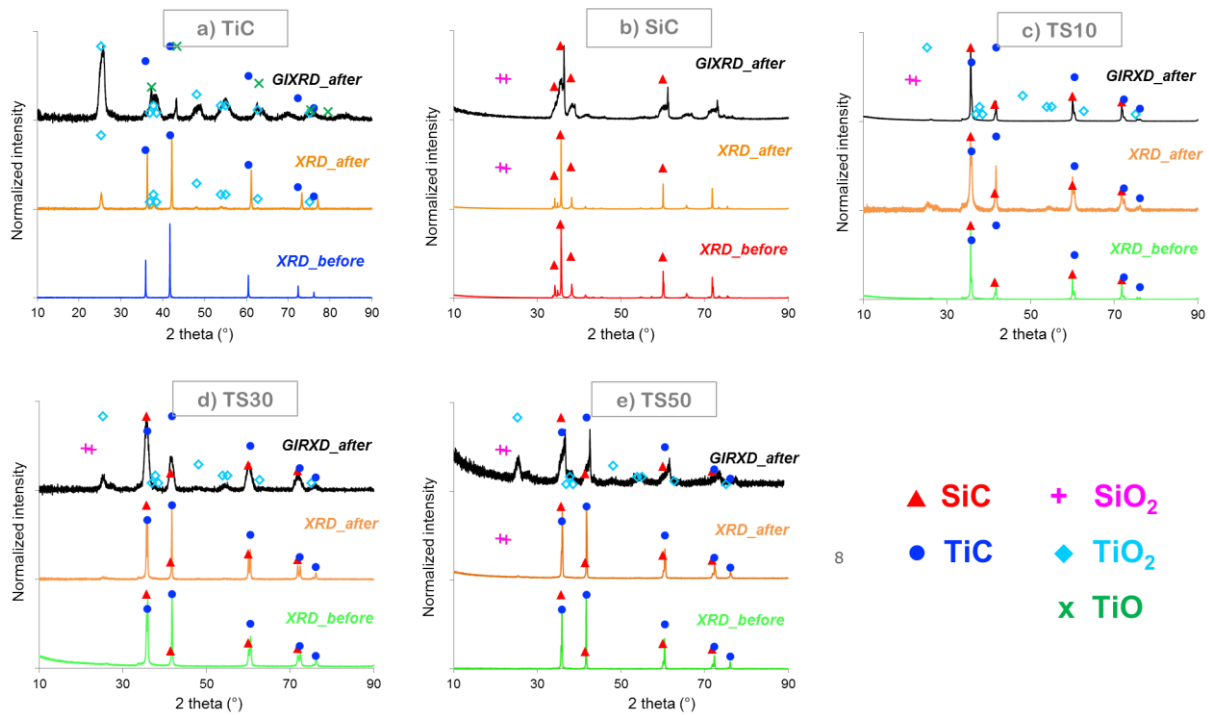
219 The surface of the pure SiC sample appears to be intact, while the presence of titanium oxides
 220 is detected on the surface of all other samples. During their oxidation TiC grains expand by
 221 volume gain and they emerge from the initially polished surface (Figure 4-a). To study the
 222 thickness of the oxidized layer, sample pieces were embedded in a resin and polished (Figure
 223 4-b). In the case of pure TiC sample, the surface is covered by a 2.3 μm thick crust of titanium

224 oxides with various morphologies. Underneath this zone, pristine TiC can be observed. In the
 225 case of the composites TS50 and TS30, the cross-section observations show no demarcation,
 226 indicating the presence of a significant layer of oxides on the surface of the sample. Only the
 227 TiC grains of the surface are oxidized, the SiC matrix seems to be intact.
 228



229
 230 *Figure 4: SEM observations after heating of a) surface of all samples and b) TiC, TS30 and TS50 in cross sections.*
 231 *The “_a” stands for “after heating”.*

232
 233 The oxidation of TiC is also evidenced by the presence of the characteristic peaks of TiO₂ in all
 234 samples (GIXRD and XRD, Figure 6). At the extreme surface of the pure TiC sample, the
 235 signature of TiO phase could be seen as well. In most cases, the SiO₂ peaks are absent,
 236 suggesting that SiC has not been oxidized, or that the resulting phase is not crystallized.
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Figure 5: Grazing Incident and classical X-rays diffractograms of the samples before and after heating at 500 °C of a) pure SiC, b) pure TiC, c) TS10, d) TS30 and e) TS50. The position of SiO₂ main peaks is given as an indication to show that this phase is not detected. The comparison between the X-rays diffractograms of all samples before heating is reported in SI 2.

244

3.3. Oxidation resistance

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In order to evaluate the oxidation resistance of the samples, thermogravimetric analyses (TGA) were performed at 1000 °C during 20 h under air on material pieces (Figure 6-a). The oxidation degree (%ox) was calculated considering the following oxidation reactions (4 and 5) [35, 47]. The mass variation due to carbon oxidation was neglected and the detailed calculation is reported in SI 4.

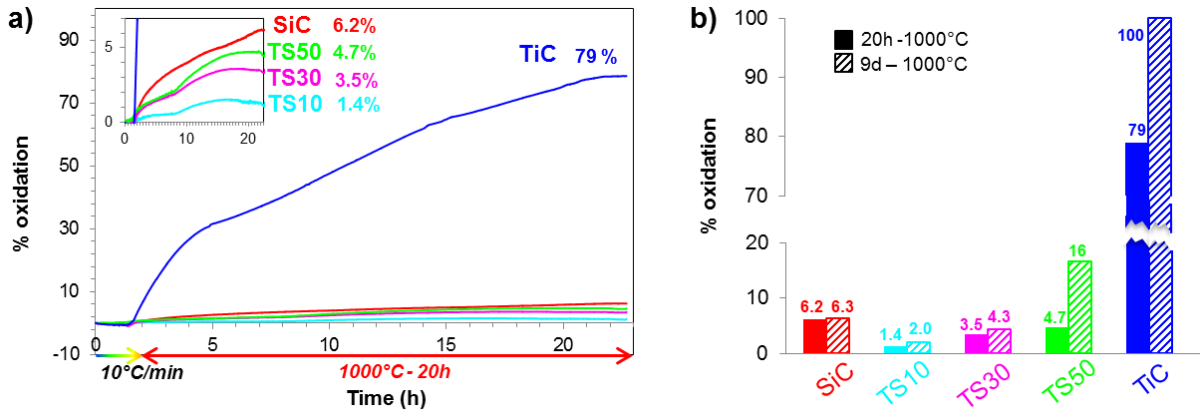
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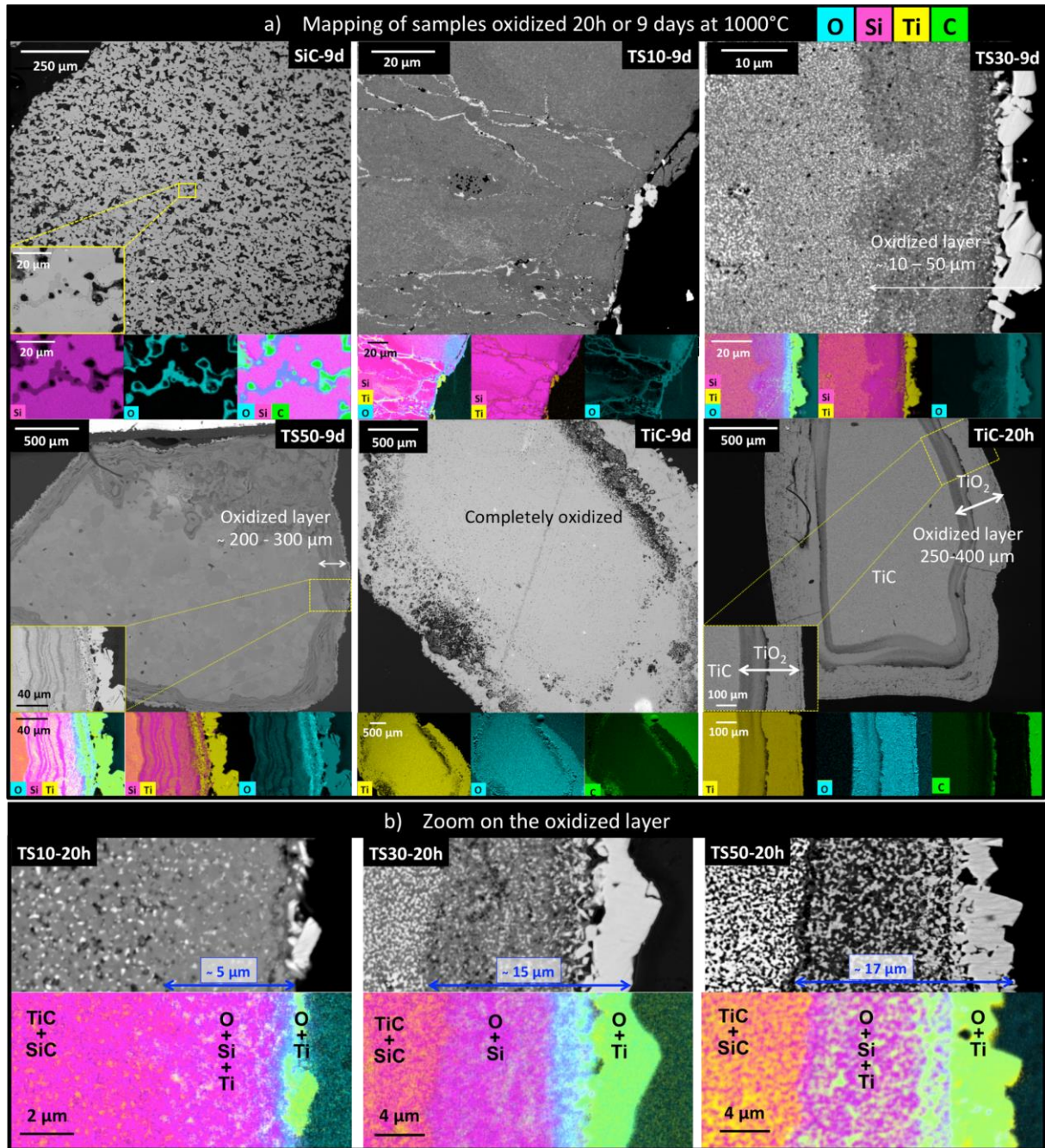
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After TGA analysis, the pure TiC sample is highly oxidized, up to 79 % while only 6.2 % of pure SiC is oxidized. The composites are less oxidized than the pure samples and their %ox increases with the TiC content. As pure SiC has a lower relative density than the other samples (74 % compared to > 90 %), the oxygen diffusion is favored which could induce the increase of the oxidation degree. Indeed, similar TGA measurements were conducted on TiC materials with various relative densities from a previous study [38]. The results reported in supporting information (SI 5) show that the weight gain increases when the relative density of the material decreases.

259 To evaluate the oxidation resistance of these samples over longer durations, sample pieces were
 260 exposed to air in a furnace at 1000 °C during 9 days. The oxidation percentage was evaluated
 261 by weighting measurements before and after oxidation (Figure 6-b). After their oxidation during
 262 20 h in the TGA apparatus and during 9 days in a furnace, the oxidized samples were embedded
 263 in a resin and polished to study their cross-sections by SEM-EDX. The most meaningful EDX
 264 mapping are reported in Figure 7-a) and the other ones are presented in SI 6.
 265



266
 267 *Figure 6: a) oxidation % as a function of time during TGA measurement (10 °C.min⁻¹ heating up to 1000 °C*
 268 *followed by a 20 h dwell at 1000 °C). b) Apparent oxidation percentage after 20 h and 9 days of oxidation under*
 269 *air at 1000 °C. The error is about 10⁻³% due to the precision of the weighting measurements.*
 270



272

273 *Figure 7: SEM-EDX mapping of polished cross sections of a) all samples after 9 days at 1000 °C, and pure TiC*274 *after 20h at 1000 °C. b) Zoom on the oxidized layer formed on TS10, TS30, and TS50 after 20h at 1000 °C.*

275

276 After 20h or 9 days at 1000 °C, the pure SiC sample presents oxidized areas covering the pore
 277 walls, even up into the center of the material (Figure 7-a). The thickness of this oxidized layer
 278 and the ox% are similar after 20 h and 9 days (Figure 6-b), which implies that the oxidation
 279 layer is protective. After 20 h at 1000 °C, the pure TiC sample presents an oxidized layer with
 280 a thickness of about 250-400 µm, surrounding the TiC pristine core. This layer is divided into

281 two sublayers, the outer tends to peel as evidenced by a C enrichment at the interface due to the
282 resin penetration. The inner layer is continuous but not protective since after 9 days at 1000 °C,
283 the sample is completely oxidized (Figure 6-b and Figure 7-a).

284 In the case of TS50 sample, after 20h the oxidation layer is continuous and much thinner than
285 that of the pure TiC (about 17 μm) (Figure 7-b and SI 6). After 9 days of oxidation, the layer
286 has grown to reach an average thickness of 200-300 μm, it presents several demarcations
287 oriented parallel to the surface. These demarcations are formed by areas depleted in Ti and O,
288 mainly composed by Si and C (SI 6). The apparent ox% is three times higher after 9 days than
289 after 20h. In the case of the TS30 sample, the oxidation layers are continuous and have close
290 thickness after 20 h or 9 days at 1000 °C (10-20 μm). The ox% has not evolved from 20 h to 9
291 days at 1000 °C.

292 The oxidation layer of TS10 sample is not continuous, some Ti-O containing aggregates are
293 present on the surface, and on the domain boundaries. These domains illustrate changes in
294 composition (Ti/Si proportion) and/or porosity in the direction of the sample thickness,
295 similarly to those observed in the direction of the sample diameter, and reported in Figure 2.
296 Depending on their composition and porosity, these domains can form oxidized pockets. After
297 9 days of oxidation, the apparent ox% has increased from 1.4 to 2 %. The oxidation layer after
298 20 h is about 5 μm thick.

299 For all nanocomposites, EDX mapping at high magnification are reported in Figure 7-b. The
300 oxidized layer can be divided into several sublayers with changes in composition. The outer
301 sub-layer is composed of Ti and O, without Si. The inner sub-layer is partly depleted in Ti, and
302 enriched in Si and O. As Underneath this oxidized layer, pristine SiC-TiC appears to be
303 undamaged.

304

305 **4. Discussion**

306 **4.1. Effects of the TiC proportion on the optical properties**

307 The expected TiC-SiC overall proportions have been confirmed by SEM-EDX and XRF. SEM
308 observations confirmed that the TiC grains have the same size in all samples but they tend to
309 form aggregates when increasing the TiC content (Figure 2).

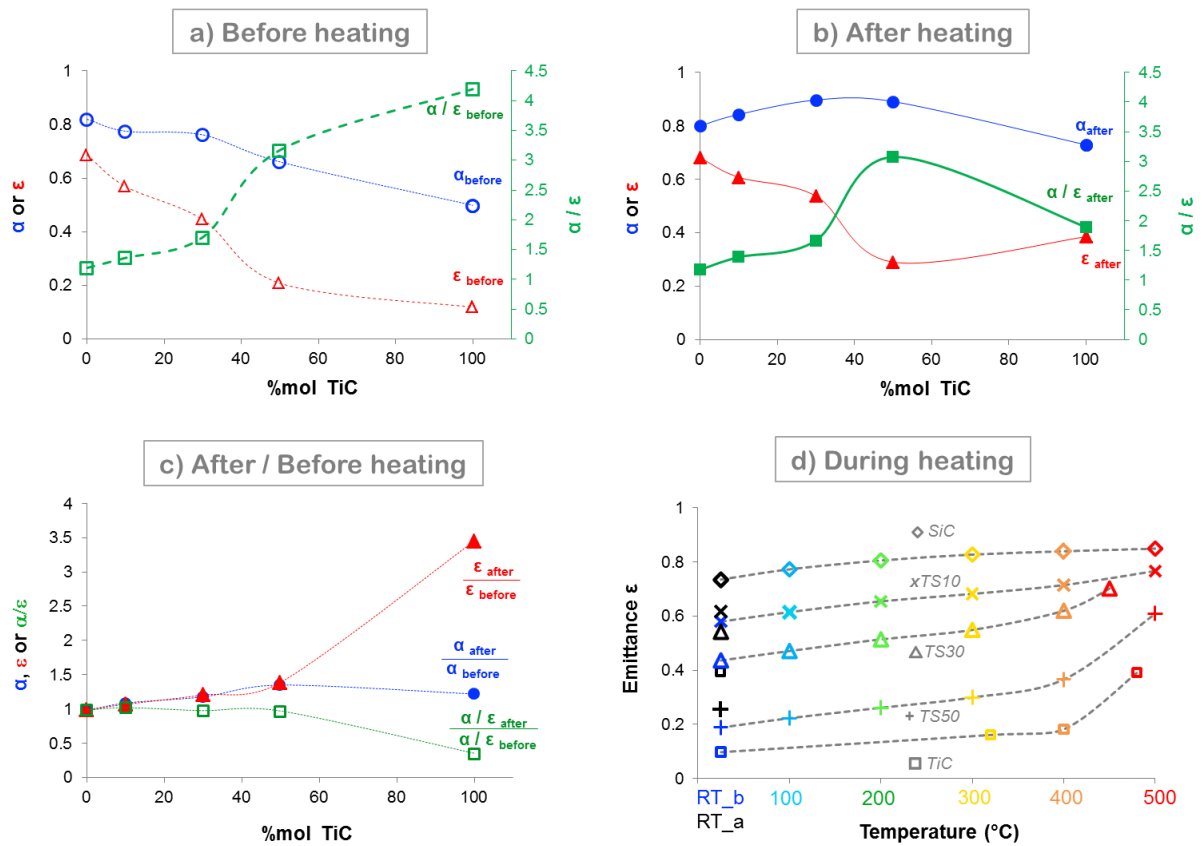
310 Before heating, the spectral reflectance at room temperature increases with the increase in the
311 TiC proportion in the entire range of analyzed wavelengths (Figure 3 and SI 3). From the
312 spectral reflectance curves measured at various incident angles, the total solar absorptance (α)
313 and the hemispherical thermal emittance (ϵ_H) were calculated using equations (1), (2) and (3).

314 The results are reported as a function of the TiC content in Figure 8-a. It appears that the
 315 increase in the TiC content induces a decrease in both the absorptance (α) and the hemispherical
 316 emittance (ϵ_H), leading to a great increase in the spectral selectivity (α/ϵ_H), as observed
 317 previously for TiC-SiC composites [38]. This increase is stronger between 30 % and 50 % of
 318 TiC than in the rest of the composition ranges.

319 During heating, the near-normal spectral IR reflectance has been measured at various
 320 temperatures (Figure 3) leading to the calculation of the total directional thermal emittance (ϵ_{8°),
 321 as reported in Figure 8-d). In all cases, the directional emittance increases with the heating
 322 temperature and the effect is higher when the TiC proportion increases. The increase in
 323 emittance with the measured temperature has already been reported for other borides and
 324 carbides [20, 48].

325 After heating and cooling, the increase in emittance is not conserved for the pure SiC sample
 326 since the hemispherical emittance values measured at room temperature before and after heating
 327 are the same (Figure 8-b). However, in the presence of TiC (pure TiC and composites), there is
 328 a difference between the absorptance and emittance values measured at room temperature
 329 before, and after heating (Figure 8-c).

330



331

332 *Figure 8: Absorptance (α), hemispherical emittance (ϵ_H) and selectivity (α/ϵ_H) calculated from room temperature*
333 *measurements a) before heating, b) after heating and c) the ratio between them, as a function of the TiC proportion*
334 *(%mol); d) directional emittance (ϵ_{θ}) as a function of the temperature of measurement.*

335

336 The hemispherical emittance after heating is a little higher than before heating for all the
337 nanocomposites and much higher for the pure TiC sample. After heating, the hemispherical
338 emittance is even higher for the pure TiC sample than for the TS50 nanocomposite (Figure 8-
339 b). For all samples except the pure SiC, the absorptance calculated from room temperature
340 measurements has increased after heating (Figure 8-c). The evolution of the absorptance after
341 heating as a function of the TiC content shows a bell shaped curve with a maximum for TS50
342 nanocomposite. As both the absorptance and the hemispherical emittance increase after heating,
343 the selectivity does not change for all samples, except the pure TiC. For the latter, the increase
344 in hemispherical emittance is too high to be compensated by the increase in absorptance, thus
345 the selectivity decreases. These changes on the optical properties can be linked to the surface
346 modifications observed by SEM (Figure 4). The TiC grains at the surface are oxidized, and the
347 presence of TiO₂ and TiO is detected by XRD and GIXRD (Figure 5). An increase in the surface
348 roughness is also reported, which could be linked to the volume gain due to the oxidation of
349 TiC into TiO₂, and to swelling due to carbon release. Previous work showed that the increase
350 in surface roughness induces an increase in both the absorptance and the emittance [38].

351

352 **4.2. Effects of the SiC content on the oxidation resistance**

353 The low relative density and high open porosity of pure SiC sample favored O penetration and
354 produced an oxidized layer on the pore walls, even up into the center of the sample. This
355 correlation between low relative density and high oxidation degree is confirmed by TGA
356 oxidation procedure applied to several TiC materials with various relative densities (SI 5).
357 However, the thickness of the oxidized layer and the %ox calculated from weight gain did not
358 increase between 20 h and 9 days. Therefore, the oxidation layer appears to be protective.
359 According to the literature, this layer could be SiO₂, as it was reported during the passive
360 oxidation of SiC at temperatures below 1400 °C [47, 49, 50]. For temperatures above 1400 °C,
361 SiC endures active oxidation releasing gaseous SiO.

362

363 Pure TiC sample is completely oxidized after 9 days at 1000 °C. The oxidation of TiC into TiO₂
364 and TiO has already been widely reported in the literature [35, 39, 51-53]. Depending on the

365 particle size, the temperature of oxidation of TiC can vary, nevertheless it starts around 380 °C,
366 and follows four stages [52]. First TiC is oxidized into oxycarbide $\text{TiC}_x\text{O}_{(1-x)}$, then it forms
367 suboxides (TiO , Ti_3O_5 or Ti_4O_9), followed by the formation of anatase (TiO_2), and finally it
368 evolves toward rutile (TiO_2). The oxidation layer is usually divided into two sub-layers; TiO_2
369 on top of sub-oxides like Ti_3O_5 , Ti_4O_7 . These two sub-layers are present on the pure TiC sample
370 oxidized after 20 h but not after 9 days. The oxidation kinetics of TiC depend on the diffusion
371 of O through the material, which explains the substoichiometry of the inner layer and the higher
372 oxidation degree for less dense samples [35, 54, 55]. After 9 days of oxidation, O has diffused
373 enough through the material to produce a single layer of TiO_2 .

374 In the case of the composites, the oxidation layer can be divided into two sub-layers. Ti is
375 concentrated at the surface, forming TiO_2 aggregates for the lowest Ti composition (TS10) and
376 a continuous layer of TiO_2 for richer ones (TS30 and TS50). Underneath, the inner layer is
377 highly depleted in Ti, which means that Ti has diffused somehow toward the surface during the
378 oxidation. The inner Si, O rich layer could be SiO_2 . This layer appears to form a continuous
379 and protective barrier for samples with enough Si (TS10 and TS30) but not for the composition
380 with lower Si content (TS50). These results are consistent with the oxidation study of TiC/SiC
381 composites by Banu et al. [39]. They observed embedded TiC particles in a SiC matrix, with
382 the presence of SiO_2 and TiO_2 after the oxidation at 750 °C under static air. Furthermore, Baux
383 *et al.* synthesized porous TiC-SiC ceramics by Chemical Vapor Infiltration (CVI) of SiC into
384 cellular TiC structures [56]. After 10 hours of oxidation at 1000 °C, TiC was oxidized into TiO_2
385 and suboxides in the core of the sample, whereas TiC parts located near the surface were
386 protected from oxidation by a layer of SiC. They concluded that this difference was due to the
387 inhomogenous penetration of SiC deposited by CVI. However, they did not report the oxidation
388 of SiC into SiO_2 nor the presence of any Ti-depleted layer underneath. To our knowledge, the
389 formation at 1000 °C of a SiO_2 layer underneath a TiO_2 crust has not been reported in the
390 literature. Therefore, ongoing work is conducted to study in more detail the processes involved
391 in the formation of these sub-layers during TiC-SiC composite oxidation.

392 **4.3. Comparison with other materials**

393 The literature reports several studies concerning the optical properties of UHTCs and especially
394 of borides and carbides. Our pure TiC sample, with a spectral selectivity of 5.0, approaches the
395 best one reported so far: dense LaB_2 ($\alpha/\varepsilon = 6.4$ [57]). The spectral selectivity of TS30 and TS50
396 composites (1.7 and 3.2) are superior to pure SiC (1-1.1 [58] and this study). They are in the
397 same range as MoSi_2 added carbides (2.2 for HfC, 2.4 for ZrC, and 2.8 for TaC [59]), pure

398 borides (2.5 for HfB_2 , 3.9 for ZrB_2 and 4.0 for TaB_2 [22, 58], 2.2 for TiB_2 [60]), and composites
399 (2.2 for HfB_2 -SiC and 2.8 for HfB_2 -HfC-SiC [61]). This comparison is given as an indication
400 since the spectral selectivity values originate from emittance measurements at different
401 temperatures. Indeed, it has been reported that the emittance measured at room temperature is
402 usually underestimated compared to the one measured at higher temperatures [12], thereby
403 impacting the spectral selectivity. However, in all cases, the samples did not experienced
404 oxidation since measurements were conducted at room temperature or at high temperature
405 measurements under vacuum or inert atmosphere.

406 The optical properties of UHTCs after exposition to oxidation are little studied so far. TaB_2
407 submitted to helium or air atmosphere during 20 min at 827 °C loses completely its spectral
408 selectivity [62], the spectral selectivity of $\text{ZrB}_2 + 10\% \text{ MoSi}_2$ decreases toward 1, and reaches
409 the one of pure SiC after heating up to 1200 °C [63]. The results obtained for HfB_2 -SiC
410 composite are better since the spectral selectivity after oxidation at 927°C during 5h is still of
411 1.3 (compared to 2.2 before oxidation) and the addition of HfC in this HfB_2 -SiC composite did
412 not improve the results ($\alpha/\varepsilon = 0.6$ after oxidation), probably because the amount of SiC was too
413 low [61]. In this context, our TiC-SiC composites are quite performant since TS30 and TS50
414 samples have a spectral selectivity of 1.7 and 3.1 after oxidation at 500°C. Even though these
415 values were obtained at lower temperatures, the oxidation tests at 1000 °C revealed the
416 formation of a protective SiO_2 layer which suggests that the TiC-SiC composites could keep
417 their interesting spectral selectivity at high temperatures.

418

419 **Conclusion**

420 This study assessed both the optical properties and the oxidation resistance of SiC-TiC
421 nanocomposite densified materials while heating up to 500 °C. The effects of the TiC
422 proportion (10 to 50 %at) were studied and compared to pure TiC and SiC samples. The spectral
423 selectivity was found to increase with the TiC content due to a high decrease in emittance and
424 despite a low decrease in absorptance. The samples were heated up to 500 °C to measure the
425 reflectance in the 1.25 to 25 μm wavelength range, and determine their optical properties at
426 various temperatures. The emittance increases with the heating temperature. After heating, the
427 pure SiC sample remains unoxidized, without any changes in its optical properties, while pure
428 TiC sample experiences severe oxidation and high decrease in its spectral selectivity. The
429 composites are also partly oxidized, and more severely as the TiC content increased. The
430 oxidation of TiC grains TiO_2 , leads to an increase in the surface roughness which induces an

431 increase in both the emittance and the absorptance. Contrary to the pure TiC sample, for the
432 composites, the increase in emittance is compensated by the increase in the absorptance.
433 Therefore, the selectivity of the composites remains the same after exposure to air at 500 °C.
434 Oxidation tests at 1000 °C during 20 h and 9 days confirmed the dramatic TiC sensitivity to
435 oxidation and the good oxidation resistance of SiC. The TiC-SiC composites form an oxidized
436 layer mainly composed of a TiO₂ outer sub-layer and a SiO₂ inner sub-layer. The latter appears
437 to be protective when the Si content is high enough (70 at% at least). According to all these
438 results, the 30 % TiC – 70 % SiC composite seems to display both high spectral selectivity and
439 satisfactory oxidation resistance, which are required properties for solar absorber applications.

440

441 **Conflicts of interest**

442 There are no conflicts to declare.

443

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452

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- 605
- 606

607

Supporting information

608

SI 1: Synthesis route and material characterization devices and conditions

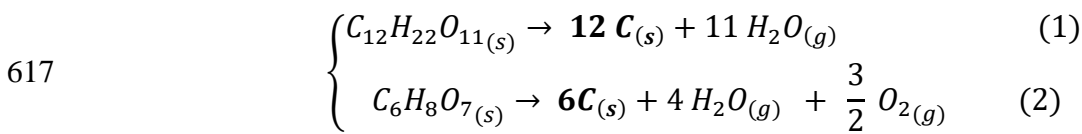
609

Synthesis

610 The nanocomposites were prepared using a semi-molecular route involving hydrolysis and
 611 polycondensation of alkoxides as metal oxide precursors and sucrose as carbon source. The
 612 resulting powders were subjected to two heat treatments to decompose the sucrose and citric
 613 acid into carbon (800 °C Equations 1 and 2) and then for the carbothermal reduction of oxides
 614 into carbide (1550 °C Equation 3).

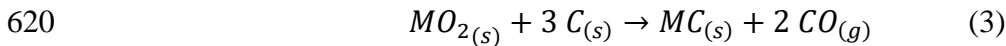
615

616 **Sucrose and citric acid decomposition - $T = 800\text{ °C}$**



618

619 **Carbothermal reduction - $T = 1550\text{ °C}$**



$$621 \quad R = \frac{12 \cdot n_{C_{12}H_{22}O_{11}}}{3 \cdot n_{MO_2}} + \frac{6 \cdot n_{C_6H_8O_7}}{3 \cdot n_{MO_2}} \quad (4) \quad F = \frac{n_{Ti}}{n_{Ti} + n_{Si}} = \frac{n_{TTIP}}{n_{TTIP} + n_{TEOS}} \quad (5)$$

622

623 The ratio R (Equation 4) quantifies the carbon content resulting from the decomposition of
 624 sucrose and citric acid according to the Equations (1) and (2). Because the decomposition of
 625 sucrose and citric acid produces not only effective carbon but also carbon gaseous species, the
 626 amount of carbon available for the carbothermal reduction is not easily predictable and varies
 627 depending on the conditions. The value of the R ratio leading to a stoichiometric carbothermal
 628 reaction is empirical. The values of R ratio are deduced according to preliminary studies [64].
 629 The relative proportions of Si and Ti in the final composite were controlled by the F ratio,
 630 defined by Equation 5. The amounts of TEOS and TTIP used in the synthesis were adapted to
 631 produce composites with increasing F ratios as described in Table 1. For the pure TiC and pure
 632 SiC references, commercial products supplied by Sigma Aldrich were used with a purity of 98
 633 % and 97.5 %, respectively.

634

Sample	TS10	TS30	TS50	TiC	SiC
R	1.68	2.39	3.18	Commercial products	
F (%at)	10	30	50	100	0
F* (%wt)	14,3	39	60	100	0
T_{sintering} (°C)	1750			1700	1950

635

Table 3: Name, R and F ratios and sintering temperature for each sample used in this study.

636 Porosity, density and roughness

637 Archimedes method was used to measure the apparent density ($\rho_{app.}$) of the sample by
638 hydrostatic weighing in water at 21 °C. The pycnometric density ($\rho_{pycno.}$) of each sample was
639 determined by helium pycnometry. The theoretical density ($\rho_{th.}$) was calculated based on the
640 average Ti / Si proportion measured by SEM-EDX and XRF analyses, and the C and O content
641 measured by elemental analyses. The relative density (D), the open and closed porosity (ϕ_{open}
642 and ϕ_{closed}) were estimated according to Equations 6, 7 and 8, respectively.

643
$$D = \frac{\rho_{app.}}{\rho_{th.}} \quad (6) \quad \phi_{open} = 1 - \frac{\rho_{app.}}{\rho_{pycno.}} \quad (7) \quad \phi_{closed} = \frac{\rho_{app.}}{\rho_{pycno.}} - \frac{\rho_{app.}}{\rho_{th.}} \quad (8)$$

644 Optical interferometry was used to measure the surface roughness Ra of the samples (Fogal
645 Nanotech – Microsurf 3D). For each sample, at least six areas of 287 μm x 481 μm , were
646 analyzed to obtain an average roughness value.

647 Morphology and composition

648 The morphology of the samples was studied by Scanning Electron Microscopy (SEM), with an
649 FEI Quanta 200 ESEM equipped with a Field Emission Gun, and with a Tescan VEGA3
650 equipped with a W thermo-cationic gun. Energy Dispersive Spectra (EDX) were recorded using
651 a Bruker SDD 5030 detector with a 123 eV resolution at the Mn ($K\alpha$) line. EDX was used to
652 confirm the composition of the synthesized products and to study the effects of oxidation.

653 The global Ti/Si proportion was also analyzed by X-Ray Fluorescence (XRF), using a Spectro-
654 Xepos apparatus with four secondary targets (Mo, Al_2O_3 , Co and HOPG Bragg crystal).

655 Carbon and Oxygen analyzers (LECO CS230 and TCH600) were used to measure the total
656 carbon and oxygen contents, respectively. The samples were heated under oxygen for carbon
657 analysis, or with graphite addition under helium gas for oxygen analysis. In both cases, the
658 formation of carbon oxides was detected and quantified by infrared spectroscopy, then related
659 to the total carbon or oxygen content in the samples. Added Fe powder was used to assist the
660 combustion in the case of carbon analysis.

661 Thermogravimetric analyses (Setsys - 1750 CS Evol, Setaram) were conducted to evaluate the
662 oxidation resistance of the samples. Sample pieces weighting about 20 mg were subjected to a
663 20 h dwell at 1000 °C. The heating rates of rise and cooling were 10 °C.min⁻¹ and 30 °C.min⁻¹,
664 respectively.

665 Structure

666 The samples were characterized by X-Ray Diffraction (XRD) using the Bruker D8 advance
667 diffractometer equipped with lynxeye detector and using Cu K α radiation ($\lambda=1.54184\text{\AA}$). Data
668 were acquired in reflection geometry (parallel beam) in the 10-90° (2 θ mode) range of angles
669 with steps of 0.019°. Silicon powder was collected and used as standard to evaluate the
670 instrumental function. TiC compound crystallized in the cubic NaCl structure type in the Fm-
671 3m space group, whereas SiC crystallized in the ZnS structure type in the F-43m space group.
672 Grazing Incident X-Ray Diffraction (GI-XRD) measurements were performed using a Bruker
673 D8 Advance diffractometer and primary optics adopting the Bragg – Brentano geometry.
674 Secondary optics were composed of long Sollers slits of 0.12° and of a point detector. GI-XRD
675 patterns were collected between 10° and 90° (2 θ mode) with a 0.02° step. The angular domain
676 was limited at higher angles by the beam knife-edge that equipped the reflectivity stage. The
677 incident angle, θ_i , was fixed to a value of 0.4°.

678 Optical properties

679 Two spectrophotometers were used to measure the total spectral reflectance of the samples.
680 Over the wavelength range from 0.25 to 2 μm , the near-normal hemispherical ($R^{\perp\circ}$) reflection
681 spectrum was acquired with a 10 nm step using a Perkin Elmer Lambda 950 spectrophotometer.
682 This apparatus was equipped with deuterium and tungsten lamps, PMT and InGaAs detectors,
683 and a 150 mm integrating sphere coated with Spectralon diffuse reflective coating. The sample
684 was illuminated at an incidence angle of 8°.

685 Over the wavelength range from 1.25 μm to 25 μm , the hemispherical directional reflectance (
686 $R^{\circ,\theta}$) was recorded at different detection angles θ from 8 to 80°, using a SOC-100 HDR
687 reflectometer (Surface Optics Corporation) coupled with a Nicolet FTIR 6700
688 spectrophotometer. A gold coated calibrated specular reflectance standard was used as
689 reference during measurements (NIST calibration). The spectral range from 1.25 to 25 μm was
690 covered by a FTIR equipped with InGaAs and DTGS/KBr detectors, coupled with Quartz and
691 KBr beamsplitters, respectively. The sample was illuminated from all directions using a 700 °C
692 (973 K) blackbody as the infrared source and a 2π imaging gold coated hemiellipsoid. The light
693 reflected by the sample at a chosen detection angle was collected by a moveable overhead
694 mirror which directed the collimated beam into the FTIR apparatus for signal treatment to
695 retrieve the reflectance spectrum. Each reflectance spectrum was derived from 64 consecutive
696 scans on the same sample. A heating plate on the sample holder enabled measurements at

697 different temperatures (from room temperature to 500 °C). The temperature of the sample was
 698 controlled by a surface thermocouple connected to PID regulation of the heating resistance. The
 699 complete description of the devices used is detailed in [43, 44].

700

701 The total spectral reflectance measured and the solar spectrum were interpolated over the
 702 wavelength range from 0.25 to 25 μm with a step of 2 nm to calculate the optical parameters,
 703 using Mathematica software. The solar absorptance α was calculated from room temperature
 704 measurements in the wavelength range 0.25 to 4 μm according to Equation 9. The near-normal
 705 thermal emittance $\varepsilon_s(T)$ and the hemispherical emittance $\varepsilon_H(T_a)$ at room temperature were
 706 calculated in the wavelength range from 1.25 to 25 μm according to Equations 10 and 11
 707 respectively. The hemispherical emittance represents the propensity of a surface illuminated
 708 from all directions of the hemisphere surrounding it to reemit radiation in the same hemisphere.
 709 Spectral transmittance was not measured, as the samples were opaque over the whole
 710 considered spectral range.

711

$$712 \quad \alpha = \frac{\int_{0.25 \mu\text{m}}^4 \mu\text{m} [1 - R_{8^\circ}(\lambda, T_a)] \cdot G(\lambda) \cdot d\lambda}{\int_{0.25 \mu\text{m}}^4 \mu\text{m} G(\lambda) \cdot d\lambda} \quad (9) \quad \varepsilon_\theta(\theta, T) = \frac{\int_{1.25 \mu\text{m}}^{25 \mu\text{m}} [1 - R(\lambda, T, \theta)] \cdot P(\lambda, T) \cdot d\lambda}{\int_{1.25 \mu\text{m}}^{25 \mu\text{m}} P(\lambda, T) \cdot d\lambda} \quad (10)$$

$$713 \quad \varepsilon_H(T_a) = 2 \int_0^{\pi/2} \varepsilon_\theta(\theta, T_a) \cdot \sin \theta \cdot \cos \theta \cdot d\theta \quad (11)$$

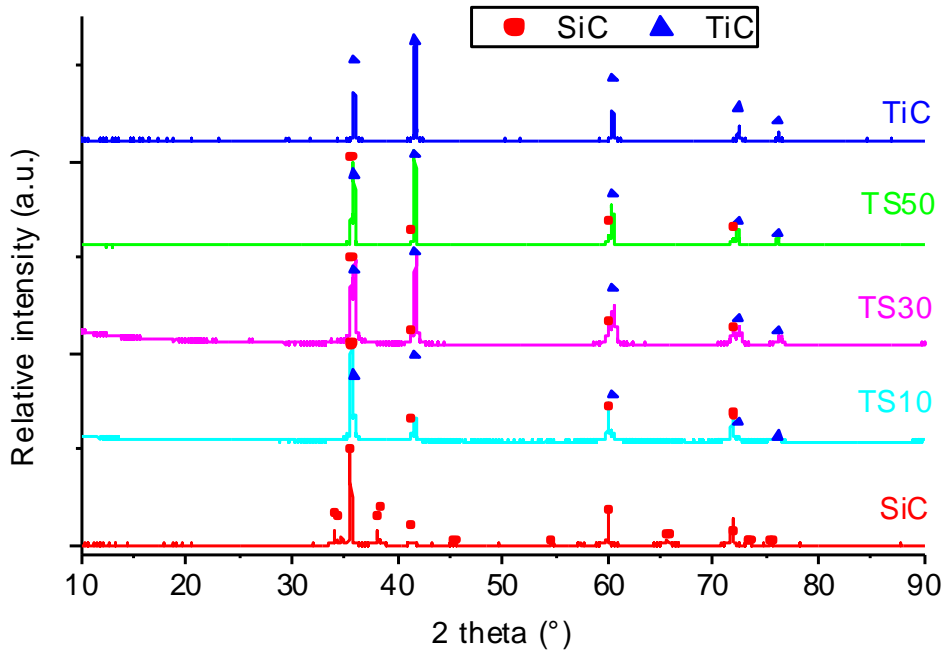
714 λ is the wavelength [μm]. $R_{8^\circ}(\lambda, T)$ and $R(\lambda, T_a, \theta)$ are the spectral reflectance of the sample
 715 measured at various temperatures (T) and a detection angle of 8°, or at room temperature (T_a)
 716 with a variable detection angle θ . $G(\lambda)$ is the standard solar irradiance spectrum (ASTM-G173
 717 AM1.5 direct + circumsolar) [W.m⁻².μm]. $P(\lambda, T)$ is the spectral emittance (exitance) of a
 718 blackbody at temperature T derived from Planck's law [W.m⁻².μm].

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SI 2: X-ray diffractograms before heating



722

723

Figure 9: a) XRD diffractograms for all samples measured at room temperature before heating.

724

725

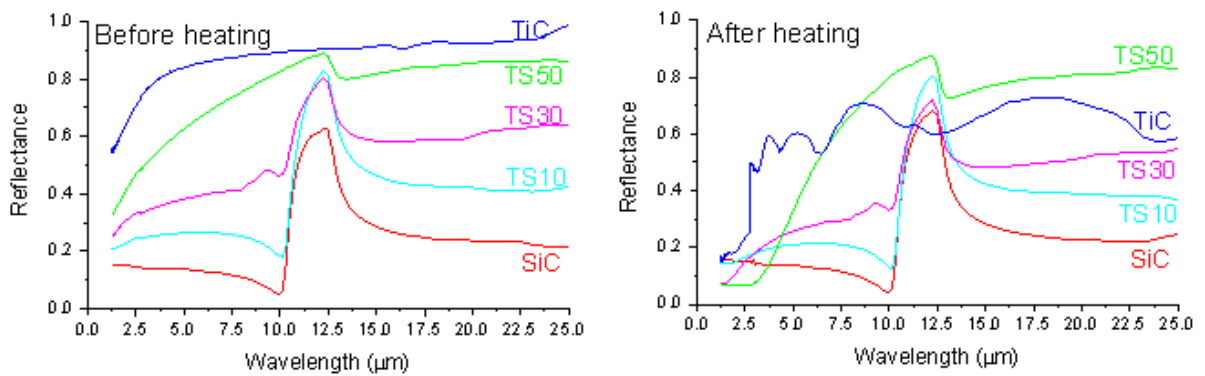
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SI 3: Reflectance curves

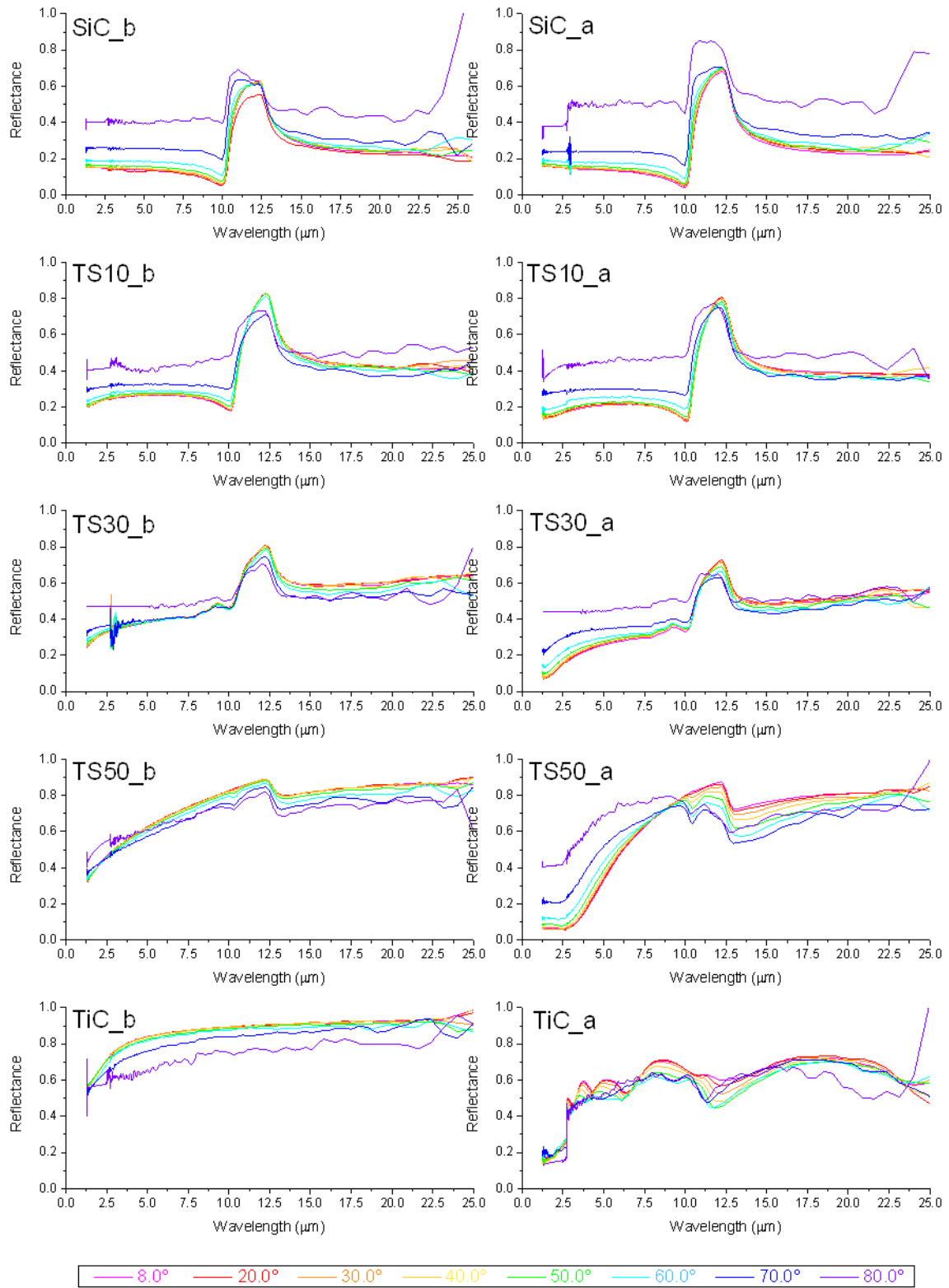


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731

Figure 10: Total near normal spectral reflectance for all samples measured with an incident angle of 8°, at room temperature before heating (left column) and after heating (right column).

732



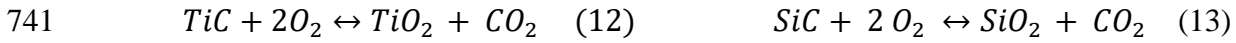
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734
735

Figure 11: Total near normal spectral reflectance for all samples measured with various detection angles at room temperature before heating (left column) and after heating (right column).

736

SI 4: Oxidation percentage calculation

737 From the TGA results, the relative mass gain $(\Delta m/m)_{exp}$ was calculated. According to the TiC
 738 and SiC oxidation reactions 12 and 13, if TiC and SiC are completely oxidized into TiO₂ and
 739 SiO₂, the maximum relative mass gain $(\Delta m/m)_{max}$ would be described by Equation 14. In this
 740 calculation, the mass variation due to carbon oxidation is neglected.



742
$$\left(\frac{\Delta m}{m}\right)_{max} = \frac{M_{oxides}}{M_{carbides}} - 1 = \frac{F \times M_{TiO_2} + (1 - F) \times M_{SiO_2}}{F \times M_{TiC} + (1 - F) \times M_{SiC}} - 1$$
 (14)

743

744 with F the TiC molar fraction (%mol) and M the molar mass (g.mol⁻¹). The maximum relative
 745 mass gain is 50 % for pure SiC, 47.6 % for TS10, 43.5 % for TS30, 40.0 % for TS50 and 33.3
 746 % for pure TiC. The oxidation percentage (%ox) is the ratio between the experimental relative
 747 mass gain and the maximum relative mass gain, as described by Equation 15:

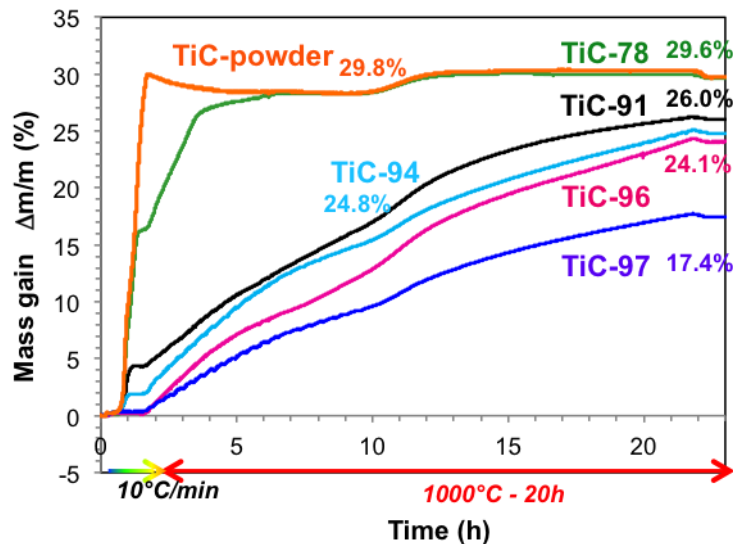
748
$$\%ox = \frac{\left(\frac{\Delta m}{m}\right)_{exp}}{\left(\frac{\Delta m}{m}\right)_{max}} \times 100$$
 (15)

749

750

751

SI 5: TG analyses of TiC samples with various densities



752

753 Figure 12: Evolution of the weight gain as a function of time during TGA measurement (10 °C.min⁻¹ rise up to
 754 1000 °C followed by a 20 h dwell at 1000 °C) for TiC samples with a relative density of 97 %, 96 %, 94 %, 91 %, 78 %
 755 and powder.

SI 6: EDX-mapping after 20 h or 9 days of oxidation at 1000°C under air.

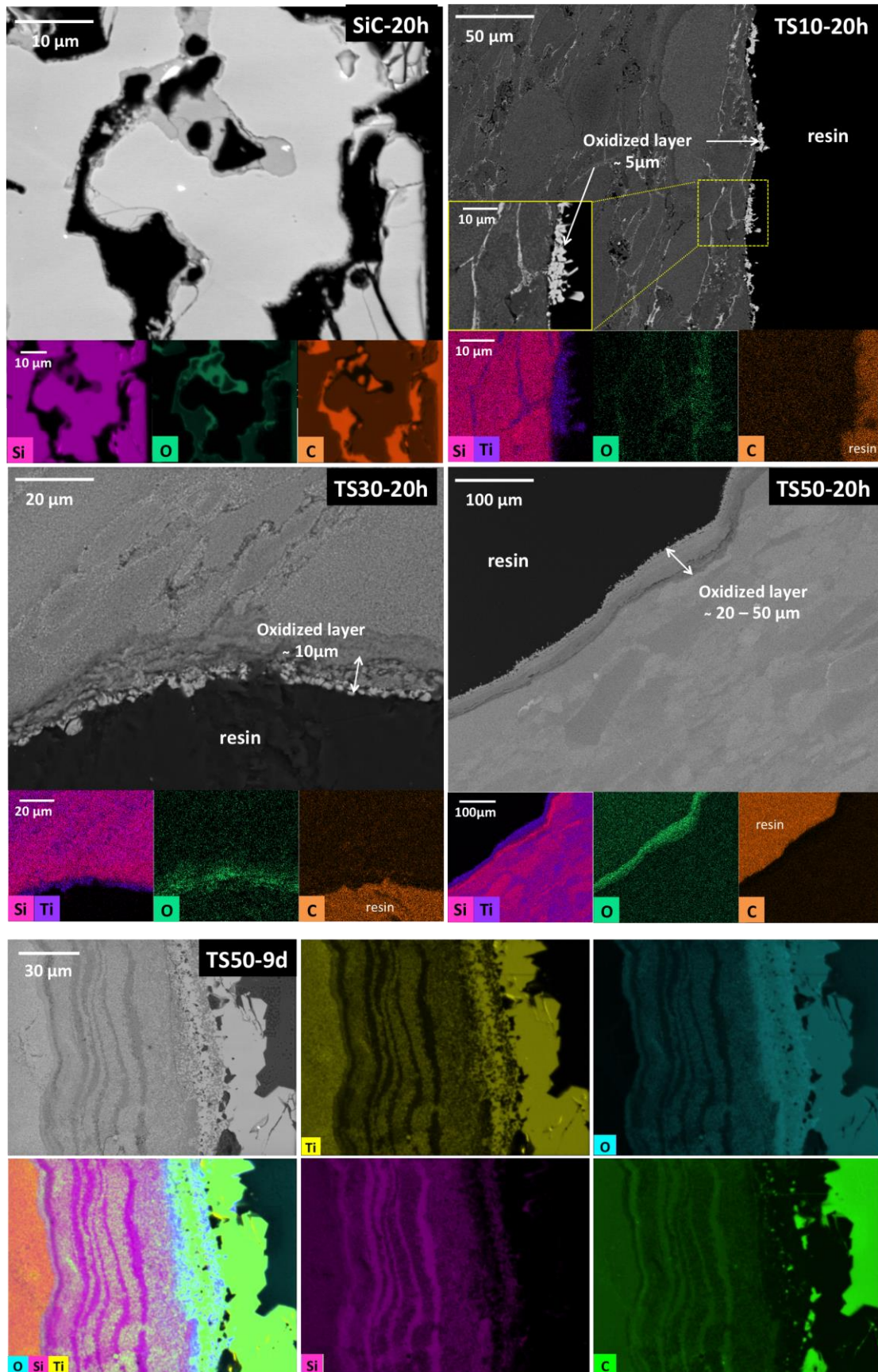


Figure 13: SEM-EDX mapping of the samples oxidized 20 h or 9 days at 1000°C under air.