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# Graphite-Si-SiC ceramics produced by microwave assisted reactive melt infiltration.

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## Abstract

A novel microstructure of graphite-Si-SiC ceramics was successfully prepared by liquid silicon infiltration of graphite-based preforms; instead of using conventional methods, the reactive infiltration process was assisted by microwaves. The effects of microwave power variation on the microstructure and the mechanical properties of infiltrated materials were studied. X-ray diffraction and Raman investigations showed the presence of both unreacted graphite and Si in addition to SiC formed at their interface. The graphitic and silicon phases were separated by a SiC network, which results more homogeneous as microwave power was increased. The amount of SiC was found to be higher in function of the growing power level; a higher conversion of graphite into SiC yielded a more dense material. The bending strength measurements confirm this, showing higher values for the samples processed using a power level of 75% of the full power compared to those obtained with 30% and 60%.

## Keywords

Reactive melt infiltration; Microwave; Graphite-based preforms; SiC; Raman spectroscopy

## 1. Introduction

Reactive melt infiltration (RMI) through a porous matrix is an alternative way to produce intermetallic, ceramic, and composite materials [1–4]. In comparison to other composite processing methods, RMI provides significant advantages such as short processing times and much lower operating temperatures with respect to the melting temperatures of produced materials. Nelson et al.[5] reported in fact that chemical vapour infiltration requires days or weeks to complete the conversion process, while RMI requires only minutes or hours to obtain

1 the final product from chemical reaction between the infiltrant and the preform. Margiotta et al.  
2 [6] obtained dense SiC carrying out the liquid silicon infiltration of carbon preforms at 1800 °C  
3 for 120 minutes; the temperature resulted much lower compared to both the melting point of  
4 SiC (2730 °C) and the temperature generally required for SiC sintering. Moreover, the  
5 materials produced by RMI show thermal properties comparable to those obtained by standard  
6 processes. Wang et al.[7] prepared ZrB<sub>2</sub>-SiC protective lamina to be used as coating on  
7 carbon/carbon composites combining pressing and Reactive Silicon Infiltration (RSI). It  
8 successfully avoids the oxygen penetration in the inner part of material thanks to the formation  
9 of a surface oxide layer. The composition of it is similar to that observed for ZrB<sub>2</sub>-SiC coating  
10 processed by CVD [8]. The processing of ZrB<sub>2</sub>-SiC coating by RSI represents a promising  
11 alternative to generally used CVD films, which show similar ablation resistance, but require  
12 long and high-cost processing methods. Moreover, Bianchi et al.[9] reported that the RSI  
13 process yields Si-SiC foam bodies showing high thermal shock resistance, comparable to that  
14 of similar foam produced by more conventional sponge replica techniques [10]. The economic  
15 advantages in term of energy and time saving make the RMI process attractive for many  
16 industrial applications such as aerospace, energy, automotive, biomedical and electronics  
17 [9,11–13].

18 Si-SiC ceramics obtained by reactive infiltration of liquid silicon into carbonaceous preforms  
19 have been widely investigated since the 70s [14]. The process is based on the exothermic  
20 chemical reaction between a porous carbon preform and molten silicon. It shows some  
21 advantages with respect to the more traditional processing methods for obtaining silicon  
22 carbide: RMI does not require the use of any sintering aids, which are instead necessary by  
23 using hot pressing and pressureless sintering [15,16].

24 RMI process is organized in three steps: (i) the manufacture of carbon/phenolic green bodies  
25 followed by pyrolysis, (ii) infiltration of the bodies by molten silicon and (iii) the exothermic  
26 chemical reaction between the liquid silicon and the solid carbon, which leads the formation of  
27 a SiC matrix:



29 The manufacture of the preforms is the first key factor that has a great influence on the  
30 properties of the final ceramic. The various carbon sources and the effects of their morphology,  
31 micrometer-scale porosity and chemical reactivity on the process have been widely investigated  
32 in the literature, as detailed [below](#).

1 According to Margiotta et al. [6], when the starting material is in powder form, the chemical  
2 reactivity of solid carbon with molten silicon is strongly dependent on both the atomic ordering  
3 and the porosity at atomic-scale level. In fact, a decrease of carbon atomic ordering and a  
4 consequent increase of porosity at atomic level should promote the development of new “active  
5 sites” favouring the reaction of carbon with molten Si.

6 Wang et al. [18] prepared glassy carbon preforms starting from a mixture of furfuryl resin and  
7 alcohol, diethyleneglycol, triethyleneglycol, water and paratoluene sulfonic acid. These  
8 components were then subjected to polymerization and pyrolysis at 700 °C. The use of glassy  
9 carbon allows control of the size and the distribution of the pores in order to maximize the  
10 infiltration process; on the other hand, with its relative high density, glassy carbon shows low  
11 reactivity toward liquid silicon and therefore it cannot be considered an ideal substrate for the  
12 liquid infiltration process [6]. The reaction between liquid silicon and glassy carbon leads to the  
13 nucleation of SiC crystals and the formation of a thin layer at their interface; it acts as a  
14 diffusion barrier preventing further reaction. The formation of silicon carbide may then proceed  
15 through slow a diffusion process or it can even be interrupted [19].

16 Many studies are based on the use of cellulosic precursors, [6,20,21] which show a higher  
17 chemical reactivity with silicon compared to that observed for glassy carbon; for these starting  
18 polymeric materials the conversion of carbon in order to obtain silicon carbide is generally  
19 fully successful. The main limit is linked to the difficulty in controlling the preform structure  
20 with pores and capillary channels of the size required for the infiltration process. In this case  
21 the dissolution of carbon into molten silicon is faster and therefore favoured with respect to the  
22 nucleation of SiC.

23 Graphite is a very common and cheap carbon source showing high thermal conductivity, good  
24 machinability and a thermal expansion coefficient close to that of silicon [22]. White et al. [22]  
25 reported that open porosity, surface roughness and Si/C contact time are the main parameters  
26 influencing the reactive wetting of liquid silicon to the graphite substrates. The use of graphite  
27 in the RMI process may be limited by the formation of cracks during the infiltration process  
28 caused by the development of internal stresses [22,23]. On the base of molar volume of the  
29 species involved, ( $V_{\text{graphite}}= 5.5 \text{ cm}^3/\text{mol}$ ,  $V_{\text{Si}}= 11.6 \text{ cm}^3/\text{mol}$  and  $V_{\text{SiC}}= 12.5 \text{ cm}^3/\text{mol}$  [23]) it is  
30 clear that the reaction between silicon and graphite leading to the formation of SiC involves a  
31 volume increase, which may induce the formation of cracks. Israel et al. [23] reported the  
32 fracture of some infiltrated samples produced by using graphite-based preforms. The study

1 shows the capillary interaction between the molten silicon and the graphite during RMI process  
2 by varying the porosity and the size of pores. Samples cracked when a graphite with a mean  
3 pore diameter around 13  $\mu\text{m}$  was used; this behaviour was not observed using others graphitic  
4 starting materials with pores under 1  $\mu\text{m}$ . White et al. [22] investigated the interaction of  
5 molten silicon with different grades of graphite, which were used as starting materials for the  
6 production of preforms. It was reported that the use of extruded graphite with high open  
7 porosity, leads to the development of internal stresses during the infiltration process, which  
8 causes the fracture of graphitic substrate. This confirms that the properties of starting graphite  
9 strongly influence the success of RMI process.

10 This paper provides a detailed microstructural, Raman and crystallographic characterization of  
11 graphite-Si-SiC materials produced by microwave (MW) assisted RMI. The starting carbon  
12 preforms were obtained by grinding up large plates of graphite to decrease the particle size to  
13 micrometric scale. The mechanical process of grain size reduction introduced many defects in  
14 the structure of graphite and increases its chemical reactivity making the infiltration process  
15 complex.

16 The successful processing of graphite-Si-SiC composites was first realized by Cornolti et al.  
17 [24] and it was linked to a careful investigation and optimization of the infiltration process,  
18 which involved the use of microwaves.

19 Unlike from conventional heating where the energy is transferred mainly through the surface of  
20 the samples, the microwave radiation provides fast volumetric heating of the irradiated  
21 component resulting in more efficient heat generation and transfer; a reduction in terms of total  
22 energy consumption and processing time with respect to the standard methods were achieved  
23 [25]. Danko et al. [26] processed silicon carbide and silicon oxycarbide ceramics by pyrolysis  
24 of preceramic polymers using standard and microwaves heating systems. The properties of  
25 materials in term of thermal stability and formed crystalline phases resulted comparable (larger  
26  $\beta$ -SiC crystallite size was observed for conventional-oven-heated samples). Moreover Breval et  
27 al.[27] compared the properties of WC samples containing 6 % and 12 % of Co sintered in  
28 conventional and microwave furnaces. The microwave sintered samples showed a higher  
29 values of hardness (from 1 to 5 GPa) than conventionally sintered samples, in addition to better  
30 resistance towards both corrosion and erosion.

31 Microwave-assisted processes allow to obtaining promising results in term of both  
32 development of materials with improved properties and new processing routes at laboratory

1 scale. However, there is a growing interest in transfer these advantages to an industrial scale.  
2 According to Banos et al. [28] the main limits that need to be overcome are mainly linked to  
3 the knowledge of the phenomena associated with the MW processes. The interaction between  
4 the microwaves and the matter is a very complex item which is nowadays a matter of study,  
5 especially when the process involves high temperatures. Another barrier is the limited  
6 knowledge of the heating mechanisms when materials are subjected to high frequency fields. In  
7 particular, the effects of electromagnetic fields on the materials' microstructure are still little  
8 known [M-M interaction]. In this context the investigation on the dielectric properties of  
9 materials is required in order to better design the MW-assisted process.

10 Different studies [29–32] investigated the materials' dielectric properties such as the dielectric  
11 constant (or real permittivity,  $\epsilon'$ ) and the dielectric loss factor (or imaginary permittivity,  $\epsilon''$ )  
12 and their variation as function of the temperature. This paper investigated MW-assisted process  
13 involving graphite-based preform and silicon, which are then converted into SiC. Both the  
14 starting materials show high microwave absorption properties: carbon materials are generally  
15 considered good absorbent of microwaves because of they can be easily heated  
16 by microwave radiation. Graphite is, for example, considered an efficient sensitizer: it converts  
17 radiation energy into thermal energy, which is then transmitted to supported chemical  
18 compounds favouring reactions which require high temperatures or which involve chemical  
19 compounds showing a low dielectric loss factor [33]. Moreover silicon absorbs very well the  
20 MW radiation at the frequency involved in the RMI process under investigation, as confirmed  
21 by Cornolti et al.[24]. The European Project HELM [34], which investigates advanced  
22 processing methods involving the use of microwaves and radiofrequencies for the processing  
23 of ceramic matrix composites, determined the dielectric properties of beta-SiC prepared by  
24 using graphite powder as carbon precursor and silicon. It was found that SiC shows a moderate  
25 value of  $\epsilon'$  in addition to a high value of  $\epsilon''$ . This combination of dielectric properties confirm  
26 the optimum interaction of SiC with microwaves.

27 The conversion of graphite-based preforms into SiC can be controlled by varying the  
28 microwave power; this paper investigates the effects of increasing microwave power on the  
29 microstructure and properties of graphite-Si-SiC materials.

## 31 **2. Materials and methods**

### 32 **2.1 Preform preparation**

1 The materials of the preforms were graphite (TIMREX KS 5-75, IMERYS, Bodio,  
2 Switzerland) and a phenolic novolac powder (BAKELITE PF GA T 10/R, Momentive  
3 Speciality Chemicals, Germany). The properties of the KS 5-75 graphite powder are: ash  
4 content 0.07 %, crystallite height  $L_c > 10$  nm, bulk density =  $0.24 \text{ g/cm}^3$ , particle size  
5 distribution  $d_{50} = 23.1 \text{ }\mu\text{m}$ ,  $d_{90} = 55.8 \text{ }\mu\text{m}$ .

6 The phenolic novolac powder employed was received in form of micro granules ( $d_{50} = 64 \text{ }\mu\text{m}$   
7 diameter). Graphite and the phenolic powder were dry mixed with a rotative mechanical mixer  
8 (EIRICH, Walldürner, Germany) for 2 hours. 20 g of compound were uniaxially cold-pressed  
9 (Ceramic Instruments, Sassuolo, Italy) at a pressure of 23 MPa for 30 seconds to obtain discs of  
10 50 mm in diameter and 5 mm in thickness. Cold pressing was chosen to achieve a reasonable  
11 porosity of the preforms after pyrolysis [35] for the following RMI stage.

12 The disks were pyrolysed in flowing Ar (300 sl/min) in an electric furnace (KEOS,  
13 Concorezzo, Italy) with the following heating cycle: 21-500°C in 12 h (heating rate of 40 °C/h),  
14 500-960 °C in 9 h (heating rate of 50°C), 1 h dwell at 960 °C and natural cooling. The pyrolysis  
15 converted the phenolic compound into volatile monomers, hydrogen and glassy carbon.

16 Table 1 shows the different weight percentages of material before and after pyrolysis process  
17 assuming a 45-55 % carbon yield [36]. A characterization of the preform porosity was done in  
18 our previous work [24]: the average pore diameter is  $2.25 \pm 0.29 \text{ }\mu\text{m}$ ; the open and closed  
19 porosities are estimated to be  $42.3 \pm 1.8$  % and  $0.7 \pm 0.3$  % respectively.

20

## 21 **2.2 Reactive melt infiltration assisted by microwave**

22 The setup employed in this research to heat by MW the preform is depicted in Fig. 1. The  
23 external  $\text{Al}_2\text{O}_3$  crucible was produced by tape casting, wrapping [37] and sintering [35] an  
24 alumina tape (0.3 mm thickness) in order to obtain a very thin wall ( $\sim 1$  mm) cylinder. The  
25 motivation was to have a container mostly transparent to MW. The vessel was then partially  
26 filled (level 1 in Fig. 1) with a mixture of 75 wt% 10  $\mu\text{m}$  grain size SiC (Ziegler, Winterthur,  
27 Switzerland) and 25 wt% of 40  $\mu\text{m}$  grain size BN powder (Henze Boron Nitride Products,  
28 Lauben, Germany). On level 1 it was placed an inner container and wicks in Sigraflex™ (SGL  
29 Carbon, Wiesbaden, Germany) filled with 50 g of silicon grains (HQ1, Sicerma, Erkelenz,  
30 Germany) with a grit size of 0.2-2.0 mm.

31 The amount of silicon was calculated to infiltrate and convert the Sigraflex™ parts and the  
32 preform into SiC whilst adding some extra amount. The preform was placed on the top of the

1 wicks. In some experiments a preform with a concentric hole was used in order to read directly  
2 the temperature of molten silicon at the bottom.

3 The cylinder was then closed with a perforated lid of Sigraflex™ to separate the reactive part of  
4 the setup from the SiC/BN powders. A BN tube was finally placed through the lid in  
5 correspondence of a hole on the preform to create an access for the pyrometer (PYROSPOT  
6 DSR10N, DIAS Infrared Systems GmbH, Schlattingen, Germany). Finally, the rest of SiC/BN  
7 powder was placed inside the Al<sub>2</sub>O<sub>3</sub> crucible in order to fill it; then the crucible was covered  
8 with an Al<sub>2</sub>O<sub>3</sub> capping. The infiltration set up was rotated in order to homogenize the  
9 temperature during MW heating. The unique spot available for the pyrometer reading was then  
10 the centre of rotation of the set up. The BN tube was carefully placed on this spot with a first  
11 rotation test with the open furnace.

12 As described in detail in a previous paper [9], the scope of the of the SiC/BN powders was to  
13 realise both a diffused MW susceptor and an insulation for thermal runaways.

14 The set-up was positioned on a rotating plate of porous alumina in the center of the microwave  
15 furnace (Frick und Mallah Microwave Technology, Peine, Germany). Rotation (20 RPM) was  
16 necessary to homogenise the MW field and avoid hot spots inside the multimode cavity. The  
17 furnace chamber was connected to four circular waveguides carrying a TM<sub>01</sub> mode at 2.45  
18 GHz. Each waveguide is supplied by an independent microwave generator delivering a power  
19 of 2 kW. Further details on the furnace and its working parameters can be found in [9]. A 2-  
20 colour pyrometer with an integrated digital camera was used to align the setup with the rotation  
21 axis of the turning plate in order to have a reliable temperature reading. The pyrometer  
22 measures the temperature in the range from 700 °C and 1800 °C; it was calibrated in our  
23 laboratory with dedicated tests on silicon and graphite. The furnace was purged and then filled  
24 with argon at 1.4 bar. Lower absolute pressures could not be achieved during MW processing  
25 due the formation of Ar plasma. Fig. 2 shows the experimental profiles of the system  
26 temperature [°C] vs time [min] obtained by varying the power lever. The maximum reached  
27 temperature cannot be reported because of it exceeds the upper limit of the pyrometer. As  
28 already reported in [9] the MW-RMI process is extremely fast: the power was kept ON till  
29 reaching the complete melting of Silicon (end of the dwell); at the onset of a second  
30 temperature peak the power was turned OFF. The temperature kept increasing, sustained by the  
31 exothermic reaction between silicon and carbon inside a quasi-adiabatic vessel. Three power  
32 levels were employed to heat up the chamber: they were corresponding to 30 %, 60 % and



1 75 % of the full power (8 kW). Higher power was avoided because of it would risk to affect the  
2 process stability: at the start up the risk concerns an arcing plasma formation and, for long  
3 experiments it is necessary avoid the waveguides' overheating.

### 4 5 **2.3 Characterization tests**

6 Three graphite-Si-SiC materials labelled P30, P60 and P75 were obtained by setting the power  
7 level at 30 %, 60 % and 75 % of the full power respectively. The three samples had a disk  
8 shape with a diameter of 50 mm and a thickness of around 6 mm. Their surfaces were initially  
9 polished with SiC grinding paper (Grit from 180 to 800) in order to remove silicon residuals  
10 after the infiltration process. The disks were cut in order to obtain samples with suitable size for  
11 the different characterization tests. Three points bending tests were performed on a set of 8 bars  
12 with size of 30x55x13 mm<sup>3</sup> by using a universal tensile testing machine (Zwick Z050, Ulm,  
13 Germany) with a span of 20 mm. A preloading of 5 N was used and the crosshead rate was 0.2  
14 mm/min according to standard ASTM C1161-18. The samples were then subjected to a second  
15 finer polishing step by using SiC grinding paper (Grit from 800 to 4000) followed by polishing  
16 cloths loaded with lubricant and progressively smaller diamond abrasives (3 μm and 1 μm  
17 respectively). The microstructure of the polished specimens and the fracture surfaces were  
18 investigated by scanning electron microscopy (SEMFEG Assing SUPRA 25, equipped with  
19 EDS Oxford INCA X-sight, Oberkochen, Germany). The micrographs have been obtained by  
20 using backscattered electrons detector, which displays the atomic number contrast allowing to  
21 better distinguish the different constituent phases.

22 Raman measurements were performed using a Raman microscope (InViaH, Renishaw, Wotton-  
23 under-Edge, United Kingdom) equipped with a green laser source (wavelength: 514.5 nm).

24 Samples named P30 and P75 were placed on a microscope glass glide and the spectra acquired  
25 in several points having different visual appearance (black, white or grey) were compared. For  
26 each measured region we started with a low magnification objective (5x) zooming-in using a  
27 20x and finally recording spectra with a 50x objective. The area of each examined spot was of  
28 about 2 μm<sup>2</sup>. Raman analysis being a volume technique, the signal is gathered from the sample  
29 surface up to a depth that varies with the optical properties of the analysed materials. In sp<sup>2</sup>  
30 rich carbon materials this depth is of a few micrometers [38]. The laser power was set at 5 mW  
31 in order to obtain a good signal-to-noise ratio avoiding in the meantime damage of the sample

1 due to excessive heating. Each measurement was carried out in extended mode ( $100\text{ cm}^{-1}$  to  
2  $3500\text{ cm}^{-1}$ ) with an exposure time of 10 s and with 3 accumulations.

3 The Raman analysis was mainly focused on three spectral regions in which the most relevant  
4 features are:

5 1) peak centred at  $520\text{ cm}^{-1}$ . This peak is typical of crystalline silicon [39].

6 2) peaks centred at  $790\text{ cm}^{-1}$ . This peak is reported in literature [40] as arising from thin films  
7 of 3C-SiC and it is associated to the transverse optical (TO) phonon modes.

8 3) peak close to  $960\text{ cm}^{-1}$ . This peak can be due either to c-SiC and/or to the longitudinal optical  
9 (LO) phonon modes of 3C-SiC.

10 4) two peaks close  $1350$  and  $1590\text{ cm}^{-1}$  respectively. These are the D and G peaks of  $sp^2$   
11 coordinated carbon atoms [41].

12 The cross section for the various peaks is different and depends on the specific environment.

13 Therefore the analysis of the peaks intensities is not sufficient in order to determine the  
14 percentage of the different phases when they coexist. However, by comparing the relative  
15 intensities of the peak related to the various phases we can verify if the amount of one phase is  
16 higher or lower in different samples [42]. To this purpose we proceed as follows:

17 1) the  $520\text{ cm}^{-1}$  was selected as an indicator for Si abundance

18 2) the  $790\text{ cm}^{-1}$  was selected as an indicator for SiC abundance. This peak was picked over  $960$   
19  $\text{cm}^{-1}$  as this last overlaps with a Si contribution

20 3) the G peak was selected as an indicator for graphite abundance. This peak was selected  
21 instead of D peak as all  $sp^2$  bonds contribute to its intensity while for the D peaks only those  
22  $sp^2$  bonds close to the edge regions of grains contribute [43]

23 4) for each sample the area (i.e. the signal intensity integrated over the peak region) of each  
24 relevant peaks is evaluated

25 5) the intensity ratios for SiC/Si and SiC/C peaks are evaluated

26 6) as an additional information about disorder in the graphite phase, the  $I_D/I_G$  (i.e. the ratio of  
27 intensities of the D and G peaks) ratio is evaluated [43]

28 7) the FWHM (Full Width Half Maximum) of the Si and SiC related peaks is computed in  
29 order to gather information on the local disorder [44] and the grain size in the Si and SiC  
30 regions [45].

31 The crystalline phases of C-Si-SiC materials were identified by using X-ray diffraction

32 (Panalytical X'PERT PRO PW3040/60, Cu  $K\alpha$  radiation at 40kV and 40mA, Panalytical BV,

1 Almelo, The Netherlands). The elaboration of XRD spectra for quantitative phase analysis was  
2 performed by using MAUD program [46,47].

3 The thermal behavior was investigated by testing samples ( $3\times3\times3$  mm<sup>3</sup> in size) to a  
4 temperature run from 25° to 1200 °C with a heating rate of 5°C/min under flowing air (50  
5 ml/min) in a thermal analyzer [TGA/STDA851°, Mettler Toledo, Columbus, Switzerland].  
6

6

### 7 **3. Results**

#### 8 **3.1. Composite microstructure**

9 Fig. 3 shows the evolution of graphite-Si-SiC microstructure by varying the microwave power  
10 level from 30 % (Fig. 3A) to 75 % (Fig. 3C). EDS analyses performed on areas with different  
11 colour appearance show that the black parts are mainly constituted of carbon. Specifically, the  
12 lamellar structure identified for these areas allows us to assume the presence of unreacted  
13 graphite. The brightest irregular spots, hereafter referred to as white areas, are mainly made of  
14 unreacted silicon.

15 The grey regions are constituted by both silicon and carbon; EDS analyses on these areas show  
16 an atomic ratio between the two elements close to 1:1 allowing us to speculate that the silicon  
17 carbide formed by reactive infiltration.

18 All the microstructures present a similarity in the phases distribution: the carbon is always  
19 isolated from the silicon by a SiC layer; moreover the silicon is surrounded by areas rich in SiC  
20 produced during reactive infiltration. A similar microstructure has been previously reported in  
21 the literature [48]. By observing a black carbon area in a larger magnification (Fig. 3D) SiC can  
22 be found among the graphite layers. It can be supposed that silicon infiltrated the plates and  
23 formed a thin SiC layer, which insulated the residual liquid silicon from carbon regions.

24 The fracture surfaces of P30, P60 and P75 samples (Fig. 4) were observed to be mainly flat  
25 indicating a brittle fracture behaviour. Graphite flakes pull-out was observed in all the samples  
26 and this phenomenon seems particularly evident in the material processed by using the highest  
27 power level (Fig. 4C and 4D). It may be assumed that the observed pull-out can promote a  
28 toughening of the ceramics.

29 In literature only few information is available about the microwaves effect on fibre/flakes pull-  
30 out. Omatete et al. [49] observed a significant fiber pull-out from the analysis of fracture  
31 surface of reaction bonded silicon nitride composites processed at 1250 °C for 8 h in a  
32 microwave furnace. The samples nitrided at the higher temperature of 1350 °C exhibited only

1 limited pull-out probably due to the fibre degradation and a strong matrix-fibre bonding. This  
2 study seems to confirm that temperature has a significant impact on the pull-out.

3 Moreover Papargyris et al. [50] reported that the fracture surface of composites produced with  
4 conventional method exhibits a more extensive fibre pull-out compared to that produced using  
5 microwaves. So the use of microwaves seems not to promote the pull-out effect. However any  
6 study is present on the effect of MW power variation on the microstructure of RMI materials; a  
7 more detailed investigation **has to be done**.

8 The presence of uniformly distributed pores of different sizes is particularly evident in sample  
9 P30 compared to specimens obtained setting a higher power level.

### 11 **3.2 Raman characterization**

12 Samples obtained using the lowest (P30) and the highest power level (P75) were examined, and  
13 the Raman spectra collected focusing on areas with different visual appearance (black, white or  
14 grey) were compared. Both precursors, i.e. graphite starting powder and crystalline silicon,  
15 were investigated in order to be used as references.

#### 17 **3.2.1 Graphite and silicon precursor analysis**

18 The Raman spectra reported in Fig. 5A evidence a high quality graphitic material with a low  
19 intensity D peak centered at  $1350\text{ cm}^{-1}$  and an intense narrow G peak centered at  $1572$   
20  $\text{cm}^{-1}$ . These peaks are very well separated and the  $I_D/I_G (= 0.16)$  ratio is typical of high quality  
21 graphite [51]. This observation is supported by the following additional facts: 2D peak (around  
22  $2700\text{ cm}^{-1}$ ) is strong and intense, left shouldered and typical of multi-layered graphite; D+G  
23 Overtone peak ( $\sim 2920\text{ cm}^{-1}$ ) is absent; and 2G peak at  $3230\text{ cm}^{-1}$  is weak and sharp.

24 The crystalline silicon Raman Spectra reported in Fig. 5B shows, as expected, an intense and  
25 very narrow peak centered at  $520\text{ cm}^{-1}$ , and a broad band just below around  $965\text{ cm}^{-1}$  [52].

#### 27 **3.2.2 P30 Sample Raman Analysis**

28 Fig. 6 is an optical image showing the grey (Fig. 6A), the white (Fig. 6B) and the black (Fig.  
29 6C) areas where the Raman spectra were measured.

30 Two different points were sampled both in the white and black zones of the material while  
31 spectra from four different points were acquired in the grey zones. All Raman spectra displayed  
32 in the figures have been background subtracted.

1 The Raman spectra of white areas are reported in Fig. 7A. These regions are rich in crystalline  
2 silicon as shown by the intense peak  $\sim 520\text{ cm}^{-1}$ , slightly downshifted and quite enlarged if  
3 compared with the crystalline precursor. The crystalline silicon structure is more disordered  
4 than that of the c-Si (crystalline silicon) precursor due to the SiC production process. The  
5 presence of an intense peak around  $960\text{ cm}^{-1}$  as it is not accompanied by the  $760\text{ cm}^{-1}$  peak  
6 typical of SiC can be attributed to the crystalline c-Si Raman spectra. No clear evidence of the  
7 presence of SiC in this region can be found. Other significant features are the presence of the  
8 graphite-related peaks at  $1350\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$  (D and G peaks) as well as of 2D, D+G and  
9 2G peaks starting from  $2960\text{ cm}^{-1}$ . This suggests the presence of unreacted graphite particles in  
10 the white region.

11 The Raman spectra of the black areas are shown in Fig. 7B. This region appears to be rich in  
12 carbon material with limited amounts of crystalline silicon and SiC indicated respectively by  
13  $519$  and  $789\text{ cm}^{-1}$  peaks. The carbon related peaks are the most intense and D and G peaks are  
14 well separated.  $I_D/I_G (= 0.88)$  is significantly higher than the value in the precursor graphite.  
15 The graphitic structure is more defective compared with the original graphitic precursor. The  
16 2D zone appears intense, left shouldered (index of multi-layered structure), and defective  
17 (presence of D+G peak). The 2G peak has typical intensity and width.

18 The Raman spectra of the grey regions are displayed in Fig. 8A. In this region a relevant  
19 amount of Si is present (sharp and intense  $519\text{ cm}^{-1}$ ) and the presence of graphitic carbon is  
20 evident too (D and G peaks sharp and intense). The presence of SiC is confirmed by the peak at  
21  $793\text{ cm}^{-1}$ .

22 The non-negligible presence of both silicon and carbon in grey regions can be explained  
23 considering a compositional inhomogeneity. This is evident from the SEM image of a grey area  
24 (Fig. 8B) which shows the presence of both white and black contaminations within the grey  
25 region.

26

### 27 **3.2.3 P75 sample Raman analysis**

28 Similarly to what was observed for sample P30, the microstructure of specimen P75 appears as  
29 a structure of spotted black, white and grey zones (Fig. 6). For this reason, we acquired the  
30 Raman spectra on these different areas to assess the compositional differences.

31 The measured Raman spectra were reported after the background subtraction.

1 The spectra of white region are reported in Fig. 9A. This zone is rich of pure c-Si confirmed by  
2 the intense peak  $\sim 519 \text{ cm}^{-1}$ , which is slightly downshifted and with a higher FWHM if  
3 compared to crystalline silicon. The crystalline structure appears to be more disordered due to  
4 the SiC production process, as previously observed in P30 sample. The presence of a weak but  
5 detectable peak at  $792 \text{ cm}^{-1}$  is due to the TO mode of SiC. This indicates the presence of a low  
6 amount of SiC. Other significant features (related to graphite) are the presence of D and G  
7 peaks at  $1350 \text{ cm}^{-1}$  and  $1580 \text{ cm}^{-1}$  respectively and evidence of 2D, D+G and 2G peaks starting  
8 from  $2960 \text{ cm}^{-1}$ . Hence, in this region disordered c-Si is dominant, but a small amount of  
9 unreacted graphite is present as well as SiC traces.

10 The Raman spectra of black region is reported in Fig. 9B. This area appears to be rich of  
11 graphitic material with limited Si and SiC presence, evidenced by the peaks at  $518 \text{ cm}^{-1}$  (Si)  
12 and  $792 \text{ cm}^{-1}$  (SiC). The graphite related peaks are by far the most intense. D and G peaks are  
13 quite narrow.  $I_D/I_G (= 0.45)$  is low but significantly higher than the value of the precursor  
14 graphite. The graphitic structure is more defective than in the original graphitic precursor. This  
15 conclusion is supported by an intense, left shouldered 2D zone (index of multi-layered  
16 structure), and the presence of D+G peak (indicating a more defective structure).

17 The Raman spectra of grey regions is shown in Fig. 9C. In this zone Si related peaks are absent  
18 while weak carbon related peaks can be observed: D and G peaks (this last is rather broadened),  
19 2D peak is weak and D+G peak can be barely seen. The peaks centred at  $794 \text{ cm}^{-1}$  and  $970 \text{ cm}^{-1}$   
20 indicates the presence of thin film of 3C-SiC deposited with different C/Si ratio. All spectra  
21 collected in the different grey points show sharp optical transverse peak (TO) and longitudinal  
22 optical (LO) SiC peak, respectively around  $794 \text{ cm}^{-1}$  and  $970 \text{ cm}^{-1}$  [53]. No peaks related to c-  
23 Si can be observed, indicating that the c-Si has fully converted to SiC (in the limit of detection  
24 of the Raman technique).

25 However, the ratio of the intensities of SiC peak at  $794 \text{ cm}^{-1}$  to carbon G peak is much higher  
26 compared to that of sample P30. Moreover, the  $I_D/I_G$  ratio is lower for sample P75 compared to  
27 P30 (0.29 and 0.98 respectively) indicating a higher level of disorder of the carbon-rich region  
28 of the latter.

29 In order to support the meaningfulness of the approach used in this paper, a Raman mapping of  
30 sample P75 has been performed (Fig. 10). Fig. 10A shows the mapped region ( $50\mu\text{m} \times 70\mu\text{m}$ )  
31 obtained using the optical microscope. This area is divided into several points; the spectra are  
32 acquired sequentially from this range of points, across the specified area of interest. Figure 10B

1 shows the mapping of the intensity of the SiC peak (brighter areas indicates higher intensity),  
2 while Fig. 10C and Fig. 10D show the mapping of the intensity of the Si and graphite  
3 characteristic Raman peaks respectively.

4 By comparing the obtained maps with the optical image it is evident that the regions which  
5 appears bright in the optical image correspond to Si-rich regions, while the dark regions mainly  
6 correspond to C-rich areas. This Raman approach is able to easily highlight the regions where  
7 the sample is richer in SiC component. Most SiC-rich regions are present in the boundary  
8 regions between Si-rich and C-rich zones while others are clearly present where Si and C  
9 signals are lower.

### 11 3.3 X-ray diffraction

12 Fig. 11 shows the XRD spectra for graphite-Si-SiC materials obtained by varying the power  
13 level during the RMI process.

14 The most intense peaks belong to  $\beta$ -SiC phase, which is considered the stable form of SiC up to  
15 2100 °C [54]. The other more common SiC polytypes such as 4H, 6H and 15R were not  
16 detected.

17 The chemical reaction between carbon and silicon leading to the formation of SiC was not  
18 complete as evidenced by the presence in XRD spectra of additional peaks assigned to both  
19 unreacted graphite and silicon.

20 The chemical composition of the starting preform (Table 1) evidences the presence of a low but  
21 not negligible amount of glassy carbon, which is a non-graphite form of carbon having a  
22 microstructural disorder between that of amorphous carbon and single-crystal graphite [55].

23 The XRD spectrum of glassy carbon usually shows broad peaks at 2theta values typical of  
24 graphite peaks [56]. No broad peaks are present in XRD spectra of C-Si-SiC materials (Fig.  
25 11). This can be explained considering that the high temperature reached during the infiltration  
26 process should allow the development from a glassy carbon structure into a graphite-like layer  
27 structure. This implies an increment of crystal structure order highlighted by the narrowing of  
28 the diffraction peaks [56,57].

29 The relative amount of formed SiC was calculated to be 49.3 wt%, 54.9 wt% and 75.7 wt% for  
30 P30, P60 and P75 samples respectively. The conversion of graphite based preform and silicon  
31 into SiC is observed to be higher by using a higher power level.

32

### 3.4 Mechanical and thermal properties

Preliminary results of mechanical and thermal properties are reported in order to understand how the microstructure of graphite-Si-SiC can influence the material properties.

The bending strength values increase by increasing the microwave power level: the average value of  $146 \pm 24$  MPa for P30 is lower with respect to  $160 \pm 16$  MPa and  $177 \pm 11$  MPa values obtained for P60 and P75 respectively. These values are comparable to those reported for commercially available SUPERSiC® material (bending strength  $\sim 147$  MPa) produced converting starting graphite based preforms to high purity silicon carbide using a reactive SiO flow [58]. However the experimental strength values result lower respect to those observed for fully infiltrated Si-SiC material [9,59].

In Fig. 12 the bending tests curves for P75 samples (reported as example) show two different behaviours. It is interesting to note that some specimens show a linear stress-strain relationship typical of brittle materials. On the other hand, samples obtained from a different part of the starting disk, report a quite higher displacement before rupture. As shown in the upper part of Fig. 12 the samples were obtained by making a series of cuts in a perpendicular direction respect to the base of the starting disk. Some of these bars showed a thin crack filled with solid silicon. This is a common defect in materials processed by RMI process. Previous studies attributed this phenomenon mainly to CTE mismatch between the formed SiC and the unreacted graphite [48,60]. The different trends in bending strength curves can be correlated to the different microstructure between samples which evidences the presence of Si-filled cracks with respect to those in which the crack is absent. The material showing a standard brittle behavior displays a homogeneous microstructure similar to those presented in Fig. 3. On the other hand, the microstructure of specimens showing the crack displays an intermediate plateau before reaching the material fracture. However, the bending strength values of the two set of samples is very similar so the presence of silicon-filled cracks seems not affecting the strength of graphite-Si-SiC materials. Similar considerations can be done for samples P30 and P60. The mechanical performance of Si-SiC materials depends on the volume fraction of silicon carbide: the higher is the amount of formed SiC, the stronger is the interconnectivity of SiC boundaries, which allow to obtain enhanced strength.

The analysis of bending strength curves cannot evidence the toughening effect supposed by observing the graphite pull out from the fracture surfaces. This conclusions has in fact to be confirmed by a more detailed study of the mechanical behavior of these materials.



1 Thermogravimetric analyses of graphite-Si-SiC material from room temperature up to 1200 °C  
2 in flowing air have been performed in order to investigate the thermal stability. Fig. 13 shows  
3 the TGA curve for sample P75, which was taken as example because it resulted the best  
4 infiltrated and densest material.

5 No change in weight was observed up to a temperature of 720 °C. For higher temperature the  
6 material starts to decrease its weight becoming stable again at a weight of about 79 % of the  
7 starting value. The one step weight decrease is probably due to the decomposition of the  
8 unreacted graphite in an oxidizing environment.

#### 9 10 **4. Discussion**

11 Graphite-Si-SiC ceramics were obtained by reactive infiltration of liquid silicon into graphite-  
12 based preforms. Starting from large blocks graphite was ground to obtain micrometer size  
13 particles; this introduced defects and enlarges its reacting surface area. Ground graphite is in  
14 fact far from its theoretical lattice stacking; many defects are present such as decreasing  
15 crystalline order, dangling bonds, irregular bond angles and angstrom-scale porosity [61].  
16 These defects are directly related to the concentration and the accessibility of “active sites”,  
17 which enhance the chemical reactivity of carbon making the infiltration process difficult.  
18 The process was assisted by microwaves, which provide a fast heating of the starting materials  
19 allowing to reduce both the consumption of energy and the processing time with respect to  
20 conventional heating. Three sets of samples were prepared by varying the microwave power:  
21 P30, P60 and P75 specimens were in fact produced by using a power of 30 %, 60 % and 75 %  
22 of the full power respectively.

23 The investigation of microstructure shows the presence of three main interpenetrated phases:  
24 black areas coming from unreacted graphitic preforms, white silicon islands and residual grey  
25 silicon carbide. The presence of both unreacted silicon and graphite put in evidence that the  
26 reaction between these two phases is not complete leaving residual starting materials in the  
27 final material microstructure. However, the grey SiC areas result the most interesting ones  
28 because of its relative amount and distribution influence the final material properties. SiC is  
29 formed at the interface between silicon and graphite and progressively grows producing a  
30 silicon carbide network. X-ray diffraction spectra confirm that silicon, carbon and SiC are the  
31 three main crystalline phases present in all the samples of graphite-Si-SiC, independently from  
32 the used microwave power.

1 SiC shows a cubic structure whose formation is expected because of the conversion into  
2 hexagonal form generally occurs at temperature higher than 2100 °C [54,62]. During the RMI  
3 process the temperature increases beyond the upper limit of the pyrometer sensor (1800 °C), so  
4 it is not possible to measure the maximum reached temperature. However Cornolti et al. [24]  
5 studied the RMI process in detail elaborating a model which is demonstrated to be in good  
6 agreement with the experimental temperature history. According to this model the maximum  
7 temperature was estimated to be around 2000°C.

8 The formation of  $\beta$ -SiC with a cubic structure is however very common in materials obtained  
9 by RMI [59,63]. Margiotta et al. [24] investigated the liquid silicon infiltration of carbon  
10 preforms derived from carbonization of crystalline cellulose and phenolic resin blends. The  
11 process performed between 1414 °C and 1900 °C evidenced the formation of  $\beta$ -SiC in addition  
12 to residual Si at all temperatures.

13 However, it is necessary to consider that the transition from  $\beta$  to  $\alpha$  forms could be affected by  
14 the other processing conditions (such as pressure, the use of microwave etc) in addition to the  
15 temperature. Therefore, it cannot be excluded the formation of a small amount of SiC with a  
16 hexagonal crystal structure. The XRD spectra did not put in evidence the formation of this SiC  
17 polytype because of they could be present in an amount smaller than the detection limit of XRD  
18 technique.

19 The intensity of SiC peaks increases from P30 to P75: the amount of this phase is therefore  
20 higher for sample P75. The formation of SiC is therefore favored by increasing the supplied  
21 MW power. This confirms the higher efficiency of the RMI process in the P75 case previously  
22 deduced from XRD measurements. Raman analyses also confirm this results; in fact in sample  
23 P75 the presence of SiC associated peaks is more evident than in P30, suggesting a higher  
24 efficiency of the process in the P75 case.

25 Moreover, Table 2 was prepared in order to compare and discuss the results coming from the  
26 Raman spectra. The main parameters which characterize a Raman peak, the center and the  
27 width respectively, were reported and compared for the starting materials (silicon and graphite)  
28 and the samples produced by setting the lowest and highest MW power (P30 and P75 samples  
29 were subdivided in their components: white, black and grey). For each sample the contribution  
30 due to Si, SiC, and carbon (D and G peaks) components was moreover considered. Last three  
31 columns report the ratio of peak areas (Si, SiC, and carbon characteristics peaks D and G).

1 These ratios show the contribution in the different regions (white, black, grey) of the various  
2 components (Si, SiC and carbon material).  
3 In particular, SiC/G and SiC/Si ratios can be used to evaluate the presence of SiC in the region  
4 under study: in fact high values of these ratios imply that an increased amount of SiC is formed.  
5 Consequently the relative amount of both Si and carbon starting material progressively  
6 decreases. Both SiC/G and SiC/Si ratios are significantly higher in P75 grey region if compared  
7 to P30.  
8 The influence of microwave power on the mechanical and thermal properties of graphite-Si-  
9 SiC materials was preliminarily investigated.  
10 The bending strength for samples increases in function of the higher used power. So it is  
11 possible to hypothesize that applying a high power the formation of vapor silicon is favored  
12 allowing the formation of an increased amount of SiC as confirmed by Raman and XRD. A  
13 visual analysis of microstructural images (Fig. 3) reveals that SiC seems to form a more  
14 continuous network for sample P75 with respect to P60 and P30. This may justify the  
15 enhancement of P75 bending strength compared to the other samples. Moreover, a higher  
16 porosity of sample P30 with respect to P75 is clear from the comparison of SEM micrographs  
17 (Fig. 3). It is well known that the presence of pores significantly affects the material  
18 mechanical properties resulting in lower bending strength.

## 20 5. Conclusions

21 Graphite-Si-SiC ceramic materials were successfully prepared by Reactive Melt Infiltration  
22 process assisted by microwave. The effects of microwave power variation on the  
23 microstructure and the mechanical properties of ceramics obtained by this process were  
24 investigated.  
25 The microstructure consists of a homogeneous distribution of interpenetrated phases. Residual  
26 graphitic areas are separated from unreacted silicon islands by a SiC network. The reaction  
27 between Si and graphite occurs at their interface and involves the formation of a growing SiC  
28 layer. However, the reaction is not complete, leaving residuals of unreacted starting  
29 components.  
30 Raman and X-ray diffraction investigations show the strong correlation between the conversion  
31 of graphite into SiC and the microwave power used. The relative amount of formed SiC  
32 increases from 49.3 wt% to 75.7 wt% by increasing the power level from 30 % to 75 % of its

1 maximum value. The increment of the relative amount of formed SiC suggests a higher  
2 efficiency of the infiltration process. Furthermore, the measurements of bending strength  
3 confirm it show higher values for samples processed by using the highest power level. The  
4 formation of a higher amount of SiC for sample P75 could explain the formation of a more  
5 continuous SiC network. The improved mechanical behavior is hence linked to a more dense  
6 material obtained by increasing the microwave power.

7

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1 **Tables**

2 **Table 1.** Change in composition of preform due to pyrolysis.

	<b>Graphite</b> [wt%]	<b>Phenolic resin</b> [wt%]	<b>Glassy carbon</b> [wt%]
Before pyrolysis	88.50	11.50	0
After pyrolysis	94.25	0	5.75

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7 **Table 2.** Raman spectra parameters for peaks under study and their ratio. All values are in  $\text{cm}^{-1}$ .

	<b>Si</b>		<b>SiC</b>		<b>D</b>		<b>G</b>		<b>Peak Ratio</b>			
	(520 $\text{cm}^{-1}$ )		(790 $\text{cm}^{-1}$ )		(1350 $\text{cm}^{-1}$ )		(1590 $\text{cm}^{-1}$ )		SiC/Si	SiC/G	D/G	
	Center	Width	Center	Width	Center	Width	Center	Width				
<b>Si</b>	520	2	0	0	0	0	0	0	0	----	----	
<b>Graphite</b>	0	0	0	0	1349	23	1575	8	----	0	0.17	
<b>P30</b>	White	520	13	0	0	1346	16	1578	10	0.00	0.00	1.04
	Black	519	10	789	7	1349	22	1578	16	0.39	0.13	0.88
<b>P75</b>	Grey	519	11	793	5	1346	20	1578	17	0.01	0.02	0.98
	White	519	14	792	21	1340	40	1576	32	0.10	0.20	0.36
	Black	518	13	792	6	1348	20	1578	9	0.45	0.05	0.62
	Grey	520	13	794	5	1345	28	1577	51	4.44	1.81	0.29

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