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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

the final product from chemical reaction between the infiltrant and the preform. Margiotta et al. [6] obtained dense SiC carrying out the liquid silicon infiltration of carbon preforms at 1800 °C for 120 minutes; the temperature resulted much lower compared to both the melting point of SiC (2730 °C) and the temperature generally required for SiC sintering. Moreover, the materials produced by RMI show thermal properties comparable to those obtained by standard processes. Wang et al.[7] prepared ZrB_2–SiC protective lamina to be used as coating on carbon/carbon composites combining pressing and Reactive Silicon Infiltration (RSI). It successfully avoids the oxygen penetration in the inner part of material thanks to the formation of a surface oxide layer. The composition of it is similar to that observed for ZrB_2-SiC coating processed by CVD [8]. The processing of ZrB_2–SiC coating by RSI represents a promising alternative to generally used CVD films, which show similar ablation resistance, but require long and high-cost processing methods. Moreover, Bianchi et al.[9] reported that the RSI process yields Si-SiC foam bodies showing high thermal shock resistance, comparable to that of similar foam produced by more conventional sponge replica techniques [10]. The economic advantages in term of energy and time saving make the RMI process attractive for many industrial applications such as aerospace, energy, automotive, biomedicals and electronics [9,11–13].

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

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

$$Si_{iliq} + C_{solid} \rightarrow SiC_{solid} \qquad [\Delta H = -68\ kJ/mol][17] \qquad \text{Equation 1}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

2. Materials and methods

2.1 Preform preparation

The materials of the preforms were graphite (TIMREX KS 5-75, IMERYS, Bodio, Switzerland) and a phenolic novolac powder (BAKELITE PF GA T 10/R, Momentive Speciality Chemicals, Germany). The properties of the KS 5-75 graphite powder are: ash content 0.07 %, crystallite height L_c > 10 nm, bulk density = 0.24 g/cm^3, particle size distribution d50 = 23.1 µm, d90 = 55.8 µm.

The phenolic novolac powder employed was received in form of micro granules (d50 = 64 µm diameter). Graphite and the phenolic powder were dry mixed with a rotative mechanical mixer (EIRICH, Walldürner, Germany) for 2 hours. 20 g of compound were uniaxially cold-pressed (Ceramic Instruments, Sassuolo, Italy) at a pressure of 23 MPa for 30 seconds to obtain discs of 50 mm in diameter and 5 mm in thickness. Cold pressing was chosen to achieve a reasonable porosity of the preforms after pyrolysis [35] for the following RMI stage.

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

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

2.2 Reactive melt infiltration assisted by microwave

The setup employed in this research to heat by MW the preform is depicted in Fig. 1. The external Al_2O_3 crucible was produced by tape casting, wrapping [37] and sintering [35] an alumina tape (0.3 mm thickness) in order to obtain a very thin wall (~ 1 mm) cylinder. The motivation was to have a container mostly transparent to MW. The vessel was then partially filled (level 1 in Fig. 1) with a mixture of 75 wt% 10 µm grain size SiC (Ziegler, Winterthur, Switzerland) and 25 wt% of 40 µm grain size BN powder (Henze Boron Nitride Products, Lauben, Germany). On level 1 it was placed an inner container and wicks in Sigraflex™ (SGL Carbon, Wiesbaden, Germany) filled with 50 g of silicon grains (HQ1, Sicerma, Erkelenz, Germany) with a grit size of 0.2-2.0 mm.

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

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

The cylinder was then closed with a perforated lid of Sigraflex™ to separate the reactive part of the setup from the SiC/BN powders. A BN tube was finally placed through the lid in correspondence of a hole on the preform to create an access for the pyrometer (PYROSPOT DSR10N, DIAS Infrared Systems GmbH, Schlattingen, Germany). Finally, the rest of SiC/BN powder was placed inside the Al_2O_3 crucible in order to fill it; then the crucible was covered with an Al_2O_3 capping. The infiltration set up was rotated in order to homogenize the temperature during MW heating. The unique spot available for the pyrometer reading was then the centre of rotation of the set up. The BN tube was carefully placed on this spot with a first rotation test with the open furnace.

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

The set-up was positioned on a rotating plate of porous alumina in the center of the microwave furnace (Frick und Mallah Microwave Technology, Peine, Germany). Rotation (20 RPM) was necessary to homogenise the MW field and avoid hot spots inside the multimode cavity. The furnace chamber was connected to four circular waveguides carrying a TM01 mode at 2.45 GHz. Each waveguide is supplied by an independent microwave generator delivering a power of 2 kW. Further details on the furnace and its working parameters can be found in [9]. A 2-colour pyrometer with an integrated digital camera was used to align the setup with the rotation axis of the turning plate in order to have a reliable temperature reading. The pyrometer measures the temperature in the range from 700 °C and 1800 °C; it was calibrated in our laboratory with dedicated tests on silicon and graphite. The furnace was purged and then filled with argon at 1.4 bar. Lower absolute pressures could not be achieved during MW processing due the formation of Ar plasma. Fig. 2 shows the experimental profiles of the system temperature [°C] vs time [min] obtained by varying the power lever. The maximum reached temperature cannot be reported because of it exceeds the upper limit of the pyrometer. As already reported in [9] the MW-RMI process is extremely fast: the power was kept ON till reaching the complete melting of Silicon (end of the dwell); at the onset of a second temperature peak the power was turned OFF. The temperature kept increasing, sustained by the exothermic reaction between silicon and carbon inside a quasi-adiabatic vessel. Three power levels were employed to heat up the chamber: they were corresponding to 30 %, 60 % and

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

2.3 Characterization tests

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

Raman measurements were performed using a Raman microscope (InViaH, Renishaw,Wotton-under-Edge, United Kingdom) equipped with a green laser source (wavelength: 514.5 nm). Samples named P30 and P75 were placed on a microscope glass glide and the spectra acquired in several points having different visual appearance (black, white or grey) were compared. For each measured region we started with a low magnification objective (5x) zooming-in using a 20x and finally recording spectra with a 50x objective. The area of each examined spot was of about 2 μm^2. Raman analysis being a volume technique, the signal is gathered from the sample surface up to a depth that varies with the optical properties of the analysed materials. In sp2 rich carbon materials this depth is of a few micrometers [38]. The laser power was set at 5 mW in order to obtain a good signal-to-noise ratio avoiding in the meantime damage of the sample

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

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

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

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

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

4) two peaks close 1350 and 1590 cm^{-1} respectively. These are the D and G peaks of sp2 coordinated carbon atoms [41].

The cross section for the various peaks is different and depends on the specific environment. Therefore the analysis of the peaks intensities is not sufficient in order to determine the percentage of the different phases when they coexist. However, by comparing the relative intensities of the peak related to the various phases we can verify if the amount of one phase is higher or lower in different samples [42]. To this purpose we proceed as follows:

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

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

3) the G peak was selected as an indicator for graphite abundance. This peak was selected instead of D peak as all sp2 bonds contribute to its intensity while for the D peaks only those sp2 bonds close to the edge regions of grains contribute [43]

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

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

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

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

The crystalline phases of C-Si-SiC materials were identified by using X-ray diffraction (Panalytical X'PERT PRO PW3040/60, Cu Kα radiation at 40kV and 40mA, Panalytical BV,

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

The thermal behavior was investigated by testing samples (3×3×3 mm^3 in size) to a temperature run from 25° to 1200 °C with a heating rate of 5°C/min under flowing air (50 ml/min) in a thermal analyzer (TGA/STDA851^e, Mettler Toledo, Columbus, Switzerland).

3. Results

3.1. Composite microstructure

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

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

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

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

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

limited pull-out probably due to the fibre degradation and a strong matrix-fibre bonding. This study seems to confirm that temperature has a significant impact on the pull-out.
Moreover Papargyris et al. [50] reported that the fracture surface of composites produced with conventional method exhibits a more extensive fibre pull-out compared to that produced using microwaves. So the use of microwaves seems not to promote the pull-out effect. However any study is present on the effect of MW power variation on the microstructure of RMI materials; a more detailed investigation has to be done.
The presence of uniformly distributed pores of different sizes is particularly evident in sample P30 compared to specimens obtained setting a higher power level.

3.2 Raman characterization

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

3.2.1 Graphite and silicon precursor analysis

The Raman spectra reported in Fig. 5A evidence a high quality graphitic material with a low intensity D peak centered at 1350 cm^{-1} and an intense narrow G peak centered at 1572 cm^{-1}. These peaks are very well separated and the I_D/I_G (= 0.16) ratio is typical of high quality graphite [51]. This observation is supported by the following additional facts: 2D peak (around 2700 cm^{-1}) is strong and intense, left shouldered and typical of multi-layered graphite; D+G Overtone peak (~2920 cm^{-1}) is absent; and 2G peak at 3230 cm^{-1} is weak and sharp.
The crystalline silicon Raman Spectra reported in Fig. 5B shows, as expected, an intense and very narrow peak centered at 520 cm^{-1}, and a broad band just below around 965 cm^{-1} [52].

3.2.2 P30 Sample Raman Analysis

Fig. 6 is an optical image showing the grey (Fig. 6A), the white (Fig. 6B) and the black (Fig. 6C) areas where the Raman spectra were measured.
Two different points were sampled both in the white and black zones of the material while spectra from four different points were acquired in the grey zones. All Raman spectra displayed in the figures have been background subtracted.

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

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

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

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

3.2.3 P75 sample Raman analysis

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

The measured Raman spectra were reported after the background subtraction.

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

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

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

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

In order to support the meaningfulness of the approach used in this paper, a Raman mapping of sample P75 has been performed (Fig. 10). Fig. 10A shows the mapped region (50µm x 70µm) obtained using the optical microscope. This area is divided into several points; the spectra are acquired sequentially from this range of points, across the specified area of interest. Figure 10B

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

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

3.3 X-ray diffraction

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

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

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

The chemical composition of the starting preform (Table 1) evidences the presence of a low but not negligible amount of glassy carbon, which is a non-graphite form of carbon having a microstructural disorder between that of amorphous carbon and single-crystal graphite [55]. The XRD spectrum of glassy carbon usually shows broad peaks at 2theta values typical of graphite peaks [56]. No broad peaks are present in XRD spectra of C-Si-SiC materials (Fig. 11). This can be explained considering that the high temperature reached during the infiltration process should allow the development from a glassy carbon structure into a graphite-like layer structure. This implies an increment of crystal structure order highlighted by the narrowing of the diffraction peaks [56,57].

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

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 ± 24 MPa for P30 is lower with respect to 160 ± 16 MPa and 177 ± 11 MPa values obtained for P60 and P75 respectively. These values are comparable to those reported for commercially available SUPERSiC® material (bending strength ~ 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.

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

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

4. Discussion

Graphite-Si-SiC ceramics were obtained by reactive infiltration of liquid silicon into graphite-based preforms. Starting from large blocks graphite was ground to obtain micrometer size particles; this introduced defects and enlarges its reacting surface area. Ground graphite is in fact far from its theoretical lattice stacking; many defects are present such as decreasing crystalline order, dangling bonds, irregular bond angles and angstrom-scale porosity [61]. These defects are directly related to the concentration and the accessibility of "active sites", which enhance the chemical reactivity of carbon making the infiltration process difficult.

The process was assisted by microwaves, which provide a fast heating of the starting materials allowing to reduce both the consumption of energy and the processing time with respect to conventional heating. Three sets of samples were prepared by varying the microwave power: P30, P60 and P75 specimens were in fact produced by using a power of 30 %, 60 % and 75 % of the full power respectively.

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

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

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

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

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

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

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

5. Conclusions

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

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

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Tables

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

	Graphite [wt%]	**Phenolic resin [wt%]**	**Glassy carbon [wt%]**
Before pyrolysis	88.50	11.50	0
After pyrolysis	94.25	0	5.75

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

		Si ($520\ cm^{-1}$)		**SiC** ($790\ cm^{-1}$)		**D** ($1350\ cm^{-1}$)		**G** ($1590\ cm^{-1}$)		**Peak Ratio**		
		Center	Width	Center	Width	Center	Width	Center	Width	SiC/Si	SiC/G	**D/G**
Si		520	2	0	0	0	0	0	0	0	----	----
Graphite		0	0	0	0	1349	23	1575	8	----	0	0.17
P30	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
	Grey	519	11	793	5	1346	20	1578	17	0.01	0.02	0.98
P75	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