Ultra-rapid, sustainable and selective synthesis of silicon carbide powders and nanomaterials via microwave heating

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Silicon carbide has been synthesised from silicon or silica combined with activated carbon or graphite via microwave heating over timescales from minutes to seconds without the need for inert atmospheres or subsequent purification. The carbide morphology and phase purity can be controlled by the microwave cavity used and the power applied and hence by the heating rate. Short irradiation times (ca. 5 minutes) in a multimode cavity using activated carbon produce single phase β-SiC nanofibres as small as 5 nm in diameter while large crystallites of α- and β-SiC can obtained in ≤1 minute using high power, single mode cavity microwave techniques.

1. Introduction
Silicon carbide, SiC, is one of the most important industrial ceramics in the world today. It finds multiple applications, for example, in refractory and structural ceramic components, coatings, abrasives, composites and as semiconducting thin films for high power/high frequency devices (for example, β-SiC (3C-SiC) has an indirect band gap of 2.2 eV at 300 K, whereas 4H- and 6H-SiC possess gaps of 3.26 and 3.02 eV respectively).1–4 Most applications have traditionally exploited unique high temperature properties such as high hardness and strength, and extreme resistance to wear and thermal shock.4 Increasingly, however, polymorphs of SiC have been proposed and studied in an energy context. Notably β-SiC is under investigation as the basis of an impurity photovoltaic,5 amorphous hydrogenated SiC has been tested as a window in increased efficiency silicon solar cells6 and the carbide has been demonstrated recently to act as a matrix for silicon nanoparticles towards the realisation of an all-silicon tandem cell.7 Additionally SiC has been investigated as a blue LED for solid state lighting8 as a nanocomposite anode with Si for lithium ion batteries9 and in composites for fusion power plants.10 Applications of SiC depend strongly on how it is synthesised and processed. The commercial Acheson process is basically unchanged after more than a century; a high temperature reduction reaction between high purity silica sand and carbon in an electric furnace.11 Finding an alternative method to reduce energy expenditure and processing time was one driver behind the many studies of microwave (MW) preparations of SiC. This becomes especially topical and urgent as industry aims

Broader context
The need to produce materials via routes that are energy efficient and sustainable has become a high priority in the 21st century. Traditionally, the processing of ceramics has been energy intensive, demanding extreme temperatures and long treatment times. Microwave processing is one alternative approach. Carbides are materials that lend themselves well to this approach since carbon is an excellent microwave susceptor. Silicon carbide, SiC, is arguably the most important non-oxide ceramic with an established history as an industrially important structural material. Now, however, SiC is emerging as a highly promising and versatile sustainable energy material with potential applications in solar cells, low energy lighting, lithium ion batteries and as composites in fusion power plants among others. These applications require control of both crystal structure and nanostructure. In this contribution we discover that not only can pure SiC be prepared in air in second timescales but also that the phase behaviour and morphology of the sample can be modified via the form of the microwave cavity and the incident microwave power. One can switch between high aspect ratio nanofibres (from 5 nm in diameter) to crystallites many microns across, primarily as a function of heating rate and reaction temperature.

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to adopt sustainable production methods in the face of growing environmental concerns and to develop an economy less reliant on fossil fuels.

Previous MW synthetic work showed that synthesis time for SiC could be cut by orders of magnitude over the Acheson process. Among challenges that remain to be overcome are: (i) to remove subsequent purification steps, post-synthesis, (ii) to design reactions that do not require reactive or cover gas environments and (iii) to reduce synthesis times (and energy expenditure) still further so that energy-efficient, continuous manufacturing becomes a possibility. We showed previously that it is possible to prepare refractory and superconducting transition metal carbides in air over second timescales using high power MWs. Here we demonstrate facile routes to synthesize β-SiC in air from Si (or SiO₂) using a multimode microwave cavity on minute timescales (≤5 min), addressing point (ii) above. We further demonstrate, for the first time, how reactions to pure SiC—addressing point (i) above—can be accomplished over second timescales (addressing point (iii)) by exploiting more sophisticated higher power MW methods (also in air). Beyond tackling these challenges of increasing product purity, reducing processing complexity (and cost) and cutting processing times, we clearly demonstrate how the morphology of the products from MW syntheses can be controlled via the mode of heating. Further we demonstrate how these approaches can be employed towards phase-selective synthesis of the cubic and hexagonal polymorphs of SiC.

2. Experimental

Multimode cavity (MMC) reactor microwave syntheses

Stoichiometric amounts of silicon (Sigma-Aldrich, 99%) and activated carbon (MAST Carbon Ltd.) (1 : 1 molar ratio; typical total sample mass of 0.265 g) were ground in a ball mill for 8 hours (Retsch PM100, 450 rpm). Selected samples underwent the same procedure replacing activated carbon with graphite (Aldrich, powder, <20 μm, synthetic). Further, silica, SiO₂ (Aldrich, 325 mesh, 99.6% metal basis), was used as a reactant with activated carbon (1 : 3 molar ratio; typical sample total mass 0.265 g) and the above procedure repeated. The mixed powders were either cold pressed uniaxially in an 8 mm pellet die (Specac, 5 tons, 10 min) dry or mixed with distilled water (either 0.15 ml or 0.2 ml) to form a thick slurry before pressing (otherwise as above). The pressed pellets were embedded in graphite (acting as an MW susceptor) in an open, 10 mm silica tube which was surrounded with low dielectric loss silica flour (Aldrich, 99.6%) (Fig. 1).

Synthesis was conducted in a multimode cavity (MMC) fed with an 800 W magnetron and operating at 2.45 GHz. No impedance matching device was employed due to the low Q factor of the cavity. All preparations were performed at ambient pressure in air. Conditions for selected samples are summarised in Table 1.

High power single mode cavity (SMC) reactor microwave syntheses

Elemental powders of Si (Sigma-Aldrich, 99%) and graphite (Sigma-Aldrich, powder, <20 μm, synthetic) (1 : 1 ratios; 0.25 g total) were ground together and pressed into 8 mm diameter pellets which were set in graphite susceptor in an open, 10 mm diameter quartz tube. The tube was placed in a silica beaker and packed with ground silica sand in order to maintain the tube in an upright position. A series of synthesis experiments were run in a TE₁₀,ₐ single mode cavity (Fig. 2). A single mode cavity differs from a traditional MMC as the presence of only one mode gives rise to very high and localized electric field intensities which are well defined in space. This definition allows the placement of the sample to be treated in the point of highest electric field. The field pattern is created by the superposition of the incident and reflected wave and is achieved through careful adjustment of a short circuit beyond the applicator. Impedance matching, required to minimize reflected power was performed using a SAIREM automatic E-h tuner. The cavity was excited using a 3–15 kW SAIREM GMP 150 SM microwave generator operating at 2.45 GHz. The generator was adjusted to produce 3 kW of microwave power over the duration of the treatments. A representative range of synthesis conditions explored in SMC experiments is described in Table 2.

Temperature readings were taken in situ using an optical pyrometer (LAND System4 Thermometer M1 600/1600 °C; ± 1 °C accuracy) with a 5 mm diameter spot centred on the sample surface. The wavelength (1 μm) of the instrument was

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**Table 1** Selected MMC samples and reaction conditions

<table>
<thead>
<tr>
<th>Sample identifier</th>
<th>1</th>
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<sup>a</sup> Activated carbon. <sup>b</sup> Graphite.
deliberately selected to minimize errors. The measurements were corrected for emissivity in the internal software of the pyrometer controller and a value of 0.7 was chosen for emissivity based on evaluation of the literature.

Characterisation

After reaction the product formed was characterized using powder X-ray diffraction (PXD) (PANalytical Xpert MPD, Cu Kα1 radiation). Initially data were used to (i) identify product phases by reference to the ICDD PDF database using the PANalytical program X’pert HighScore Plus and (ii) to derive cell parameters for Si-C phases by least squares fitting. Crystallographic parameters and quantitative phase fractions of crystalline components were obtained by Rietveld refinement against PXD data (collected for 2–12 h over a range of 5 < 2θ/C14 < 85 with a step size of 0.017/C142) for each dataset (using GSAS and EXPGUI packages16,17).

Raman spectra were collected at room temperature using a Horiba LabRAM HR confocal microscope system with a 532 nm green laser. A hole aperture of 50 m, 600 g mm−1 grating and a Synapse CCD detector were used.

Field emission scanning electron microscopy (FESEM) was conducted under high-vacuum conditions using a Hitachi S4700 microscope with 10 kV accelerating voltage and secondary electron detection to study the morphology of the sample. Transmission electron microscopy was performed using a FEI Tecnai T20 (FEI, Eindhoven, Netherlands) operated at 200 kV acceleration voltage using a LaB6 filament with images recorded using a Megaview III CCD camera (Olympus SIS GmbH, Garching, Germany). Conventional bright field and dark field diffraction contrast imaging was used in combination with selected area diffraction to characterize the nanostructure and relate this to the crystallography of the nanofibres. Samples for SEM of sufficient thickness were prepared by depositing powder on to a carbon tab. Samples for TEM were prepared by sonicating the powders in ethanol and then pipetting drops of the suspension onto holey carbon film Cu grids.

3. Results and discussion

MMC syntheses

The success of sample preparation was intimately dependent on the use of the water binder. With graphite as a carbon source, dry-pressed powders proved to be the only way of obtaining pellets that maintained their integrity during pressing; addition of any volume of water in these cases (even <0.15 ml) produced thin suspension-like slurries which could not be contained adequately in the pellet die. Even dry samples, however, were difficult to press. Samples prepared from activated carbon could be pressed dry or using various volumes of added water. However, those pressed dry showed no evidence of reaction. Of the activated carbon samples pressed with a water binder, those samples using silicon were most easily handled with smaller water volumes, while for those pressed with silica, the reverse was the case. Optimum conditions for the reagents used are reflected by samples 1–13 (Tables 1 and 2), which consistently produced carbide products and will be the main focus hereafter. We will return to the effects of added water in the discussion below.

PXD of samples prepared from silicon and activated carbon, 1–5, illustrate that close to single phase β-SiC (99 wt% by Rietveld refinement) can be synthesized in air after only 2 min (Fig. 3). We note, in fact, that graphite reflections are almost certainly from surrounding susceptor powder that was not successfully removed from the product pellet since control experiments in which activated carbon was heated alone do not yield graphite by PXD. No silica reflections were evident for any irradiation times. At 5 min and above, diffractograms were present for the β-SiC samples synthesized from Si + C in a MMC: (a) 1, (1 min irradiation time); (b) 2 (2 min); (c) 3 (3 min); (d) 4 (5 min); (e) 5 (10 min). Reflections from graphite (●) are also indicated.
obtained that clearly demonstrated that it is possible to produce β-SiC as a single phase material.

Pellets produced with graphite, 6–8, always fractured during reaction in the MMC reactor, tended to disintegrate and were difficult to recover. Powder patterns from these Si + C samples always contained graphite peaks, even after relatively long irradiation times. Further, only at long irradiation times (e.g. 8) was there no evidence of residual silicon. As with the activated carbon reactions above, no silica reflections were evident for any of the irradiation times employed.

When silicon was replaced by silica in reactions with activated carbon (9–13), it was immediately obvious that (at times violent) pellet fracturing was prevalent during the course of reactions commensurate with the evolution of gas. Further, the observation of plasma in the open tubes would also suggest gaseous evolution of products as might be expected from the oxide starting material. Ex situ PXD revealed that the course of these reactions was much more complex than that of reactions from Si + C. As can be seen in Fig. 4, reactions at relatively short irradiation times yield β-SiC as the major phase. After 3 minutes (9) this is accompanied by graphite (possibly again from residual susceptor material) and SiO₂ (both quartz and cristobalite). By 5 minutes (10), SiO₂ phases are almost negligible but at extended irradiation times (11, 12) the silicon dioxide phases (both quartz and cristobalite and predominantly the former) increase in phase fraction and the phase fraction of carbide diminishes.

Rietveld refinements for the Si + activated carbon samples, 1–5, were performed using the zinc blende structure of β-SiC as a starting model. The background (modelled using a reciprocal intercalation function; function 8 within GSAS), scale factor, zero point and cell parameters were refined in initial cycles. Peak widths and profile coefficients (peak shape was modelled using the Thompson-Cox-Hastings pseudo Voigt function; peak shape function 2 within GSAS) and isotropic temperature factors were subsequently refined. Ensuring that all observed reflections were fitted, graphite was input as a secondary phase where relevant and phase fractions refined. Attempts to refine the occupancy of the C site in β-SiC resulted in site occupancy factors (SOFs) that fluctuated at values slightly in excess of unity and hence the SOF was set at 1. Attempts to include oxygen or nitrogen on the C site also produced physically meaningless values and did not improve the quality of the fit. All refinements converged smoothly in final cycles. Data for 1–5 clearly demonstrate that the structure and stoichiometry of the carbide are invariant with time (e.g. Table 3 for 1, 2 and 4; Fig. 3 and 5). The cubic lattice parameter is in excellent agreement with literature values as are the Si–C and Si–Si distances (1.8877(2) Å and 3.0826 (2) Å respectively). We find no evidence of oxygen-inclusion in the bulk material. This is corroborated by semi-quantitative EDX data which confirm only Si and C are present.

SEM images for silicon + activated carbon samples show that 1 min reactions (1) yield submicron sized irregular particles (of the order of 50–100 nm across) partially fused together to form a porous matrix (Fig. 6a). Reactions beyond 1 min yield significant reductions in particle size and increased particle anisotropy, culminating in the growth of SiC nanofibres. Between 2 and 5 min (2–4), the samples are dominated by colonies of nanofibres appearing to grow between clusters of nanoparticles (nanofibres from 2 are shown in Fig. 6b). EDX data from spot and area scans suggest that all these samples (1–5) contain Si and C only.

Evident from the SEM images of 2–5 is that the nanofibres in these samples are typically of high aspect ratio, measuring from 5–30 nm in diameter and exhibiting lengths of the order of 2–20 μm. There is neither any significant change in the yield of nanofibres nor of the structure of the nanofibres as irradiation times increases across samples 2–5. Interestingly, if the volume of added water is increased, nanofibres are not observed until

<table>
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<th>Table 3 Crystallographic data from Rietveld refinements against PXD data. Shown are data for 1, 2 and 4</th>
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<td><strong>C 4c (¼,¼,¼), Uiso</strong></td>
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<td><strong>Rwp</strong></td>
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<td><strong>X²</strong></td>
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irradiation times of 5 minutes or greater. Further, yields of fibres are lower and both the particles and fibres themselves are of larger dimensions than those prevalent in 2–5. The volume of water binder, therefore, appears quite critical to nanofibre growth.

When graphite is substituted for activated carbon as the carbon source, SEM micrographs reveal that particles similar in habit to those seen at short reaction times with activated carbon (e.g. 1: Fig. 6a) are formed, but in contrast to the activated carbon samples, the size distribution of the particles is not nearly as uniform (commonly agglomerations of particles from ca. 200 nm to 1–2 μm across). Nanofibre formation is never observed in graphite samples whether from short (3 min; 6) or long (30 min; 8) irradiation times. Similarly micrographs from silica + carbon reactions (9–12) show no evidence for nanofibre formation, although agglomerates of particles typically 100–200 nm across are observed at short irradiation times (9 and 10).

Raman spectra of 1–5 exhibit a very strong band at ca. 790 cm\(^{-1}\) corresponding to the Transverse Optical (TO) Brillouin zone centre Raman-active mode in β-SiC (3C-polymorph; zinc blende structure).\(^{19,20}\) Nanostructured samples (for example, 2–5) show additional weaker bands at ca. 520–535 cm\(^{-1}\) and a shoulder on the strongest TO band (ca. 760 cm\(^{-1}\)) which could be attributed to acoustic (transverse and longitudinal) phonon modes and TO (from points of the Brillouin zone other than the centre) phonon mode scattering respectively. Broad features from 850–980 cm\(^{-1}\) can be attributed to Longitudinal Optical (LO) modes. Collectively these latter bands originating from acoustic phonon, TO and LO modes are associated with stacking faults often presaging formation of the 4H polytype of α-SiC,\(^{21}\) but equally are a feature of β-SiC nanofibres (particularly those in the lower size range) as noted below in the discussion of the TEM data. Peaks observed at higher wavenumber in some samples (ca. 1350 cm\(^{-1}\) and 1580 cm\(^{-1}\)) likely originate from residual graphite powder susceptor consistent with patterns obtained from PXD. By way of example, the Raman spectrum of 5 is shown in Fig. 7.

The details of the nanostructure of the nanofibres are revealed using transmission electron microscopy (TEM) as shown in Fig. 8. Fibres a few 10 s of nm in thickness are frequently observed and dark field imaging using suitable reflections frequently reveals a parallel striped structure within each wire, with the stripes having an irregular spacing of the order of a few nanometres as shown in Fig. 8a. Comparison with diffraction patterns (e.g. Fig. 8b) reveals that the stripes always run perpendicular to \{111\} directions. Moreover, the growth direction is always along a \{111\} direction. Higher magnification images, as shown in Fig. 8c, show that the stripes are a result of twinning on \{111\} planes of the β-SiC structure, in this case perpendicular to the growth direction. This frequent planar faulting also manifests itself as streaks in diffraction patterns perpendicular to the stripes, as shown in the diffraction pattern of Fig. 8b. It is clear from this that the SiC forms nanowires with frequent twinning, but that the twinning is neither frequent nor regular enough that this qualifies as a specific polytype other than β-SiC. Stacking faults and \{111\} twins are, in fact, relatively well documented in β-SiC nanofibres, especially in fibres of diameters of the order of 10 s of nm, including those that have been synthesised previously via microwave plasma CVD or vapour transport methods.\(^{22–24}\) These planar defects have been associated with the growth process itself rather than with a phase transition to one of the hexagonal SiC polytypes, irrespective of
whether, for example, the carbide nanofibres grow via a Vapour–Liquid (VL) or Vapour–Liquid–Solid (VLS) mechanism.

SMC syntheses

Results from syntheses performed in the TE10 SMC reactor demonstrated that under these conditions graphite could be successfully used as a source of carbon and synthesis times could be improved at least ten-fold from the fastest reactions in the MMC. PXD demonstrated that phase-pure $\beta$-SiC was obtained from a dry pellet of Si + C (graphite) after 20 s ($14$; Fig. 9a). Reactions performed at 10 s ($13$) produced $\beta$-SiC but from PXD samples contained graphite as a minority phase (ca. 15 wt%). Reactions for longer periods (e.g. 20 s, 40 s; $14, 15$) yielded $\beta$-SiC with 6H-SiC ($\alpha$-SiC) present as a secondary phase (17.1(1) wt% from Rietveld refinement against PXD data for $14$, for example). In situ optical pyrometer measurements taken during the course of reactions afforded temperatures in excess of 1873 K. The heating rate over the course of these reactions exceeds 500 K s$^{-1}$. SEM images of $14$ (Fig. 9b) demonstrate a striking contrast to those from samples made in the MMC (Fig. 6) with products composed of well-formed, faceted crystallites 5–10 µm or more across. Increasing the irradiation time leads to further crystal growth; crystallites of $15$ were typically 20 µm across. These observations suggest that the strongly contrasting heating rate in the different cavities supports the formation of different product morphologies.

Consideration of the effect of the carbon source on the SMC reactions leads to two interesting observations. First when activated carbon replaces graphite the crystallite size of the carbide product appears reproducibly smaller for approximately equivalent irradiation times. No nanocrystalline products, either particles or fibres, are observed, however, for any durations (in contrast to MMC reactions). Second, for longer irradiation times (for example, samples $17$ and $18$, therefore) SiC products contain not only $\beta$-SiC (i.e. 3C-SiC) but also appreciable 6H-SiC as a secondary phase ($\geq 20$ wt%). Optical pyrometry evidenced that both the heating and cooling rates in the SMC Si + activated carbon reactions ($16–18$) were extremely high. Activated (disordered, amorphous) carbon typically couples more efficiently to MWs than graphite achieving higher heating rates and peak temperatures.$^{25}$ It seems likely that these factors favour the formation of metastable 6H-SiC. Increasing the applied power and/or optimising the cavity could therefore be exploited to maximise the heating rate and the reaction temperature and in principle enable hexagonal polymorphs of SiC ("$\alpha$-SiC") to be prepared in preference to the cubic polytype.

Discussion

The reactions to form SiC from elemental Si are relatively straightforward in that the conversion is a 1-step process:

$$\text{Si} + \text{C} \rightarrow \text{SiC} \quad (1)$$

The above reactions in the MMC reactor produce $\beta$-SiC and so one can conclude that that the reaction temperature is predominantly in a regime below 2373 K.$^{26}$ However, and as corroborated by Raman spectra and the presence of a shoulder on the leading edge of the $\beta$-SiC (111) PXD reflection, the direct

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Fig. 7 The Raman spectrum of $5$, a, b, c and d denote bands originating from acoustic phonon modes, non-zone centre and Brillouin zone centre transverse optical modes and longitudinal optical modes respectively.

Fig. 8 TEM micrographs of $\beta$-SiC nanofibres ($2$) synthesised in a MMC from Si + C showing (a) dark field image of a nanowire exhibiting frequent twinning, (b) [011] selected area diffraction from the right hand end of this nanowire and (c) higher magnification bright field image of a SiC nanowire demonstrating frequent twinning perpendicular to the growth direction.

Fig. 9 (a) PXD pattern and (b) SEM micrograph of SiC (including 17 wt% 6H-SiC) synthesised in the single mode MW reactor by irradiation at 3 kW for 20 s ($14$).
observation of twinning in the TEM images and streaking in the SAED patterns implies stacking faults associated with nanostructured β-SiC and/or the eventual transition to α-SiC polymorphs. For SMC reactions in particular where only relatively large carbide crystallites are observed, the latter explanation for defects is more likely and hence a peak temperature in excess of 2373 K is plausible. Previous reports have suggested that, in fact, reaction (1) conventionally proceeds via the dissolution of carbon in liquid Si and precipitation of SiC from the supersaturated melt. Si melts at 1687 K (below the peak temperature recorded in SMC syntheses) and it is therefore possible that a similar process occurs in a microwave field, although we have no direct evidence from analysis of samples at short reaction times that this is the case.

It is well established that the power dissipated in the material (or power density) is proportional to the electric field strength inside the material squared. Which in turn is a function of the cavity dimensions and design. The comparative use of an MMC and a SMC gives rise to the creation of power densities orders of magnitude apart. Electron micrographs of material processed in the MMC indicate that fibres grow at the interfaces between particles. It is postulated here that the reason for this is the enhanced heating rates at such interfaces as a result of Maxwell Wagner or interfacial polarisation. Such effects create highly localised and selective temperature rises which may explain the formation of the SiC nanowire structures, possibly crystallising and growing from molten silicon as carbon is dissolved. In this respect, the use of a binder would appear to be essential to enable both reaction and nanofibre growth to occur in the MMC environment. The binder is integral in achieving intimate mixing and allowing the intergrain void space to be minimised as a result of successful pelleting. Although, for example, all syntheses involving silicon and carbon were ball milled prior to mixing, the inherent smaller particle size and higher surface area of the activated carbon over graphite (confirmed by SEM micrographs of the starting materials) also acts so as to maximise interfacial contact on mixing and pressing. Hence it is not surprising that a combination of activated carbon and binder provides the optimum conditions for nanofibre growth. Further, if our postulate of Maxwell Wagner polarisation is indeed correct, one can understand how the MMC reactions employing water bound Si + activated carbon lead to pure β-SiC in much shorter reaction times than equivalent dry pressed Si + graphite preparations. It is even possible that water, as a polar, liquid MW susceptor, acts so as to promote initial local dielectric heating at grain boundaries. Interestingly if the water volume is increased then the beneficial binding effects begin to be countered (increased reaction times). We also see similar detrimental effects on reaction time and phase purity in preliminary experiments in which other solvents of varying polarity and viscosity (e.g. acetone, ethylene glycol) replace water. These alternative solvent experiments are being investigated further by us for a wider range of liquids, but the role of water as primarily a binder would appear to be corroborated in that the loss tangents of ethylene glycol (1.350) and acetone (0.054) are respectively greater and less than that of water (0.123). In MMC syntheses without a binder, reaction from Si and C to SiC does not proceed to completion despite the excellent and well-documented MW susceptor properties of both graphite and activated carbon. This suggests that the power density inside the material is insufficient to enable the reaction temperature to be reached. By contrast complete reaction in the SMC is possible using graphite and without using a binder. This would lend weight to the supposition that higher reaction temperatures are achieved in the SMC and that reaction occurs via a liquid Si melt (producing larger β-SiC crystallites as a result). During our experiments we noted that the reflected power was high during the initial 1–2 s of the experiment. However, after 2 s the reflected power dropped to essentially zero indicating that the dielectric loss had increased to the point that very high coupling efficiency occurred. Almost certainly this will be consistent with melting of the materials present and the induction of thermal runaway in the material. This behavior is consistent with the dielectric properties of SiC as measured by cavity perturbation. The dielectric loss of SiC begins to increase dramatically at 1200 °C in these studies rationalising observations of thermal runaway.

In both MMC and SMC syntheses from Si + C the presence of surrounding graphite is pivotal not only as a MW susceptor but also as a reductant providing a low partial pressure of O2 in the environment surrounding the reaction. In the former context, the MW reactions are driven by the MW susceptibility of the carbon reactant and surrounding graphite; silicon being lower loss than graphite. That these reactions can be performed in air is important in terms of designing convenient and relatively inexpensive scaled-up processes.

By contrast to the Si + C case and as has been documented previously, the reactions to SiC from SiO2 and C ideally follow two steps:

\[ \text{SiO}_2 + C \rightarrow \text{SiO} + \text{CO} \]  

(2)

\[ \text{SiO} + 2\text{C} \rightarrow \text{SiC} + \text{CO} \]  

(3)

Notable, therefore is that the first step is a reduction and the second a reduction–carburisation and that each step requires the evolution of gaseous products; SiO, CO in reaction (2) and CO in reaction (3). Also well established in the literature is that a side reaction can occur in the solid state (at ca. 1400 °C) between remaining SiO2 and SiC as it forms:

\[ \text{SiC} + 2\text{SiO}_2 \rightarrow 3\text{SiO} + \text{CO} \]  

(4)

From our ex situ PXD evidence, it is apparent that despite initial fast formation of β-SiC (9 and 10), at longer irradiation times the relative yield of the carbide is diminished (11 and 12). This would support the initial generation of carbide by reaction (2) and reaction (3) and subsequent solid state reaction under reaction (4). That at longer irradiation times diffraction patterns are dominated by SiO2 (and crystalline carbon phases are absent) suggests that gaseous SiO generated by reaction (4)—and reaction (2)—reacts with air to oxidise to SiO2. Despite the surrounding graphite, this is not unlikely since the other observation in the SMC SiO2 + C reaction is that high localised gas pressures (from SiO and CO) are generated very quickly disintegrating the pellet and scattering graphite susceptor, exposing the sample to air. The importance of controlling the gaseous environment and especially the SiO and CO partial pressures has...
been stressed previously in synthesis of SiC from SiO$_2$.\textsuperscript{34} It remains a challenge to perform synthesis of single phase SiC in the SMC from SiO$_2$ in air.

4. Conclusions

In summary, we have reported the synthesis of high purity $\beta$-SiC in air in timescales from 5 min to 20 s. The selection of Si and C sources, the use of water as a binder and the choice of applied MW source (power, cavity) are variables that can be harnessed successfully to control carbide purity and processing time. Significantly, the mode and therefore the rate of MW heating can be exploited to dictate the carbide morphology from nanowires to large crystallites. Potentially, also, one can exert a similar control over phase behaviour from $\beta$-SiC (3C-SiC) to the various $\alpha$-SiC polymorphs (e.g. 6H-, 4H-SiC). Such a degree of control (under energy-efficient conditions) is important in designing materials with tailorable structural and functional properties and vital if SiC is to achieve its potential in a host of new energy-focused applications. These outcomes can be understood broadly in terms of the reaction chemistry and microwave interactions but it is clear that the key to gaining complete control over phase formation, crystal growth and to understanding reaction mechanism will be via state-of-the-art in-situ measurement techniques. Such studies offer the best opportunities for progress towards designing scaled-up flow processes.

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References