Synthesis of graphite by chlorination of iron carbide at moderate temperatures

Svetlana Dimovski, Alexei Nikitin, Haihui Ye and Yury Gogotsi*

Drexel University, Department of Materials Science and Engineering and A. J. Drexel Nanotechnology Institute, Philadelphia, Pennsylvania, 19104, USA.
E-mail: gogotsi@drexel.edu; Fax: 1 215 895 6760; Tel: 1 215 895 6446

Received 29th September 2003, Accepted 27th October 2003
First published as an Advance Article on the web 12th November 2003

Synthesis of graphite by extraction of iron from iron carbide by chlorine is reported in this work. This process is attractive because it can produce well-ordered graphite at temperatures as low as 600 °C, providing an opportunity for low-temperature solid-state synthesis. Thermodynamic simulation was used to determine the composition of the reaction products under equilibrium conditions and select the initial process parameters such as temperature and chlorine/carbide molar ratio. The interlayer spacing and crystal size of the produced graphite were calculated from X-ray diffraction measurements. The degree of orientation of the graphitic layers was determined by Raman spectroscopy. Three temperature regimes have been identified. At temperatures below 500 °C, amorphous or disordered carbon is formed as shown by Raman spectroscopy and TEM studies. Well-ordered graphite microcrystals are formed by solid-state growth between 600 and 1100 °C. Above the eutectic temperature in the Fe3C-SiC system, 1130 °C, the growth of large graphite crystals occurs from the liquid phase, similar to the formation of kish graphite by precipitation of carbon at high temperatures from supersaturated molten iron. Iron chlorides, the main impurities in the material synthesized by the solid-state growth, can be removed by using excess chlorine gas or by a separate wet chemical purification step. Preparation of graphite doped with iron for catalytic purposes is also possible using this process.

1 Introduction

It has been previously shown that selective etching of carbides is an attractive technique for the synthesis of various carbon structures. Carbon produced by extraction of metals from carbides is denoted carbide-derived carbon (CDC).1 Leaching in supercritical water,2,4 high-temperature treatment in halogens5 and vacuum decomposition can be used to remove metals from carbides, producing carbon coatings, powders or bulk shapes. In order for the chlorination reaction to proceed, molecules of Cl2 (g) must be transported to the carbide/carbon interface and molecules of metal chloride must be transported away. Linear reaction kinetics have been demonstrated for the chlorination of SiC6 implying that the carbon film is nanoporous and allows easy permeation of Cl2 molecules. This phenomenon allows transformation of a carbide particle or a bulk component to any depth until it is fully converted to carbon. The CDC formed by selective etching in halogens demonstrate a variety of carbon structures depending on experimental conditions. Amorphous and nanocrystalline graphitic carbon,6 nanotube-like structures of and nanocrystalline diamond6 have all been reported. However, ordered graphite was only found in small amounts as a thin film on the surface of SiC crystals.10 Very high temperatures, exceeding 2500 °C and even approaching 3000 °C, are usually required for solid state synthesis of graphite.11 It is also known that metals of the iron subgroup can catalyze graphite growth. This has been demonstrated in the synthesis of graphite crystals (kish graphite) from molten iron supersaturated with carbon, in which graphite flakes are formed either during cooling of the melt or by evaporation of iron.12 An increased degree of graphitization in CDC produced by chlorination of TiC in the presence of small amounts of Fe, Ni and Co has been recently demonstrated.13 However, the interaction of iron carbide with chlorine or other halogens has not been reported in the literature. This paper describes the formation and evolution of graphite in CDC produced by extraction of iron from iron carbide using chlorine gas.

2 Materials and experimental

2.1 Materials

Iron carbide powder for this study was provided by Hazen Research, Inc. Chlorination experiments were done on the as-received powder. Scanning electron microscopy, energy-dispersive X-ray spectroscopy (EDS), wide angle powder X-ray diffraction (XRD), and Raman spectroscopy analyses were conducted to characterize the original material. The average particle size was measured to be ~0.5 μm. These particles form grain-like iron carbide clusters (av. size ~350 μm). The XRD pattern fully matches that of synthetic Fe3C (ICDD file 35-0772), and no other compounds were detected in the raw powder. EDS analysis showed traces of oxygen, probably originating in the very thin surface layer of intrinsic iron oxide and/or CO2 and water absorbed from the air, and aluminium, most likely from the sample holder.

Chlorine (BOC Gases, 99.5%) was dried with concentrated sulfuric acid and anhydrous calcium sulfate. Purging was done with 99.998% pure argon (BOC Gases).

2.2 Thermodynamic simulation

The ChemSage v4.14 advanced SOLGASMIX-based Gibbs energy minimization program from GTT, Germany, was used to estimate equilibrium amounts of reaction species as functions of the incoming amount of chlorine gas (per mol of Fe3C) and chlorination temperature for different amounts of chlorine. The calculations were done for a closed system with a constant total pressure. The solid phase was treated as a mechanical mixture of compounds with unit activities, and the gas phase was considered a mixture of ideal gases.
2.3 Synthesis
The apparatus used to treat Fe₃C with chlorine at atmospheric pressure has been described elsewhere.¹ In brief, Fe₃C was loaded in a quartz boat and placed in a horizontal quartz tube reactor, which was purged with argon gas until the desired reaction temperature was reached. The sample was then exposed to flowing Cl₂ gas for 3 h, and purged again with argon during the cooling period, as described in refs. 1 and 14. Constant reaction temperature and gas flow rate were maintained during a single experimental run. The interaction of iron carbide with chlorine at temperatures ranging from 400 to 1200 °C was investigated; other parameters were fixed during all runs. Carbon collected from the quartz boat was purified, when necessary, by washing away residual impurities with 10% HCl followed double distilled water three times in sequence, and dried carefully at a temperature of about 100–150 °C.

2.4 Characterization
The chlorinated samples were analyzed using a Philips XL-30 environmental field-emission (FE) SEM. SEM analysis was always accompanied by EDS analysis to verify that the analyzed material was carbon. TEM samples were prepared by dispersing the synthesis products in isopropyl alcohol over a copper grid with a lacey carbon film, and transmission electron microscopy (TEM) analysis was performed using a JEOL JEM-2010F (200 kV). A Gatan image filter for energy filtered imaging and electron energy loss spectroscopy (EELS) was used to identify carbon areas and impurities. Raman microspectroscopy (Renishaw 1000) with the excitation wavelength of 514.5 nm (Ar ion laser) with a range of 800–2000 cm⁻¹ and exposure time of 10 s was used to analyze the degree of carbon ordering. The spectra were collected from at least five different points of each sample with a 2-μm spot size. Low laser power was applied to avoid damaging and heating the sample. GRAMS 32 v5.2 spectral analysis software was used for peak fitting and deconvolution. The in-plane crystallite size of graphite, \( L_a \), is shown to be inversely proportional to the ratio of D band at 1350 cm⁻¹ and the G band at 1580 cm⁻¹ \( (I_D/I_G) \) ratio. It can be calculated as: \( L_a = 4.4(I_D/I_G)^{-1} \) (nm) according to Tuinstra and Koenig's work for 2.5 nm < \( L_a < 3000 \) nm.

X-Ray diffraction was done using a Siemens D-500 diffractometer utilizing Cu-Kα radiation (1.406 Å). The data were collected as step scans, with a step size of 0.05° (2θ) and a count time of 2 s step⁻¹ between 10 and 80° (2θ).

3 Results and discussion
3.1 Reaction thermodynamics
Since iron chlorides are more thermodynamically stable than CCl₄, at high temperatures chlorine reacts selectively with the metal at the carbide surface by the reactions:

\[
\begin{align*}
\text{Fe}_3\text{C} + 9\text{Cl}_2 &\rightleftharpoons 6\text{FeCl}_3 + 2\text{C} \\
\text{Fe}_3\text{C} + 3\text{Cl}_2 &\rightleftharpoons 3\text{FeCl}_2 + \text{C}
\end{align*}
\]

The formation of chloride dimers such as Fe₂Cl₆ and Fe₂Cl₄ in the gas phase is also possible under certain conditions (Fig. 1). Thermodynamic modeling can be utilized to estimate the effect of various process parameters on CDC formation and predict optimal synthesis conditions.² Thermodynamic analysis shows that a small amount of chlorine (Fig. 1(a) and (b)) results in the formation of solid FeCl₂ in the sample, and that relatively high temperatures (above 1000 °C) are needed to remove iron salts from CDC. Excess chlorine (Fig. 1(a) and (d)), shifts the reaction toward the formation of Fe₂Cl₆(g), while carbon may be consumed to form CCl₄(g) at temperatures below 400 °C. At higher temperatures, CCl₄(g) is not stable, which enables the formation of a solid carbon phase. Intermediate regimes (Fig. 1(c)) result in the removal of iron compounds as gaseous reaction products. However, some solid FeCl₂ may remain in the system. Further reduction of iron from its salts to metallic form.

![Fig. 1 Thermodynamic analysis of iron carbide chlorination: (a) equilibrium amounts of species vs. incoming amount of chlorine gas per mol of Fe₃C at 400 °C, (b)-(d) equilibrium amount of species vs. chlorination temperature for: (b) \( n = 1 \) mol of Cl₂(g), (c) \( n = 4 \) mol of Cl₂(g) and (d) \( n = 8 \) mol of Cl₂(g).](image-url)
iron using H₂ gas may enable the design of CDC-metal catalyst systems. Thermodynamic calculations of the SOLGASMIX type, such as shown here, provide information about closed systems in equilibrium. The experimental system used in this work was an open system and gaseous reaction products were continuously removed with the gas flow, shifting the reaction equilibria (1) and (2) to the right and favoring the formation of carbon. Reaction kinetic limitations also play the role in an actual product composition. Caution must be taken in the interpretation of the thermodynamic calculation results, in which further refinement is clearly possible; however, these results do provide some general guidelines and are generally in good agreement with experimental results. They can be used to predict regimes suitable for the synthesis of CDC from iron carbide.

3.2 Raman spectroscopy analysis

Typical Raman spectra of Fe₃C-derived carbon powders synthesized at various temperatures are shown in Fig. 2. Raman analysis shows that Fe₃C was successfully converted into carbon with various degrees of ordering, depending on the reaction temperature. Three main temperature regimes can be identified here. At temperatures below 500 °C, chlorination yields amorphous or disordered carbon. Broad disorder-induced D (1353 cm⁻¹) and graphite G (1596 cm⁻¹) Raman bands can be found in the spectrum from the sample obtained by chlorination at 400 °C (Fig. 2(a)). A relatively high I₆/I₉ ratio of ~0.90 (Fig. 3), corresponding to in-plane crystalline size of graphite L₆ < 4 nm, indicates that amorphous carbon is produced under these conditions.

Although the D and G bands are the most prominent features in Raman spectra of CDC, the actual Raman scattering data cannot be fitted with two peaks in the case of highly amorphous structures. Such difficulties were observed for Fe₃C-derived CDCs produced below 500 °C. Instead, for an adequate representation of these spectra, three additional broad peaks of relatively low intensities located in the vicinity of 1225 cm⁻¹ (unassigned) 1620 cm⁻¹ (D') and 1500 cm⁻¹ (D'') were included. Peak fitting (Fig. 4) was conducted following the procedure described in ref. 14.

At reaction temperatures of 600–1100 °C, the D and G bands become well-defined and clearly separated (D at ~1353 cm⁻¹, G at 1582 cm⁻¹). In addition, a weak D' band appears as a shoulder around 1620 cm⁻¹ (Fig. 2(b)). The shift of the G peak position towards that of ordered graphite (1582 cm⁻¹) and decrease of its full width at half maximum (FWHM) value to ~35 cm⁻¹ indicates the onset of graphitization. Increasing of the reaction temperature increases the intensity of the G band relative to the intensity of the disorder-induced D band, decreasing the I₆/I₉ ratio from 0.44 (in average) at 600 °C to about 0.13 at 1000 °C (Fig. 3), which corresponds to L₆ ≈ 30–55 nm. For comparison, the I₆/I₉ ratio of CDCs produced from SiC at the same reaction temperature is close to one. Thus, the presence of iron in the system facilitates graphite nucleation and growth at much lower temperatures, which is in agreement with previous publications showing the catalytic effect of iron on graphitization.

Above the eutectic temperature in the iron-Fe₃C system (1130 °C), growth of large graphite plates and flakes occurs from the liquid phase. Here, carbon precipitates in the form of highly ordered graphite crystals from molten iron supersaturated with carbon. The Raman spectrum for chlorination at 1200 °C is shown in Fig. 2(c). The D band disappears, and a very strong and narrow (FWHM = 16 cm⁻¹) G band at 1582 cm⁻¹ shows that perfect graphite crystals are formed under these conditions.

3.3 Powder X-ray diffraction

Typical X-ray diffraction patterns of three different carbon powder samples are shown in Fig. 5. Two 002 and two hkl0 diffraction peaks can be distinguished in the patterns of samples produced at 800 and 1000 °C. The 002 (2θ ≈ 26.9°) and 004 (2θ ≈ 54.9°) peaks correspond to the parallel graphene layers. The 100 (2θ ≈ 43°) and 110 (2θ ≈ 77.8°) diffraction peaks are characteristics of the 2D in-plane symmetry along the
graphene layers. Based on its XRD pattern, the powder synthesized at 500 °C is not graphitized, which is in agreement with Raman analysis. This low-temperature sample also contains traces of iron chlorides.

Further analysis of these XRD profiles showed that the width of the 002 peak decreases as the reaction temperature increases. Its position is approximately the same at both 800 and 1000 °C, which indicates that the graphite interplanar spacing (0.334 nm) is developed in these powders at temperatures as low as 800 °C. This is also in agreement with the TEM and Raman analysis. As the reaction temperature increases, the 10l band also splits into 100 and 101 peaks.

XRD data for selected samples are shown in Table 1. The interplanar spacings, d002 and d004, were evaluated from the positions of the 002 and 004 peaks respectively by applying Bragg’s equation. The crystallite size Lc along the c-axis was calculated from the 002 peak using the Sherrer formula with a value of constant K = 0.9.17 The crystallite size La along the basal planes was calculated from the 100 peak, using the Warren–Bodenstein formula with a value of K = 1.77.18 Lc values of 45–50 nm were obtained from the XRD pattern analysis. They agree with the values of 30–55 nm estimated from the Raman spectroscopy using Tuinstra and Koenig’s equation.

3.4 Scanning and transmission electron microscopy

The effect of the reaction temperature on CDC microstructure is illustrated in Figs. 6 and 7. An SEM micrograph of ‘as-received’ Fe3C is shown in Fig. 6(a). The full conversion of Fe3C to carbon is possible without affecting the original Fe3C grain morphology. Drastic changes in CDC texture were, however, observed with an increase of reaction temperature. At lower reaction temperatures (< 500 °C), the overall volume of the original Fe3C grains is converted to a fluffy, disordered carbon by formation and evaporation of volatile iron chlorides (Fig. 1(d)). Chlorination at mild regimes yields a grainy (for 600 °C, Fig. 6(b)) or striated (for 800 and 1000 °C, Fig. 6(c)) texture suggesting formation of graphite lamellae. A very different carbon microstructure was achieved after chlorination at 1200 °C, as shown in Fig. 7. Several millimeter-size graphitic spheres (one shown in Fig. 6(a)) were observed. Opening the spheres revealed that they are hollow inside, and their walls are built of very thin graphite flakes (Fig. 7(b)). The inner surface of the spheres was found to be overgrown with graphite crystals. An example is shown in Fig. 7(c). Fig. 7(d) and (e) show the morphology of exfoliated graphite, which is formed during the synthesis process due to removal of iron salts that intrinsically intercalate graphite. However, it is important to note that neither XRD nor TEM and Raman analysis found intercalation compounds in CDCs after their synthesis. Moreover, EDS analysis showed no traces of iron and chlorine in the samples. Above the eutectic temperature in the iron–Fe3C system, the liquid phase is formed producing melt droplets. Upon interaction with chlorine, iron is easily removed from the iron–carbon melt, which thus becomes supersaturated with carbon. Planar graphite nucleates and grows from this supersaturated melt. By adjusting the process parameters, it might be possible to grow millimeter-size crystals of graphite. The surface of graphite crystals synthesized at 1200 °C is shown in Fig. 7(c).

TEM images of CDC powders produced at different temperatures are shown in Figs. 8–10. Similar to the SEM image in Fig. 6(b), Fig. 8(a) shows the agglomerated microstructure of the CDC powders produced at low temperatures (400–600 °C). The HRTEM image (Fig. 8(b)) shows that the
particles produced at 400 °C are mainly built of amorphous carbon, while minor local ordering and formation of turbostratic graphite can be found at the edge of the particles even at this very low temperature. For comparison, in CDC produced from other carbides, such as Ti₃SiC₂, graphitic carbon was not found below 700 °C. The measured crystallite size along graphite basal planes for 400 °C is on average less than 5 nm, which is in good agreement with the $L_a$ value estimated from the Raman spectra.

Much stronger graphitization has been observed during high temperature CDC synthesis. CDC powders produced at 800 °C contain thin sheets of graphite (Fig. 9). Amorphous carbon can still be found, but in significantly smaller quantities (less then 10 vol%). When the synthesis temperature is 1200 °C, TEM images (Fig. 10) show that perfect graphite crystals with an interplanar distance of 0.334 nm are produced, indicating complete graphitization.

Thin graphite flakes produced at 600–1100 °C may find applications in lithium batteries and supercapacitors. Currently, similar flakes are produced in a complex process including graphitization at above 2500 °C, followed by intercalation and exfoliation of graphite. Here we demonstrate that

Fig. 7  SEM micrographs of a graphite sample produced by chlorination of Fe₃C at 1200 °C.

Fig. 8  TEM micrographs of amorphous carbon and turbostratic graphite in a sample produced by chlorination of Fe₃C at 400 °C.

Fig. 9  TEM micrographs of thin graphite flakes in a sample chlorinated at 800 °C.
synthesis of graphite from iron carbide can be done in one step at moderate temperatures.

4 Conclusions

Chlorination of Fe₃C at temperatures of 400 °C and above results in the formation of carbon and solid or gaseous iron chlorides. Three temperature regimes have been characterized. Amorphous carbon is formed at temperatures of 400–500 °C. Flakes and ribbons of nanocrystalline graphite form at 600–1100 °C, while graphite ordering increases with temperature. Formation of microcrystalline graphite and millimeter-size graphite crystals occurs above the eutectic point in the Fe/Fe₃C system.

Acknowledgements

We thank Julius Chang and Jerome P. Downey for providing the iron carbide sample. This work was supported by DARPA via an ONR contract. The purchase of the Raman spectrometer and environmental SEM was supported by NSF grants DMR-0116645 and BES-0216343. TEM work was performed in LRSM, University of Pennsylvania.

References


Fig. 10 TEM micrographs of well-ordered graphite in a sample produced at 1200 °C.