

Formation of filamentous carbon through dissociation of chromium carbide under hydrothermal conditions

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Abstract Synthesis of filamentous carbon through the decomposition of chromium carbide was studied employing hydrothermal technique in the pressure and temperature range of 100–200 MPa and 350–800 °C respectively. It was found that chromium carbide dissociates into chromium oxide in the presence of water at temperature <400 °C. But, the formation of free elemental carbon as filamentous particles was noticed in the presence of organic compounds at temperatures above 600 °C. The organic compounds are known to dissociate to C–O–H supercritical fluids under hydrothermal condition. The supercritical fluids generated by the dissociation of organic compounds have great influence on the decomposition of chromium carbide. The scanning electron microscopic (SEM) studies of the experimental run products show that the fibrous or filamentous form of carbon was found with a few spherical shaped carbons, in the chromium carbide–organic compound runs. These carbon particles were solid curved filaments with a mean diameter of 50–100 nm. Micro Raman spectroscopic studies show that the filaments have sp^2 -hybridized carbon atoms.

Introduction

The synthesis of diamond [1], the discovery of fullerene [2] and carbon nanotubes [3] have inspired interest in carbon studies especially with regard to the synthesis of free elemental carbon. Apart from its well known allotropic forms i.e., diamond and graphite, several other new solid forms of carbon have been reported in recent times. They are onion like carbon, diamond like carbon, disordered graphite, filamentous carbon, carbon nanocells, carbon beads, carbon spheres, etc., [4–7]. Classifications of these new forms of carbon were given based on the nature of arrangement of carbon atoms and their basic structural units [8–12]. These new solid forms of carbon have interesting arrangements of carbon atoms with varying bond strengths and have general structure of sp^2 -hybridized bonding. However, the physical, chemical as well as mechanical properties of each of these new forms of carbon vary significantly and hence find application in the field of electronics, catalysis, adsorption and energy storage materials. Among these new solid forms of carbon, filamentous carbon finds application in various fields due to its unique properties such as low specific gravity and high flexibility, chemical inertness, mechanical strength, thermal conductivity and stability in an inert atmosphere [13]. Recently, filamentous carbon and its composites are also being extensively used as new class of tissue scaffolding materials [14]. This versatile nature of the carbon fibers/filaments led to extensive research on the development of the different precursor materials from which they could be processed [15].

Carbon nanofibers or filaments with well-defined specific structures may be grown on metallic surfaces and these structures can be utilized as adsorbents, in thermoplastic composites, as construction materials and in microelectronics [16]. These new forms of carbon were

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synthesised under extreme conditions with low energetic efficiency and high cost, and the production of filamentous carbon is usually achieved by catalyzed disproportionation of carbon monoxide or hydrocarbons [17]. There are very few attempts to synthesize carbon polymorphs through liquid route at relatively low pressure and temperature conditions in a closed system. Gogotsi et al. [18] have reported the formation of filamentous carbon through decomposition of paraformaldehyde in a closed system employing hydrothermal technique. Jablonski et al. [19] have examined in detail the formation of filamentous carbon in the C–O–H–Ni, C–O–H–Fe, and C–O–H–Co systems at ambient pressure. The filamentous carbon found in the above studies shows low graphitization and conical layer morphology. Libera et al. [20] synthesized bamboo-like carbon filaments under hydrothermal condition. In pursuant of the preparation of newer forms of carbon under hydrothermal condition, the authors have reported the formation of spherical shaped carbon [21] and the formation of nano crystallites of sp^3 -hybridized carbon—‘diamond’ [22, 23] through the hydrothermal decomposition of silicon carbide under varying partial pressures of water and carbon dioxide. In pursuit of preparation of newer forms of carbon under hydrothermal condition, the authors used chromium carbide as carbon source and studied its dissociation under hydrothermal condition in the presence water and organic compound. It was found that the chromium carbide dissociates in water at temperatures <400 °C, into chromium oxide and carbon dioxide, but in the presence of organic compounds it decomposes into chromium oxide and free elemental carbon at temperature above 600 °C and 100–200 MPa. The SEM and the micro Raman studies indicate the presence of nano sized filamentous carbon along with chromium oxide.

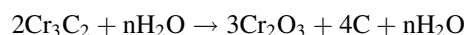
Experimental

The experiments were carried out using the conventional Tuttle-Roy externally heated pressure vessels made up of Rene MRA-114 super alloy steel. The starting mixture were commercially available chromium carbide (~300 mg) and water/organic compound (~300 mg), taken in a sealed gold tubes of 50–60 mm length and 4.5 mm outer diameter with wall thickness of 0.1 mm. The organic compounds used in the present investigations were malonic acid, glycolic acid, ascorbic acid, malic acid, stearic acid, citric acid, formic acid and oxalic acid. The sealed gold capsules were ensured for any leakage through extended heating at 100 °C in hot air oven before placing them in the vessel. The pressure vessels with the initial water pressure of 20–30 Pa, were inserted into the pre-heated furnace and pressure and temperatures were monitored till the desired

P-T conditions were attained. The duration of the experimental runs was 60–120 h, and the vessels were quenched by compressed air blast. The run product was carefully removed by cutting the capsules and were dried and examined under microscope. The run products were further characterized by X-ray diffraction studies (XRD). The high resolution Scanning electron microscopy (SEM) was performed using Hitachi, Model S-4000, Japan. The Laser Raman spectroscopy was performed using the CT64000, Jonin, Yvon Atago Bussan, Japan, with wavelength of 514.5 nm is used in the present study. Scans were taken over the wave number range 1000–1800 cm^{-1} .

Results and discussion

Hydrothermal decomposition of chromium carbide in the presence of water was studied with water as pressurizing media and the conditions of the experiments are described in Table 1. This was carried out following the studies made by Gogotsi and others, on the decomposition of silicon carbide in the presence of water. These authors have confirmed by both theoretical estimates [24, 25] and the experimental studies [26]; the formation of free elemental carbon through the decomposition of silicon carbide in the presence of water alone. Here, we found that the decomposition of chromium carbide in the presence of water and the probable reaction is as follows:



But we observed in the present experimental study under pure water system the chromium carbide decomposes at temperatures as low as 350 °C, the only solid phase observed is green color powder of chromium oxide and there is no free elemental carbon formation. Probably the carbon is converted into carbon dioxide by consuming the required oxygen available inside the capsule.

Further, experiments were also performed to fix the reaction boundary at 100 MPa and 200 MPa, the univariant phase boundary for the above reaction lies around 350–400 °C. The experimental results pertaining to the construction of chromium carbide—water system will be published elsewhere.

Earlier we had found the formation of free elemental carbon in the form of spherical shaped particles and the sp^3 -hybridized nanocrystallites, by using organic compounds instead of water through the decomposition studies of silicon carbide [21–23]. Thus, we extended this study to decompose chromium carbide under the influence of organic compounds and the results of this study were shown in Table 1. The argument that the C–O–H fluids could be the source for the formation of diamond and

Table 1 Representative experimental conditions for formation of filamentous carbon

Sl. No.	Starting charge	Solvent	Temperature in °C	Pressure in MPa	Duration in days	Product
1	Cr ₃ C ₂	Water	200	100	3	Chromium carbide
2	Cr ₃ C ₂	Water	250	100	2	Chromium carbide
3	Cr ₃ C ₂	Water	300	200	5	Chromium carbide
4	Cr ₃ C ₂	Water	350	100	3	Chromium oxide
5	Cr ₃ C ₂	Water	350	200	3	Chromium oxide
6	Cr ₃ C ₂	Water	400	100	4	Chromium oxide
7	Cr ₃ C ₂	Water	400	200	3	Chromium oxide
8	Cr ₃ C ₂	Malonic acid	500	100	3	Chromium oxide
9	Cr ₃ C ₂	Glycolic acid	500	100	2	Chromium oxide
10	Cr ₃ C ₂	Ascorbic acid	600	100	3	Chromium oxide
11	Cr ₃ C ₂	Malic acid	600	100	3	Chromium oxide
12	Cr ₃ C ₂	Stearic acid	650	150	3	Chromium oxide + Filamentous carbon
13	Cr ₃ C ₂	Citric acid	700	200	3	Chromium oxide + Filamentous carbon
14	Cr ₃ C ₂	Formic acid	700	150	3	Chromium oxide
15	Cr ₃ C ₂	Oxalic acid	750	150	2	Chromium oxide + Filamentous carbon + spherical shaped carbon
16	Cr ₃ C ₂	Malonic acid	750	150	3	Chromium oxide + Filamentous carbon + spherical shaped carbon
17	Cr ₃ C ₂	Glycolic acid	800	200	3	Chromium oxide + Filamentous carbon + spherical shaped carbon
18	Cr ₃ C ₂	Ascorbic acid	700	150	2	Chromium oxide + Filamentous carbon
19	Cr ₃ C ₂	Malic acid	700	150	3	Chromium oxide
20	Cr ₃ C ₂	Stearic acid	800	150	4	Chromium oxide + Filamentous carbon
21	Cr ₃ C ₂	Citric acid	800	150	4	Chromium oxide + Filamentous carbon
22	Cr ₃ C ₂	Formic acid	800	200	5	Chromium oxide
23	Cr ₃ C ₂	Oxalic acid	800	200	5	Chromium oxide + Filamentous carbon + spherical shaped carbon

graphite in nature [27, 28] as well as the theoretical calculations [29] on the sp^2 - and sp^3 -hybridized carbon formation in the C–O–H system encouraged us to explore to use organic compounds to generate the ideal C–O–H fluid environment. We had also discussed about the diamond growth region by comparing the C–O–H ternary plots of organic compounds used [21]. It is interesting to note that the chemical species fall on the tie lines emerging from three corners representing the C–O–H to meet at the OH or C₁H_x or CO radicals. Similar diagrams are discussed by Bachmann et al., Rumble III et al. and discussed by DeVries et al. [30–32]. The organic compounds under hydrothermal condition decompose to generate the C–O–H supercritical fluid such as H₂O, CO₂, CO, C₁H_x, OH Etc. and increased atomic hydrogen concentration and provide highly reducing atmosphere with low oxygen fugacity inside the capsules [33]. It is well known fact that the ability of these super critical fluids is to dissolve the non-volatile

solids under hydrothermal conditions [34]. This will help not only in dissociation of metal carbides but also in the formation of free elemental carbon at relatively low temperature and pressures. The XRD studies of the run products is not useful in the characterization of carbon phases, as the bulk of the carbon phases are disordered graphitic in nature that have strong absorption for X-rays. Hence the XRD pattern of the run product shows only the pattern matching with that of chromium oxide and no lines corresponding to any of the reported carbon phase were found even after stripping the lines corresponding to that of chromium oxide. The representative X-ray diffraction patterns of chromium oxide are shown in Fig. 1. The examination of the run products under high resolution Scanning Electron Microscopy (HRSEM), indicates the formation of fibrous or filamentous type carbon along with some spherical shaped carbon in all experimental runs at temperatures above 600 °C and pressures above 100 MPa.

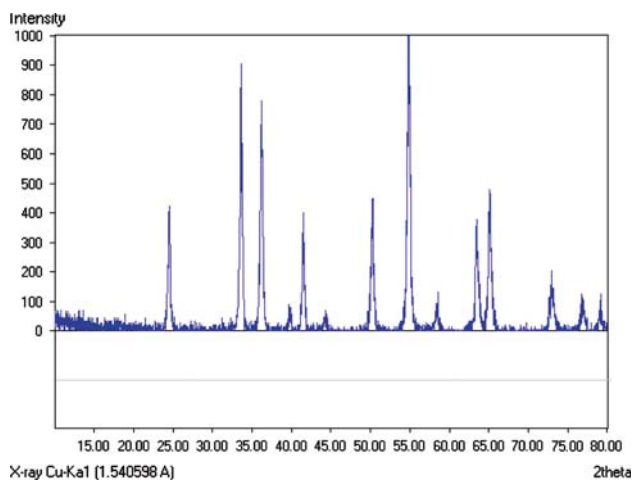


Fig. 1 Representative X-ray diffraction pattern of chromium oxide obtained through decomposition of chromium carbide under hydrothermal condition

The fibrous or filamentous carbons dominate in proportion to that of spherical carbon particles and were solid curved with a mean diameter of 50–100 nm (Fig. 2).

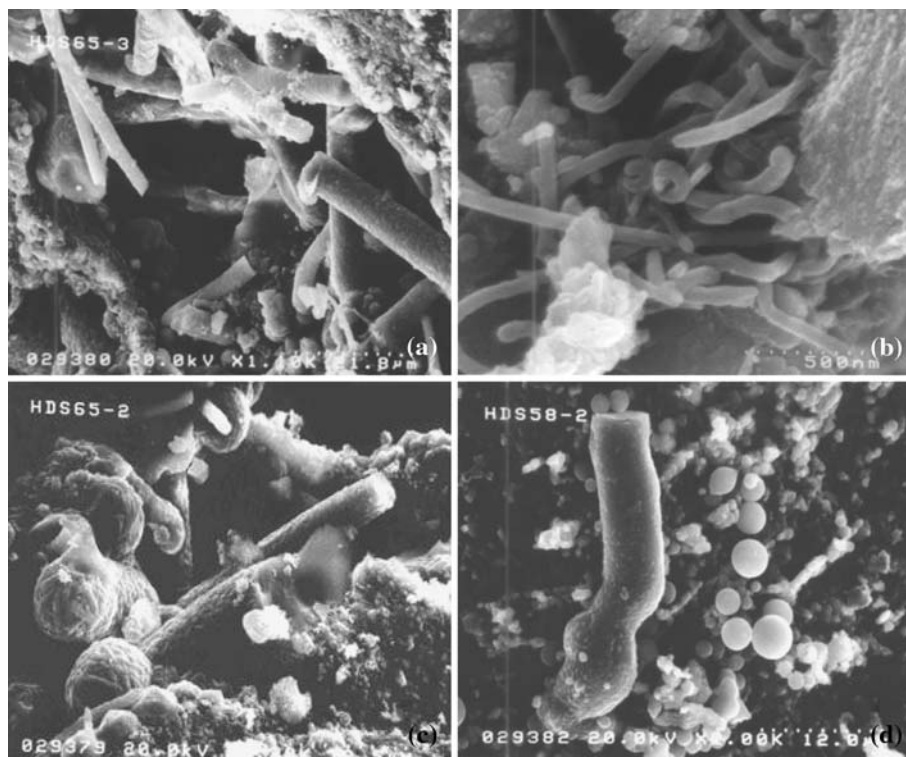
Micro Raman spectroscopy is the most simple and powerful tool for analyzing and identifying more or less all different forms and allotropes of carbon and carbonaceous materials [35]. The micro Raman spectral studies were applied to all sample, carbon formation was detected in all experiments conducted at and above 600 °C. The

spectrums indicate the presence of two prominent broad bands appearing at 1590 cm^{-1} and 1330 cm^{-1} , corresponding to the G band and D band respectively. The G band is assigned to the C–C stretching vibrations of sp^2 hybridization of carbon atoms in a two-dimensional hexagonal lattice, i.e., E_{2g} of graphite [36] and the D band corresponds to vibrations of carbon atoms with dangling bonds in plane terminations. The positions of these G and D bands and analysis of their relative intensities, i.e., I_D/I_G , also confirm that the filamentous carbon is of disordered graphitic type. A typical Raman spectrum comparison of all the filamentous carbon particles obtained through decomposition of chromium carbide in this study is presented in Fig. 3. All the results discussed here were replicated and showed good reproducibility. The G-band at 1580 cm^{-1} appears to shift up with increasing disordered graphitic nature. This clearly indicates the formation of sp^2 -hybridized carbon and spectra so obtained are also compared with that of the spectra obtained for the commercial spec pure graphite sample.

Conclusion

The synthesis of filamentous carbon from C–O–H fluids has been demonstrated in this study. The hydrothermal method has great potential for the preparation of carbon particles with varying morphologies, presumably with less thermal strain. The closed system, low temperature growth

Fig. 2 SEM images showing (a–c) filamentous particles (d) filamentous and spherical particles



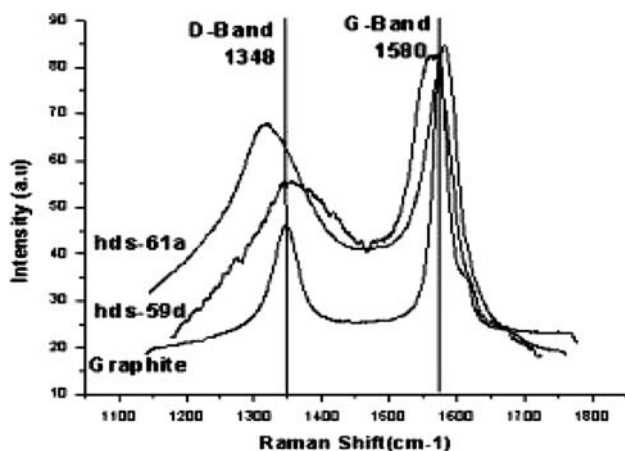


Fig. 3 Micro Raman spectra of filamentous (hds-61a) and spherical shaped (hds-59d) aggregates of carbon particles compared with that of spec pure graphite (Gr)

with suitably tailored atmosphere to produce oxidizing or reducing conditions is an excellent way to produce carbon polymorphs, which are often unattainable by other means. Thus, hydrothermal technique allows the synthesis of phases, which could not be stabilized by any other methods at such a low P-T conditions. By varying the relative proportion of chromium carbide to organic compound ratio, as well as by varying the partial pressures of C–O–H fluids generated inside the capsule we can control particle size and shape. The formation of filamentous carbon under hydrothermal conditions through the dissociation of chromium carbide at relatively low temperature and pressure has obvious advantageous compared to that of conventional growth techniques is of particular interest because of their possible applications in the field of microelectronics, as energy storage materials, as catalysts and in robotics. Besides, the polymer–filamentous carbon composites could act as a new class of tissue scaffolding materials, due to their versatile nature of having high initial strength, rapid growth and benign tissue reaction, further it is being histologically and mechanically similar to natural structures. The studies on the preparation of such composites of polymer–filamentous carbon are in progress and will be published elsewhere.

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