RESULTS AND DISCUSSION

This chapter deals with the salient results obtained by hydrothermal experimental studies carried out to synthesize the carbon polymorphs. The run products obtained were discussed with the aid of the characterisation tools, mainly SEM and Micro Raman spectroscopy. Besides, experimental runs on the hydrothermal phase equilibrium studies of carbides in the water medium were carried out to construct the phase diagram for dissociation reaction. An attempt was made to retrieve the thermochemical parameters of the carbides. In addition to carbides as the source of carbon, a few other carbon source materials were explored for the synthesis of carbon polymorphs through hydrothermal treatment and the results are presented at the end.

5.1 Introduction

The results of the experimental investigations pertaining to the synthesis of carbon polymorphs are presented and these results are discussed with the aid of the various characterisation tools. The characterisation tools employed in the present investigation are stereo binocular microscope for visual observation, powder X-Ray diffraction studies for structural characterisation, scanning electron microscopic studies for morphological studies, FTIR and laser micro Raman for spectroscopic studies. The X-ray diffraction studies is of less significance for the characterisation of carbon phases, as the carbon atoms especially the disordered or less ordered carbon molecules shows greater absorption for radiation. As presented in the chapter IV, the results of the experimental studies are also presented as sub systems based on the type of carbon source used for the synthesis. The results of decomposition of carbide systems were given first and other carbon source materials such as activated carbon, filamentous carbon and shungites are given in the later part of this chapter.
5.2 Synthesis of carbon polymorphs using carbides as source of carbon

5.2.1 Silicon carbide – water system

The visual observation of the run products of this system (see Table 4.1) is composed of white powdery material with out much crystallinity. The products are homogenous except for a tint of grey colored material. The X-ray diffraction studies of the products shows only the lines of silica phase. The silicon carbide - water system was also studied by Yoshimura et al. (1986) [1]; Gogotsi and Yoshimura (1994) [2]; Gogotsi et al. (1995, 1996) [3-4], under hydrothermal conditions by taking the silicon carbide in the form of powder (β-SiC), amorphous fiber (commercially available Tyranno fibers) and sintered silicon carbide powder. Accordingly they proposed the following reactions (r1-r4) for the hydrothermal treatment or corrosion / leaching of silicon carbide studies, support the formation of free elemental carbon. However, they have noticed only the formation of CO, CH4, and silica phase. Eventually, Gogotsi et al. (2000) reported the formation of sp2-bonded carbon by hydrothermal treatment of β-SiC powder in the temperature range of 600-800 °C and pressure >500 MPa, the run products were first washed in HF to remove silica phase before subjecting it to Micro Raman spectroscopy. The XRD and micro Raman spectroscopic studies indicated the formation of graphitic carbon, diamond and amorphous carbon. However, bulk of the material is composed of graphitic and amorphous carbon, with a small quantity of sp2-hybridized carbon [5]. The presence of diamond was confirmed through sharp Raman reflections ~1330 cm\(^{-1}\). They claimed that the growth of nanocrystallites of diamond under hydrothermal conditions is due to the phenomenon of hetero-epitaxial growth over the diamond seed which is due to the interaction of water and silicon carbide and in situ generation of C-O-H fluids. But, the scientific community is not convinced with the observation of Raman shift since they have invariably used the diamond seed. Similarly, Roy and co-workers [6-11] have attempted to synthesise diamond by hydrolysis of silicon carbide powder at P-T condition of 150 MPa and 800 °C and reported the formation of both amorphous and
sp$^3$-bonded carbon; the sp$^3$-bonded carbon was confirmed by the presence of sharp 1332cm$^{-1}$ Raman spectral line. They also reported that the silicon carbide to water ratio is a critical factor for the formation of diamond and stated that this ratio should be $\sim 27$ wt%. However, the deviation in percentage of water in the system did not result in the Micro Raman shift at $\sim 1332$cm$^{-1}$. Thus, they have attributed the formation of diamond as mainly due to the hypothesis that the exposure to high atomic hydrogen concentration while dissociation leads to the direct precipitation of sp$^3$-bonded carbon. However, they have failed to explain the source for the generation of high concentration of atomic hydrogen in the system. In the present study, it was surprising to note that there was no formation of any kind of carbon phase, with the similar kind of starting charge and water as fluid medium in the temperature range of 300 to 800 °C and 50 to 200 MPa pressures. Even though the experiments were replicated, only the silica phase was found (see Fig.5.1).

![Figure 5.1](image)

**Fig. 5.1.** Powder XRD patterns of quartz crystals obtained by decomposition of silicon carbide

Thus the product obtained could be attributed to mainly due to the dissociation followed by oxidation reaction of silicon carbide, the oxygen required for the reaction is consumed from the atmosphere prevailed inside the capsule and thus the possible reaction ($r_5$) is:

$$\text{SiC} + 2\text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}_2 \ldots r_5$$

Systematic experiments were carried out with a sole purpose to understand the phase equilibrium of dissociation reaction of silicon carbide in water medium. It was found in the literature that extensive experimental studies have been carried out to explore the possibility of diamond synthesis under hydrothermal conditions using silicon carbide as source of carbon. But, very little attention was given to understand
the stability and thermochemical behavior of the silicon carbide and such a study is lacking. Therefore, a systematic hydrothermal runs were carried out to determine the conditions of equilibrium for silicon carbide – water system in the P-T range of 50-200 MPa and 300-800 °C. It was intended to retrieve the thermodynamic parameter of silicon carbide using the constructed phase diagram. The dissociation of silicon carbide to silica and carbon dioxide curve is having a straight line relationship and the corresponding equilibrium temperature and pressures are:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
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<tr>
<td>330</td>
<td>48</td>
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<tr>
<td>360</td>
<td>110</td>
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<tr>
<td>380</td>
<td>160</td>
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<tr>
<td>410</td>
<td>200</td>
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### 5.2.2 Silicon carbide – wollastonite - water /organic compound system

After failing to notice the formation of any significant amount of carbon phases through decomposition of silicon carbide in water alone, the decomposition of silicon carbide is carried out in the presence of wollastonite with water and other organic compounds as solvents. Several experiments (Table 4.2) were carried out in the temperature range of 700 – 800 °C at 200 MPa of water pressures. The resultant product was wollastonite, quartz and calcite crystals (see Fig. 5.2) along with vapour. Here, the wollastonite partially reacted and dissociated to form calcite and silica, and the silicon carbide dissociated into silica and vapor, yet the formation of free elemental carbon was not noticed. Though the expected reaction $r_6-r_7$ (given below) indicates that there is a provision for the free elemental carbon formation but, no traces of carbon particles are found in the run products.

\[
2\text{SiC} + \text{CaSiO}_3 + 6\text{H}_2\text{O} \rightarrow \text{CaCO}_3 + 3\text{SiO}_2 + \text{C} + 6\text{H}_2 \ldots \ldots r_6
\]

or

\[
\text{SiC} + \text{CaSiO}_3 + 3\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{SiO}_2 + \text{C} + 2\text{H}_2\ldots \ldots r_7
\]
As mentioned earlier, there are several reports on the precipitation of carbon as graphite, diamond or amorphous phase by hydrothermal treatment of silicon carbide [8-11] with water as fluid medium, and they have attributed the formation of carbon phases as mainly due to the effect of C-O-H supercritical fluids generated through the interaction of carbide and water. Inspired with their argument, it was felt that the need for the generation of C-O-H supercritical fluid is utmost important. It was felt that the supercritical fluid generated by the interaction with silicon carbide and water is insufficient to create a congenial environment for the precipitation of free elemental carbon, since, none of the above mentioned experimental approaches have been able to generate sufficient amount of C-O-H fluid environment in their system. Hence, in the present study the organic compounds were taken along with the starting mixtures in order to generate the sufficient amount of C-O-H supercritical fluids in the system. Thus, experimental study on the synthesis of carbon polymorphs was pursued further by decomposing silicon carbide in the presence of wollastonite and organic compound.

Fig. 5.2. SEM image of calcite crystals
Supercritical fluids (SCF)

A fluid is supercritical when its temperature or pressure is higher than their critical values [12-14]. Most of the interesting applications of SCF occur at 1<T/Tc<1.1 and 1<P/Pc<2 [15-16]. Under supercritical conditions the fluid exists as a single phase having some of advantageous properties of both liquid and gas [17-18]. Further, supercritical fluids are known for their high density, diffusivity and low viscosity to give high dissolving power and facilitating mass transport. It also accelerates the interactions between the starting charge materials. This dissolving power of SCF can be tuned further by varying the temperature and pressure.

The organic compounds used in the present investigation are:

- Malic acid – C₄H₄O₄
- Malonic acid – C₃H₄O₄
- Glycolic acid – C₂H₄O₃
- Stearic acid – C₁₈H₃₆O₂
- Succinic acid – C₄H₆O₄
- Formic acid – CH₂O₂
- Sucrose – C₁₂H₂₂O₁₁
- Oxalic acid – C₂H₂O₄
- Citric acid – C₆H₈O₇
- Ascorbic acid – C₆H₈O₆
- Acetic acid – C₂H₄O₂

Most of these organic compounds are oxidized completely under the hydrothermal conditions to form molecules of H₂O, OH, CO₂, CO, C₁Hₓ radicals and atomic H. These are known to produce highly reducing environment with low oxygen fugacity and increased atomic hydrogen concentration inside the capsule. Further, it is interesting to note that all the chemical species of the organic compounds when plotted in a C-O-H trilinear diagram (Fig. 5.3), fall on or around the intersection point of three tie lines emerging from three corners representing C-O-H to meet at OH, CO and C₁Hₓ radicals. This region is considered as the diamond growth region as indicated by Bachmann et al. [19] who has shown with similar trilinear diagram that the C-O-H fluids are in equilibrium with graphite and diamond, around the marked region along the tie line joining the CO and H (Fig. 5.4). DeVries et al. (1994) [20] have also indicated the possibility of precipitation of carbon in the C-O-H system.
Fig. 5.3. Plot of C-O-H species of organic compounds used in the present study.

Fig. 5.4. Ternary Plot given by Bachmann et al. summarizing the C-O-H range for CVD diamond formation [19].
The visual observation of the run products of silicon carbide - wollastonite - organic compound system under optical microscope indicates that it has a mixture of both white and dark colored powdery material. The white portion has lots of shiny quartz crystallites and their SEM images are given in Fig. 5.5. The dark colored portions have no visible morphological feature. When examined by X-ray diffraction studies the white portion has two distinct phases comparable to wollastonite and silica (quartz/tridymite phase). The XRD of dark portion in most of the runs do not give diffraction lines of any carbon phase, this may be due to lack of ordering and strong absorption for X-rays. In a few runs the XRD pattern of dark portion has diffraction line corresponding to the carbon phase of JCPDS file no. 18-0311 and 22-64 (see Fig. 5.6). The dark portion of the run products were further subjected to High Resolution Scanning Electron Microscopy (HRSEM). Bulk of the material is just irregular particles without much observable morphology and very few particles found to be as spherical particles (see Fig. 5.7).

The expected reaction ($r_8$ & $r_9$) for the silicon carbide - wollastonite - organic compound system for a few selected organic compounds, suggests the formation of calcite, quartz and carbon phases. However, in the present study, it was found that the wollastonite persists and no calcite formation was observed along with precipitated carbon phase. This may be due to the fact that the generation of C-O-H supercritical fluids has enhanced the stability limit of wollastonite, resulting in its persistence and no calcite formation (see Table 4.4). Thus the presence of wollastonite in the system has no influence either on the breakdown of silicon carbide or on the formation of carbon phase. Hence, it was concluded that the use of wollastonite is of no consequence with regard to the formation of free elemental carbon. Because of the above said reason the dissociation of silicon carbide runs were pursued further without wollastonite in the system.

\[
\begin{align*}
\text{SiC} + \text{CaSiO}_3 + \text{C}_4\text{H}_4\text{O}_4 \ (\text{malic acid}) & \rightarrow \text{CaCO}_3 + 2\text{SiO}_2 + 4\text{C} + 2\text{H}_2 \\
\text{SiC} + \text{CaSiO}_3 + \text{C}_3\text{H}_4\text{O}_4 \ (\text{malonic acid}) & \rightarrow \text{CaCO}_3 + 2\text{SiO}_2 + 3\text{C} + 2\text{H}_2
\end{align*}
\]
Fig. 5.5. SEM micrograph of quartz crystals (a) aggregate (b&c) enlarged image of rhombic crystals
Fig. 5.6. The XRD pattern of dark portion showing diffraction line correspond to the carbon phase and quartz.
Fig. 5.7. SEM images of irregular carbon particles in silicon carbide-wollastonite-water system
5.2.3 Silicon carbide – organic compound system

In silicon carbide – organic compound system without excess water, the run products show a significant improvement in the yield of carbon (Table 4.3). It was known [21] that the presence of slightest amount of water in the system inhibits the formation of diamond. Hence, rest of the experiments were performed with no excess water and the amount of water molecules in the system is restricted to the water molecules produced by the oxidation of organic compounds. The black portion of the run product was subjected to XRD, SEM, FTIR and Laser Micro Raman spectroscopic studies.

High resolution scanning electron microscopic (HRSEM) images of the run products obtained from the silicon carbide – organic compound system, show the majority of the black portion of the run products is composed of glassy or irregular and spherical shaped carbon particles. The spherical shaped particles are found either as discrete or linked to one another as chains or clusters (see Fig. 5.8). The spherical particles are porous in nature and the dimension of the pores varies between 20 - 30 nm and the wall thickness ranges from 2-3 nm (see Fig. 5.9). The spherical particles of carbon found in this study are of particular interest because of their porous nature and its possible applications in catalysis and energy storage [22].

In the run products of HDS-56 and HDS-57 where the starting materials were silicon carbide along with malonic acid and glycolic acid respectively, the following interesting observations are made. Though, the bulk of the run products are similar in many aspects with rest of the runs on silicon carbide – organic compound system (see Table 4.3), a careful and closer observation by HRSEM of the spherical particles obtained in these runs shows that they have an opening and in each of these opening certain kind of fluid material flows out, indicating the exchange of fluid which is entrapped inside the spherical particles during their precipitation (see Fig. 5.10). Some of the spherical particles show the development of scale like material over its surface having metallic luster and the thickness of these scales are of a few nanometers. These scales are presumed to have formed at the contacts of the spherical particles with that of the inner walls of the gold capsule. This indicates that the scales are formed due to
Fig. 5.8. SEM images of spherical carbon particles (a) particles surrounding quartz crystals (b&c) particles linked as chains or aggregates
Fig. 5.9. SEM images of porous spherical carbon particles (a) discrete particles (b) enlarged image showing irregular pores (c) porous particles with vent/opening
Fig. 5.10. SEM images of carbon particles showing fluid like material oozing out through the vent
localized melting and recrystallisation of carbon particles (see Fig. 5.11a). Further these spherical particles are hollow and broken into two halves or more number of smaller pieces. The broken pieces of these carbon spherules exhibit the growth of nanocrystallites on their inner wall and the crystallites show well developed octahedral facets (See Fig. 5.11 b, c, d, e & f). These crystallites are of very minute in size and their size ranges from 10 to 30 nm. The growth of these crystallites resembles geoids i.e. the growth of zeolite crystals in the cavities and vugs of volcanic lava flows. The experiments of silicon carbide with malonic acid and glycolic acid were repeated in order to check the reproducibility of the results. However, there is not much difference in the results as well as on the yield of carbon particles and it is found that the results are reproducible and not just accidental or coincidence of a particular situation during experimentation. The energy dispersive spectra (EDAX) obtained for these crystallites indicate that they were composed essentially carbon (~98.90 At. %) the EDAX spectra along with the qualitative analytical results are given in Fig. 5.12.
Fig. 5.11. SEM images of carbon particles (a) scaly material adhered to the surface of spherical particles (b & c) octahedral crystals at the inner walls of the spherical particles
Fig. 5.11. SEM images of carbon particles (d, e & f) octahedral crystallites grown at the inner walls of the spherical particles
Spectroscopic characterisation of the carbon particles was carried out using FTIR and laser micro Raman. The FTIR of these particles show strong absorption in the range 1250-1260 cm\(^{-1}\), which is characteristic of diamond polytype. Except this absorption, the others do not correspond to any of the carbon bonding. The β-SiC used as the source of carbon has been completely decomposed, as it is evident from the absence of absorption in the 3300 cm\(^{-1}\) region (see Fig. 5.13).
Laser micro Raman spectroscopy is a very useful tool especially for characterisation of carbon in micro to nanosize particles. In Raman scattering - the inelastic scattering of photons by excitations of a molecule or a solid, provides a spectroscopic technique for the identification of symmetries of the bonding and structure of carbon atoms. Hence, micro Raman spectroscopy is commonly used to characterize carbon materials. The carbon – carbon bonding might take place in many ways to form molecular and crystalline structures. Carbon is known to form single, double and triple bonds resulting in linear chains, strongly anisotropic layered materials, three dimensional solids and novel molecular solids as spherical or cylindrical carbon shells. The large differences in the Raman spectra of the various forms of carbon such as graphite, diamond, fullerenes, carbon nanotubes and other unusual forms make Micro Raman technique more attractive for distinguishing one form of carbon phase to another. The prominent regions in Raman spectra to be observed in carbon studies are spectrum corresponding to the D and G bands and intensity ratio i.e. $I_D/I_G$. The G band is related to the vibrations in $sp^2$-hybridization of carbon atoms in a two dimensional hexagonal lattice and the D band are associated with vibrations of carbon atoms with dangling bonds in plane terminations.

The representative run products having carbon particles were subjected to micro Raman studies. The spherical particles of carbon found in the dissociation runs of silicon carbide and organic compound (HDS-58 and 39) show two distinct types of strong and sharp bands. The spectra of the above mentioned runs are shown along with that of pure quartz and β-SiC powder (see Fig. 5.14).
The run product of HDS-58 has D band and G band peaks at around 1356 and 1590 cm\(^{-1}\) respectively, which is more characteristic of glassy or disordered carbon, whereas in HDS-39, the positioning around 1336 and 1560 cm\(^{-1}\), which are referred to D and G band of C-C stretching vibrations respectively. This kind of spectra could be attributed to a particular type carbon structure and similar kind of spectra were described by Vischer et al. (1993) and Gogotsi et al. (1996) and have been discussed at length with regard to the positioning of the D and G band [23-24]. Further, a few more spherical particles which are hollow and porous in nature found in runs of malonic acid and glycolic acids are quite distinct to other spherical and irregular carbon particles. When these particles were examined by micro Raman studies the spectra obtained show near \(sp^2\)-hybridization, the D and G band are positioned at around 1359 and 1581 cm\(^{-1}\), the spectra of run products of HDS-40, 56 and 57 are shown along with the spectra of spec pure graphite for comparison in Fig. 5.15. When the micro beam of laser Raman strikes the shining scaly material adhered to the outer surface of the spherical particles or the crystallites found in the inner walls of some of the broken halves of the spheres in run products of HDS-56d, clearly indicates that the
spectra show the sharp D band in the 1332 cm\(^{-1}\) region and a shallow broad peak of G band at 1590 cm\(^{-1}\) region. This spectrum matches well with that of commercially available diamond powder from HYPREZ, Co., USA. The spec pure graphite spectrum, clearly deviates with the positions of diamond powder spectral positions of D and G band regions (Fig. 5.16), thus clearly indicating the formation of \(sp^3\)-hybridized carbon under hydrothermal conditions. The formation of diamond phase is evident from the HRSEM, supported by EDAX along with Micro Raman studies. The formation of diamond phase is attributed to the influence of SCF, which creates a congenial atmosphere inside the capsule. The localized migration of these fluids entrapped inside the spherical particles recrystallise resulting in the formation of nanoscale crystals. The formation of nanoscale diamond crystals under hydrothermal conditions or sub-natural condition is a breakthrough in carbon science and this report is the first of its kind. So far one can find in the literature that there are ample reports on the growth of diamond over the diamond seed but no reports on the nucleation and crystallisation under hydrothermal conditions [25-26]. Hitherto, the synthesis studies of diamond have invariably used the diamond seed materials and metal catalysts under hydrothermal as well as high pressure conditions using belt apparatus or split sphere techniques. The crux of this study is the synthesis of diamond well below the

Fig. 5.15. Micro Raman spectra of spherical and irregular carbon particles (HDS 40, 56 and 57)
Berman – Simon line and without the use of any metal catalysts or diamond seed material, unlike in previous works as reviewed in the chapter II of this thesis.

5.2.4 Chromium carbide – water system

It is for the first time the chromium carbide is being explored as source of carbon to synthesise carbon polymorphs under hydrothermal conditions. Among several metal carbides like nickel carbide, zirconium carbide, tantalum carbide etc., chromium carbide is preferred for the present investigation, as it was reported in the literature that chromium and other transition metals are being used as metal catalysts in high pressure synthesis of diamond studies. Similar to the silicon carbide decomposition studies as dealt in the previous part of this chapter, the chromium carbide decomposition studies were carried out. Accordingly, the synthesis of carbon polymorphs through the decomposition of chromium carbide in water medium and also phase equilibrium study for this system were carried out.

**Fig. 5.16.** Micro Raman spectra for scaly / nano sized crystallites (HDS – 56d).
The details of the experimental conditions of decomposition of chromium carbide in water medium along with the run products obtained are given in Table 4.4. Although there is enough scope for the formation of carbon phase in the expected reaction \((r_{10})\) but the visual observation of the run product indicates that it is composed of green powdery material only without much crystallinity. The products are homogenous and there is not even a trace of carbon material. Even after the experiments were repeated only the chromium oxide phase was noticed in X-ray reflections (Fig.5.17).

\[
2\text{Cr}_3\text{C}_2 + 9\text{H}_2\text{O} \rightarrow 3\text{Cr}_2\text{O}_3 + 4\text{C} + 9\text{H}_2 \quad \ldots \quad r_{10}
\]

Therefore, the product obtained could be attributed mainly to the dissociation followed by oxidation reaction of chromium carbide. The oxygen required for the reaction is consumed from the atmosphere prevailed inside the capsule and also from water molecule and thus the reaction \((r_{11})\) can be written as:

\[
2\text{Cr}_3\text{C}_2 + 8\text{O}_2 + n\text{H}_2\text{O} \rightarrow 3\text{Cr}_2\text{O}_3 + 4\text{CO}_2 + \text{H}_2 + (n-1) \text{H}_2\text{O} \quad \ldots \quad r_{11}
\]

**Fig. 5.17.** Representative X-ray diffraction pattern of chromium oxide obtained through decomposition of chromium carbide.
The absence of carbon phase in the experimental run products may be due to the fact that the whole of carbon might have oxidized to carbon dioxide, since the reducing conditions created inside the capsule was not sufficient enough to prevent the oxidation of carbon produced through dissociation. Further, the systematic hydrothermal phase equilibrium studies of decomposition of chromium carbide in water medium was carried out in the temperature range of 200 - 500 °C and 50 – 200 MPa pressures. The experimental bracketing of the reaction boundary was done and the equilibrium temperature with corresponding equilibrium pressure given below:

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pressure (MPa)</th>
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<tbody>
<tr>
<td>310</td>
<td>48</td>
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<tr>
<td>350</td>
<td>110</td>
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<td>370</td>
<td>160</td>
</tr>
<tr>
<td>380</td>
<td>200</td>
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</table>

### 5.2.5 Chromium carbide – organic compound system

The results obtained in the silicon carbide – organic compound system did encourage us to explore further similar studies on chromium carbide. Besides the formation of free carbon particles in silicon carbide organic compound system, some of the interesting and unusual forms of carbon such as spherical carbon particles and the nanocrystallites were noticed. Hence, it is important to understand the nature of carbon phase formed under the influence of C-O-H supercritical fluid and the effect of catalytic activity of chromium metal. The details of the experiments and the run products obtained in this system are given in Table. 4.5.

The predicted reactions involving some of the organic compounds \((r_{12} & r_{13})\) for the above system show that there is enough scope for the formation of carbon along with chromium oxide as given below.

\[
2\text{Cr}_3\text{C}_2 + 2\text{C}_4\text{H}_4\text{O}_4 \text{ (malic acid)} + \text{H}_2\text{O} \rightarrow 3\text{Cr}_2\text{O}_3 + 12\text{C} + 5\text{H}_2 \ldots \ldots r_{12}
\]

or

\[
2\text{Cr}_3\text{C}_2 + 2\text{C}_3\text{H}_4\text{O}_4 \text{ (malonic acid)} + \text{H}_2\text{O} \rightarrow 3\text{Cr}_2\text{O}_3 + 10\text{C} + 5\text{H}_2 \ldots \ldots r_{13}
\]
In most of the experimental runs, the formation of carbon phase and chromium oxide, at temperatures above 600 °C in the pressure range of 150 – 200 MPa was noticed. The carbon particles precipitated in these runs is either spherical or ovoid in shape along with the formation of filamentous carbon. The HRSEM study of the run products of the chromium carbide - organic compound system indicates that the filamentous carbon particles are dominant than that of the spherical or ovoid particles (see Fig. 5.18). The filaments are solid, straight or curved, with mean diameter ranging from 50 – 100 nm. Micro Raman spectroscopic studies of filamentous carbon indicate that the presence of two prominent peaks corresponding to D and G band appear at 1350 cm$^{-1}$ and 1585 cm$^{-1}$ region (see Fig. 5.19).
Fig. 5.18. SEM images showing (a, b) filamentous carbon (c) filamentous carbon with spherical particles
The recent studies on unusual forms of carbon has attracted the scientific community as these are considered to be the new class of materials since they find applications in fields ranging from micro electronics, catalysis, adsorption, energy storage and in biomedical engineering. The filamentous carbon because of its unique properties such as low specific gravity, chemical inertness, high flexibility and mechanical strength is being extensively used in biomedical applications like tissue scaffolding material.

5.3 Retrieval of thermodynamic properties of carbides

Phase equilibrium studies carried out to understand the stability and decomposition of silicon carbide ($\beta$-SiC) and chromium carbide ($\text{Cr}_3\text{C}_2$) in water medium presented in the chapter IV section 4.6.1.1 and 4.6.2.1. The well bracketed equilibrium Pressure and temperature tabulated in the previous section of this chapter provides very useful information. It also provides a means of retrieving some of the thermodynamic properties for the phases involved. Limited thermodynamic data are available in the literature for these compounds, which have been derived either by calorimetric

![Micro Raman spectra of filamentous carbon (HDS-70) compared with spec pure graphite](image-url)
methods, electrochemical methods or under extreme temperature conditions. However, retrieval of thermodynamic parameters using the equilibrium reaction studies i.e., phase equilibrium diagrams has drawn limited attention of material researchers. There have been no reports on the derivation of thermodynamic parameters using hydrothermal phase equilibrium diagrams constructed for the reactions involving carbide phases. There are several approaches to retrieve the thermodynamic parameters from the decomposition reaction boundaries. If the relationship exhibited by the equilibrium reaction boundary in the P-T plane is simple straight line or near straight line, then the most effective way of retrieving the thermodynamic parameters is by using Clausius-Clapeyron relationship. This actually relates the slope of the reaction boundary with that of the thermodynamic parameters such as entropy or enthalpy as well as with that of volume of reaction. If one can determine the exact volume of reaction of the phases involved and also the slope of the boundary, then it is simple to estimate the thermodynamic parameters.

The Clapeyron equation states that:

$$\frac{dP}{dT} = \frac{\Delta S_r}{\Delta V_r} \quad \text{or} \quad \frac{dP}{dT} = \frac{\Delta H_r}{T \Delta V_r}$$

An extensive compilation of thermodynamic data presented by Robie and Waldbaum, Holland and Powell, CRC Handbook [27-29], were used for other phases involved in the reactions while attempting to retrieve thermodynamic parameters for carbide phases. The predicted reaction for the experimental phase equilibrium studies of silicon carbide (r$_3$) and chromium carbide (r$_{11}$) in water medium, involves the dissociation of carbide phase followed by the oxidation by utilizing the atmospheric oxygen available inside the capsule. Equilibrium temperature and pressures are presented in the previous section of this chapter. However, an attempt to retrieve thermodynamic parameters for the carbide phase using the equilibrium P-T conditions and the thermodynamic data for the phases other than carbide involved in the reaction, retrieval exercise was futile. In the absence of any analytical data on volatile generated inside the capsule, quantitative estimation of thermodynamic data is not possible. However, the change in entropy and enthalpy of reaction calculated using Clapeyron relationship, reaction slope and volume of reaction (from Holland and Powell, CRC Handbook) deviates much from that of reported data. Hence, it was
concluded that more quantitative phase equilibrium studies are needed for such thermodynamic calculations.

5.4 Other carbon source materials

The products obtained in some of the exploratory experiments using activated carbon, filamentous carbon and shungite show no significant results when treated them under hydrothermal conditions with water and C-O-H supercritical fluids. The X-ray diffraction studies indicate that the graphitic carbon was observed in the activated carbon runs. However, the filamentous carbon and natural shungite remain unreacted under the chosen experimental conditions. Since, the natural shungite needs very high activation energy to break its bonding, no reaction was observed. The organic compounds decomposed in the above mentioned experiments were converted either to vapors of CO$_2$, H$_2$O or methane, as observed while opening the capsule.

The resultant product obtained in few exploratory runs clearly indicates that it is necessary to carry out more experiments using a range of solvents, which can provide high activation energy under hydrothermal conditions. The results obtained in the present investigations demonstrate a new route for the hydrothermal studies on carbon. Interesting newer materials can be produced especially by using host of organics in the starting charge and is going to be very rapidly growing field in carbon science.
Reference