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Hydrothermal synthesis and characterization of micro to nano sized carbon particles

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Experiments under hydrothermal conditions were carried out to study the formation of elemental carbon through the decomposition of β-Silicon carbide (β-SiC) in the presence of organic compounds. The organic compounds were known to dissociate at low P-T conditions and produce the C–O–H supercritical fluids, which will have great influence on the decomposition of β-SiC. These hydrothermal runs under the influence of supercritical fluids will not only help in dissociating the silicon carbide into SiO_2 and free elemental carbon but also control the type of carbon phase formation. The Scanning Electron Microscopic (SEM) studies of the run products indicate the formation of the micron sized carbon particles having characteristic shapes like spherical/ovoid, scaly with metallic lustre and in some runs we find the formation of nano sized octahedral crystallites. Micro Raman study of these carbon particles reveals that bulk of the carbon formed in these runs were disordered / sp^2–hybridized carbon but we also noticed the formation of black scales over the spherical particles and the octahedral crystallites which exhibits the sp^3-hybridization having the characteristic sharp band at 1332 cm^{-1}, comparable to that of diamond powder. The octahedral crystallites are formed at the inner walls of the hollow spherical carbon particles. In any of the experimental runs we haven't used either the metal catalysts or the diamond seed with the charge material. Thus, the nucleation and formation of nano sized octahedral crystallites of diamond (sp^3-hybridized carbon) in the present study at lower P-T conditions compared to that of its formation in nature is a significant breakthrough in the study of diamond synthesis.

1. Introduction

Elemental carbon is known to exist in two well known polymorphic forms viz. graphite (sp^2 hybridized) and diamond (sp^3 hybridized). These two forms of carbon are known to exist in nature under highly contrasting conditions and possess very different physical and chemical properties. Besides graphite and diamond, there are reports on new solid forms of carbon [1–4], which have unusual shape and size and are mainly of sp^2-hybridized. They are carbon nano tubes (bucky tubes), fullerenes (bucky balls), carbon onions (bucky onions), filamentous carbon, nano cells and nano beads. These new solid forms of carbon have attracted intense interest owing to their several outstanding properties such as high specific surface area, good mechanical stability, chemical inertness, and porous nature having large pore volume. Preparation of graphite and diamond as well as the new solid forms of carbon have met with relatively fair amount of success and most of them need high energy processes like high temperature arc discharge / laser ablation [5, 6] and the chemical routes like chemical vapour deposition (CVD) and chemical vapour transport (CVT) [7, 8]. But, in all

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these high temperature processes, the yield is very low and such techniques are inefficient for commercial production. Thus, a simple and high yielding route for the preparation of these materials is to be developed to its full potential. Therefore, the authors have explored a simple and moderately low temperature and pressure hydrothermal technique to synthesis the elemental solid carbon [9, 10]. Our study is mainly focused on the synthesis of sp^3-hybridized and other new forms of sp^2-hybridized carbon under hydrothermal conditions. Here, we present the recent experimental results of the hydrothermal runs carried out by decomposition of silicon carbide in the presence of organic compounds. The organic compounds in the present P-T studies were expected to decompose into C–O–H supercritical fluids. It is a well known fact that the C–O–H fluids in nature are the source for the formation of some of the poorly crystallised carbon, graphite and diamond [11]. The study of solid and gaseous inclusions in diamond also indicated the C–O–H fluids as the source for nucleation and growth of diamonds in nature [12]. Thus, we have chosen some selected organic compounds to study the formation of carbon under hydrothermal conditions. The characterization of the run products through SEM studies indicates the presence of nano sized octahedral crystallites along with spherical and ovoid shaped carbon particles and micro Raman study show that the majority of the carbon particles are disordered in nature and few samples shows sp^2 and sp^3 — hybridization.

2. Experimental details

The experiments were carried out in the pressure temperature range of 200–300 MPa and 600–800°C using externally heated Roy-Tuttle test tube type autoclaves (MRA-114 R/S) made up of Rene / Stellite super alloy steel. The starting charge was β-SiC powder having specific area less than 8 $m^2.gm^{-1}$ was used along with organic compounds. The organic compounds used in the present investigation are of reagent grade formic acid, oxalic acid, malonic acid, maleic acid, glycolic acid, and citric acid. The starting materials comprising of β-SiC and organic compound without water were sealed in annealed gold capsules (50–60 mm length and 4.5 mm i.d having a wall thickness of 0.1 mm), thus restricting the amount of water in the system to the water released through the dissociation of organic compounds. We found that the excess water in the system would decrease the yield of carbon precipitation and the thermodynamic calculation of Jacobson *et al.* 1995 [13] indicated that the formation of free carbon is expected in the low water to carbide ratio. Further, in the high-pressure metal – carbon experimental system the free excess water in the system inhibits the formation of diamond [14] and the formation of graphite is more favourable. The sealed capsules were placed in the autoclaves after ensuring for any leakage. The autoclaves were inserted into the preheated furnace and the temperature and pressure were monitored until the desired P-T conditions were established. The runs were arrested by quenching it through air blast and then dipping the autoclaves in a water bath. The capsules were removed carefully and were cut open. In most of the runs the gas with pungent smell was evolved and the run products were carefully dried and subjected to characterization using powder X-Ray diffraction studies (XRD) and Scanning Electron Microscopy (SEM). Micro Raman spectral analysis of the run products was carried out using spectrometer in micro mode (T64000, Atago-Jubin Yuon, France-Japan, Ar+ laser with an excitation wave length of 514.5 nm). The experiments were replicated in order to check the reproducibility of the results.

3. Results and discussion

We have reported earlier [9, 10] the decomposition of silicon carbide in the presence of organic compound at temperature above 700°C and pressure above 100 MPa. It was found that the silicon carbide decomposes to either quartz or cristobalite along with free carbon particles in the presence of both water and organic compounds, but the yield of carbon particles has improved when there was no excess water in the system. The carbon particles formed were discrete or linked spherical shaped particles having pores, the pores were elongated irregular in shape with pore diameter of 20 to 30 nm. Thus demonstrating that the C–O–H super critical fluids produced through decomposition of organic compounds will have great influence in decomposing the silicon carbide and precipitating the free elemental carbon. However, the hypothesis of organic origin for graphite and diamond (at least a part of it) and methane is a more favourable transport medium for the synthesis of diamond in chemical vapour transport technique [15, 16] as well as the varying scenario of natural diamond formation has encouraged us to carry out more rigorous experiments. Hence, by varying the relative proportion of silicon carbide to organic compound ratio the experiments in the silicon carbide – organic compound systems were carried out. Thus, varying the partial pressures of C–O–H fluids generated inside the capsule and to study its effect on the stabilisation of carbon phase. We have earlier discussed about the diamond growth region by comparing the trilinear plots of C–O–H of organic compounds used, with that of the similar diagram of Bachmann *et al.*, Rumble III, Hoering, and discussed by DeVries [17–19], indicate favourable chemical environment for the diamond formation. Further, Benndorf, [20] is of the opinion that the increased concentration of atomic hydrogen and the C_1H_x radicals by dissociating the organic compound in a closed system is an ideal environment for the stabilization of carbon phase especially for the sp^3 — hybridized carbon under the subnatural conditions. In the present study we have not only noticed the improvement in the yield of carbon particles but also change in the shape of the carbon particles precipitated, spherical, ovoid and scaly material having metallic lustre Fig. 1 (a–d).

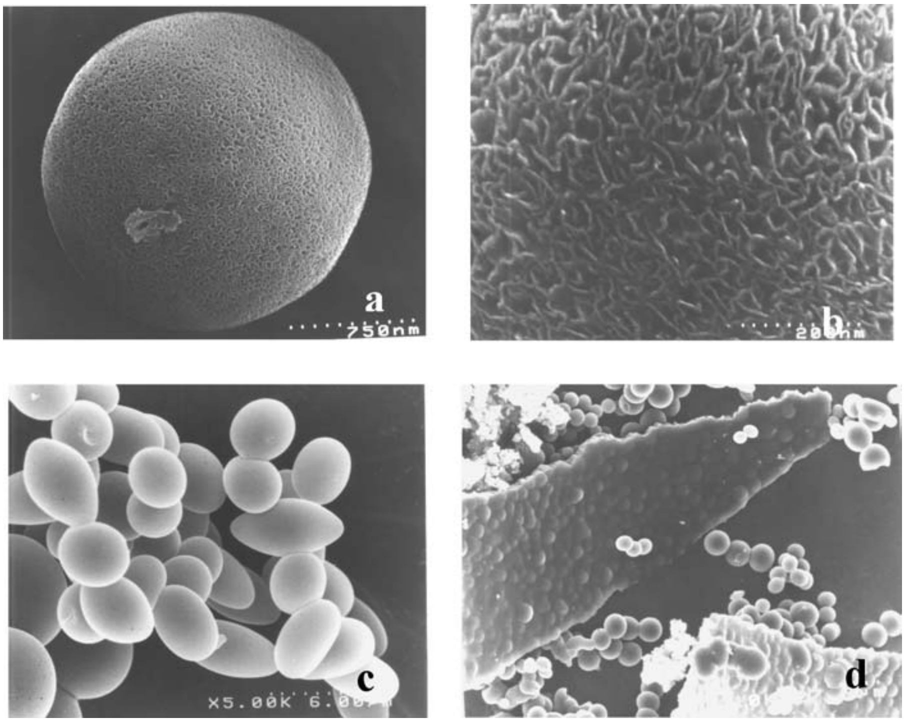

Figure 1 a–d: SEM images showing (a) spherical particle (b) enlarged image of pores (c) ovoid shaped carbon and (d) spherules with scaly material.

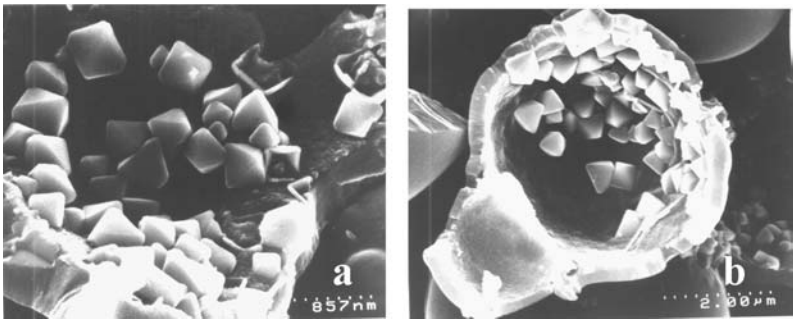

Figure 2 a–b: SEM images of carbon particles showing well developed octahedral facets adhered to the inner walls of the broken spherical particles.

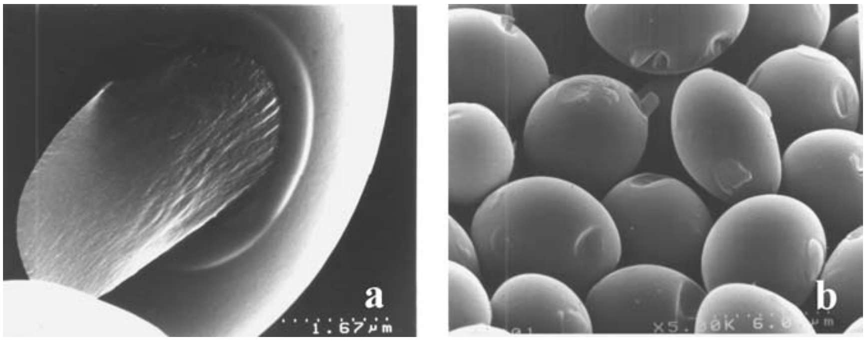

Figure 3 a–b: SEM images showing fluid like material coming out of solid spherical and ovoid particles.

Careful examination of these carbon particles under high resolution Scanning Electron Microscope, we found that some of the spherical particles are porous, hollow and the broken pieces of these carbon particles exhibit the growth of very minute crystallites which are adhered to the inner walls spheres and these crystals shows well developed octahedral facets Fig. 2a and b.

The growth of these crystallites resembles the zeolite crystals grown in vugs and cavities of volcanic flows. We have also noticed different stages in the development of hollow and porous carbon phase formation, i.e. fluid like material is coming out of the solid spherical or ovoid particles through a vent and resulting in hollow ovoid or spheres (Fig. 3a and b). Quantification of the

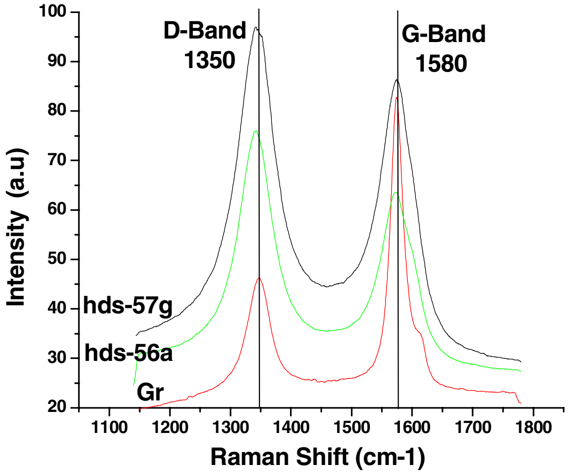

Figure 4 Micro Raman spectra of spherical (hds-56a) and ovoid shaped (hds-57g) aggregates of carbon particles compared with that of spec pure graphite (Gr).

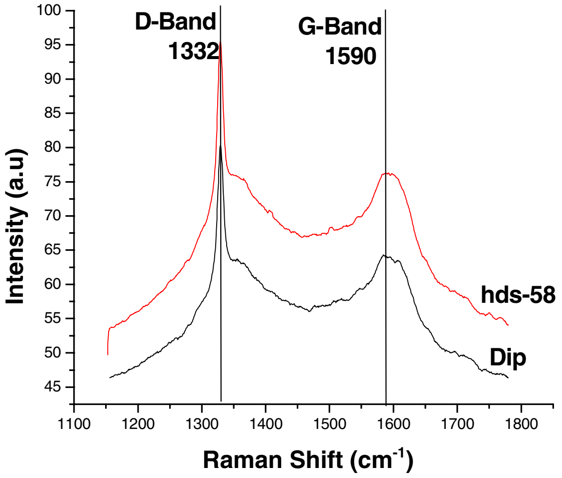

Figure 5 Micro Raman spectra of porous spherical particles (hds-58) compared with that of the commercially available diamond powder (Dip).

mechanism leading to the formation of desired shape and type of carbon formation is difficult since the phenomenon observed as above is not unique to any of the particular condition of formation, and the yield of these crystallites was also very poor. We are still working on the improvement in the yield of such crystallites as well as achieving homogenised run product.

The XRD studies of the run products is not much useful for the characterization of carbon phases, as bulk of the carbon phase is found to be of disordered nature and has strong absorption for X-rays. However, the XRD pattern shows only the pattern matching with the quartz/cristobalite and no lines corresponding to any of the reported carbon phase were found even after stripping the lines corresponding to the quartz/cristobalite.

Raman spectroscopic study of the run products indicates that the bulk of the carbon particles exhibit the broad spectrum with prominent peaks at 1350 and 1580 cm^{-1}, which are referred to D and G-band of C-C stretching vibrations. The G-band is from the carbon atoms forming hexagonal lattice, and the D-band is associated with vibrations of carbon atoms in dangling bond in plane terminations which is characteristic of sp^2 — hybridization corresponding to graphitic or disordered carbon material. Fig. 4 shows the typical representative Raman spectrum for spherical and ovoid shaped aggregates of carbon particles (hds-57g, hds-56a), along with the spec pure graphite sample. The Raman spectra obtained for a few selected scaly material having metallic lustre and for the nano sized crystallites adhered to the inner walls of the porous spherical particles (hds-58) is shown in Fig. 5 along with the spectrum of commercially available diamond powder (Hyprez — Engis, USA). This spectrum has a sharp peak at 1332 cm^{-1} and a shallow broad peak at 1590 cm^{-1}.

4. Conclusion

SEM and Raman spectroscopic observations of the run products have clearly demonstrated the formation of carbon particles under hydrothermal conditions. Besides, the spherical and ovoid shaped carbon particles, the significant observation is the formation of nano sized diamond crystals. Hitherto, the attempts on the hydrothermal synthesis of diamond/sp^3 — hybridized carbon have succeeded in the overgrowth of seeded diamond crystal and some even used the metal catalysts but the present study we haven't used either the diamond seed or the metal catalysts. Thus, demonstrating the fact that, not only over growth but also the nucleation and crystallization of diamond was possible under hydrothermal conditions. However, the relative proportion of crystallites formed compared to that of disordered carbon particles is very poor. Hence, we have been working further on the improvement in the yield and the size of the crystallites.

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