CHAPTER – VI

Conclusions

The author would like to sum up the results presented in this thesis on the hydrothermal experimental work carried out to synthesize the carbon polymorphs using carbides as well as some exploratory study on other carbon source materials. This is just a beginning and more extensive work has to be carried out on the hydrothermal synthesis / growth of carbon polymorphs especially the diamond phase. The present study is a step closer towards complete realization of hydrothermal synthesis and growth of gem quality (clear & flawless) diamond crystals and also, the new class of carbon materials like unusual forms such as filamentous carbon, carbon onions, fullerene, carbon nanotubes and nano cells. As Professor Rustum Roy puts it “the hydrothermal synthesis / growth of diamond will be a fourth revolution in the study of carbon science”. Although it was planned to study the synthesis of carbon polymorphs, more emphasis was given to produce diamond and other unusual forms of solid carbon phases under hydrothermal conditions.

The following are the salient outcome of the present doctoral work.

- All hydrothermal experimental runs for the synthesis of carbon polymorphs were carried out using Tuttle – Roy reactors in the P-T range of 100 - 200 MPa and 700-800 °C.

- The synthesis of carbon polymorphs was studied through the dissociation of silicon carbide with water as a fluid medium. The results obtained indicate that the dissociation of silicon carbide was followed by *in situ* oxidation of the silicon and carbon; hence the resultant products were only quartz and vapor phases.

- The decomposition of silicon carbide in the presence of wollastonite was carried out in water medium. Though the wollastonite and silicon carbide dissociate under hydrothermal conditions, but the run product shows wollastonite, quartz and calcite along with vapor phases. Yet no precipitation of carbon particles was noticed in any of the run products.
Further, the dissociation of silicon carbide in the presence of wollastonite was studied using organic compounds as solvents. It was intended to dissociate the silicon carbide under the influence of C-O-H supercritical fluids generated by organic solvents. The resultant products are unreacted wollastonite, well crystallized quartz along with small amount of carbon particles. The persistence of wollastonite is due to the C-O-H supercritical fluids environment inside the capsule, which has enhanced the stability of wollastonite. The irregular and spherical shaped carbon materials are of disordered or graphitic carbon with near $sp^2$ – hybridization.

The experimental runs were pursued without wollastonite, i.e with silicon carbide and organic compounds only. The run products show significant improvement in the yield of carbon particles along with crystalline quartz. The carbon particles exhibit spherical shape and they hosts nano crystallites of $sp^3$ – hybridized carbon “Diamond” at the inner walls.

The formation of $sp^3$ – hybridized carbon “Diamond” nanocrystallites is one of the significant break through in the study of carbon science. So far the synthesis of diamond is successfully carried out under HPHT condition or CVD/CVT and other high energy consuming techniques. Hydrothermal studies on diamond could so far able to show the over growth or phantom growth on diamond seed in the presence of metal catalysts. Here, author has clearly demonstrated for the first time, the nucleation and growth of diamond crystallites under hydrothermal conditions without the use of either metal catalysts or diamond seed.

Chromium carbide is also used as a source of carbon for the synthesis of carbon polymorphs. The run products in water medium are just a chromium oxide, whereas under the influence of C-O-H supercritical fluid in addition to chromium oxide the filamentous carbon was present along with spherical / ovoid shaped particles. The filamentous carbon particles are dominant over spherical or ovoid shaped particles. The filaments were solid and elongated with a mean diameter of 50 -100 nm.
A more systematic hydrothermal experimental runs were carried out in the P-T range of 50 – 200 MPa and 300 – 800 °C for phase equilibrium studies on the decomposition reactions of silicon carbide and chromium carbide with water as a fluid medium. The P-T plane obtained for the above study and considering the probable reaction, an attempt is made to estimate the thermodynamic parameters but due to lack of data on the exact nature of volatiles and its quantitative analysis, thermodynamic quantification was not possible at the moment.

Scope for future work

In the present investigation the author has used a few carbides as source of carbon and there are many more carbides unattempted. Water and few organic compounds were used in the present study as solvents, but there are several other organic compounds, hydrocarbons and aromatic hydrocarbons which are to be explored for the possibility of synthesis and growth of diamond as well as other newer forms of carbon. In addition to carbides as source of carbon, there are host of other carbon containing materials such as coal, carbon nanotubes, carbon black, fullerenes, shungites, diamond like carbon, fibrous carbon, carbon soot and carbon beads to be explored for the synthesis of carbon polymorphs.

Many of the above said carbon source materials have been used in synthesizing diamond and other forms of carbon, but very little attention was given to understand and quantifying the reactions involving them. The paucity of thermochemical data for many of the above said carbon source material is a hindrance in quantifying reactions involving these phases. Hence it is also utmost important to carry out systematic more phase equilibrium studies in water and other organic solvents. This will provide a useful tool to retrieve the thermodynamic parameters.

In addition to synthesizing carbon polymorphs under hydrothermal conditions, another important field to be explored is the preparation of polymer- carbon composites, which could act as a new class of materials having applications as
high strength materials and catalysts due to their versatile nature. Further, it being histologically and mechanically similar to natural structures, hydrothermal synthesis of these composites under controlled C-O-H supercritical fluids environment can be attained.

- The studies using organics under supercritical hydrothermal conditions for the preparation of organic-inorganic hybrid nanocrystals is an emerging field. The present study demonstrates that, there is a great possibility of obtaining organic-inorganic carbon based hybrid materials with a perfect control over the size and morphology of the particles. Also, such a study would help in producing polyscale carbon phases. This area is untouched in science.