CHAPTER 7
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SUMMARY AND FUTURE SCOPE OF THE WORK

Compact High Temperature Reactor (CHTR) and Advanced Heavy Water Reactor (AHWR) need high density isotropic type graphite and also carbon-carbon composite for various critical structural components. The present work dealt with preparation and characterization of the carbon/carbon composites. The objective of this work was to develop carbon composite materials with reasonably high density as well as amorphous isotropic carbon for use in thermal reactors. An amorphous structure is needed in order to avoid accumulation of Wigner energy. This was achieved by carrying out development of carbon-carbon composites by using different precursors. Subsequently efforts will be taken up for the fabrication of some test components for evaluating the performance of the same in our novel reactors.

The composites were prepared using petroleum coke, carbon black PAN carbon fiber both chopped and matted. These materials were characterized for their properties. The petroleum coke based samples were found to be amorphous at lower temperatures (below 800°C), but they tend to graphitize at higher temperatures. They also showed the accumulation of Wigner energy, which limits their use as neutron scatterer in the Advanced Heavy Water Reactor (AHWR). As these samples were found to be graphitizable in nature, the next sets of samples were made from chopped PAN fiber and phenol formaldehyde resin as binder, which was non-graphitizable in nature. The composite made with 20 vol% fiber heat treated at 1000°C showed the desired property in
terms of amorphousness and isotropicity. The samples with lower volume percentage of fiber (10 vol%) developed crack during processing. The increase in the percentage of fiber volume enhances stress-graphitization as observed in the case of 50 vol% fiber based sample. The samples with 20 vol% fiber tended to develop anisotropy when heated to 2000°C. Basically the shape of the fibers causes the development of stress at fiber matrix interface. This problem was eliminated by choosing the spherical shape of the second phase (carbon black). Carbon black-phenolic resin composites have been prepared through a novel technique. It was found that the carbonization of the phenolic resin pieces prior to composite preparation helps in many ways. The shrinkage of the product was found to be lesser as the volatile matter evolved during carbonization was lesser. Thus the possibility of crack formation also reduces. Therefore higher rate of heating could be employed there by helping in the decrease in production cost. Composite with a density up to 1320 kg/m³ was obtained without any impregnation by this method as compared to 1270 kg/m³ with the PAN fiber based sample after four cycles of impregnation. The structural characterization suggests that the carbon black-phenolic resin carbon composite fulfills the criterion of the scattering material. Its C_p value was found to be more than that of the graphite, which suggests a reduced probability of release of Wigner energy. This material has to be densified to impart additional irradiation stability. Further composite fabrication using 2-D matted PAN carbon fiber for the development of carbon-carbon composites was carried out. The carbonization of the preforms to remove the volatiles was subsequently followed by densification of these samples using liquid impregnation technique. To achieve the required density the impregnation was carried out with varying process controls and characterized after
suitable heat treatments. Optical microscopy with polarized light, electron microscope, XRD analysis, X-ray Tomography and Micro Laser Raman spectroscopy was used to characterize the microstructure and get a clear understanding of the microstructural details and to estimate the degree of graphitization that is achieved finally. C/C composites with density of 1470 kg/m$^3$ were developed with two cycles of impregnation and carbonization. These composites were found to be amorphous in nature from the XRD even after heat treatment up to 1800$^\circ$C. Further work on irradiation stability was carried out to see the stability of these materials under irradiation.

As the main aim of this was to develop a composite for advanced reactor applications, hence due concern would be given to the radiation damage studies of these materials by conducting relevant irradiation experiments. The carbon-carbon (C/C) composite samples have been irradiated at varying fluencies with thermal neutrons at APSARA Reactor in Bhabha Atomic Research Center, Trombay. The energy spectrum for irradiation was 98% thermal neutron component for which neutron energy was up to 0.55 eV and 2% is epithermal component (above 0.55 eV). It was observed from the XRD analysis of the irradiated and unirradiated samples that the value of $d_{002}$ peak for the unirradiated samples is higher than that of the irradiated samples indicating the tendency to get ordered structure. This was also inferred from the Raman spectroscopy. The $I_G/I_D$ ratio of irradiated samples was found increase with increasing fluence when compared to unirradiated samples initially but decreased further with increasing fluence. The stored energy with respect to the fluence level was obtained from the DSC, which indicated that simple defects created due to low fluence of irradiation are annealed by heating accompanied by release of the stored energy at lower temperature. On the other hand the
complex defects are formed require high temperatures are required for annealing these defects. The flux/fluence used is lower than the actual scenario in the upcoming compact high temperature reactor; however the present study could definitely be an initial step in the direction of investigation of damage caused by neutrons on carbon/carbon composite materials for its use in the upcoming reactor. Currently the available flux was low in the range of $10^{12}$ n/cm$^2$/s. However, these samples have to be evaluated by irradiating at a higher dose for potential nuclear application. There were severe limitations of not being able to use the fluence of $10^{20}$ n/cm$^2$. However, an extension of work on carbon-carbon composites irradiation with higher flux in some international neutron irradiation facility would be taken up in near future. Currently some irradiation studies with high energy neutrons are being carried out. However these investigations are out of scope of the present work and hence will be taken up in future.

In order to ensure the long life of the components in the reactors these are need to be coated with pyrolytic carbon (PyC) and silicon carbide (SiC) for improved mechanical, chemical and irradiation stability. PyC and SiC are to be deposited by chemical vapour deposition (CVD) technique. Although carbon-carbon composite materials possess excellent properties, they are prone to oxidation at high temperatures as conventional carbon materials when exposed to oxidizing atmospheres. Hence they can be used in environment consisting of vacuum or inert gases. As these carbon-carbon composites will experience high temperature and severe environment it is necessary to coat these composites with suitable protective layer coating. Hence protocol for SiC coating was developed using chemical vapor deposition technique on the 3D surface of the C/C composite block in a hot wall vertical reactor at temperature of 1400°C. The effects of the
process coating parameters on deposition rate and morphology of CVD coated SiC were studied. The coating was identified as β-SiC from XRD analysis. In the present studies it was found that not only the content of hydrogen but also the content of argon in the total gas mixture affects the deposition rate and the morphology of the SiC deposit. The effect of argon was found to be more pronounced than the hydrogen gas in the present system. It was possible to achieve the SiC coating using the commercially available MTS. Further work on studies of oxidation behavior of these coating will be taken up in near future course of work. Alternative chlorine free precursors are being developed which also will be used for the SiC coating as MTS is highly corrosive in nature. Consequently, intense research over the past years have been focused on the elaboration of SiC based materials from precursors such as silane plus hydrocarbon, organosilicon single compound precursors and organosilicon polymer. Among the SiC precursors most focus is on the compounds, which are non corrosive, non toxic and environment friendly.

**An extension of the present work not included in thesis**

Apart from the coating of the carbon-carbon composites, development of protective coatings for the containment of fission products within the fuel particle is also being studied. The CHTR fuel is designed to operate at high temperatures, withstand high burn-up and has long core resident time. A typical CHTR fuel bed consists of prismatic BeO moderator block with centrally located graphite fuel tube carrying fuel compacts. Schematic of fuel particle is shown in Fig. 7. 1. A typical TRISO coated fuel particle has a kernel (500 μm diameter) comprising of fissile, fertile and burnable poison materials followed by four coating layers.
The functional requirements and proposed dimensions of these layers are as follows: (a) Low-density pyrolytic carbon (PyC) buffer layer: This porous layer (90 μm thick) acts as an absorber for fission recoils and provides volume to accommodate fission products and kernel swelling. (b) Inner high-density PyC layer: This layer (30 μm thick) serves as a barrier to gross diffusion of fission products and fission gases. This is to protect integrity of subsequent SiC layer. (c) Silicon carbide (SiC) interlayer: This layer (30 μm thick) contains gaseous fission products released by the kernel and thus acts like a pressure vessel. This also acts as a pressure vessel. It contains gaseous fission products released by the kernel and thus acts like a pressure vessel. This also acts as an additional diffusion barrier to metallic fission products. The thickness needs to be adequate to withstand the developed pressure and corrosion attacks by fission products. (d) Outer high-density PyC layer: This layer (50 μm thick) as well as inner PyC layer, on irradiation, puts SiC layer into compression to limit stresses. Additionally it provides chemical protection to SiC layer. It also provides bonding surface for making compacts. There is much importance of SiC in nuclear energy applications. In TRISO-coated fuel
particles for high temperatures reactors (CHTR, HTGR), one of the layers is SiC coating. In particular, the SiC layer acts as a diffusion barrier to metallic fission products and a miniature pressure vessel of the particle. The Fig. 7.2 shows the SEM images of the TRISO coated particle containing the SiC layer sandwiched between the PyC prepared as an extension of the present work.

Fig. 7.2: SEM images of the TRISO coated zirconia particle
Coating has been developed using surrogate 500 μm zirconia microspheres. Three isotropic layers of graded density of pyrolytic carbon and silicon carbide over a buffer (porous) carbon layer was coated over the spherical particle. The coatings were developed using a high temperature spouted bed reactor. Uniform coating of pyrolytic carbon was obtained using acetylene gas. The SiC coating was developed using methyl trichlorosilane (MTS). The SEM images of the coated particles showing the different layers of uniform thickness are shown in Fig. 7.2. Raman Spectroscopy verified the β-SiC phase of isotropic layer of silicon carbide.