Summary

Natural biological system has largest variety of efficient and elegant multifunctional materials. Because of their multipurpose and multifunctional performance, interest has aroused to develop biomorphic based processing approach for developing oxide and nonoxide based structural and multifunctional materials. Various techniques such as replication, infiltration and sacrificial template have been used to develop materials for various applications by utilizing their common geometries. Porous cellular structure in wood behaves like lightweight solids providing significant surface area and specific permeability for water, metal/nonmetal or other minerals for growth. In the present work, porous SiC with wood like microstructure has been develop from pine wood as a starting material. The porous cellular structure of pine wood was used as a template and silica was added in different forms to make C/SiO$_2$ composites. Carbothermal reduction was carried out to develop SiC by using different precursors. The resulting SiC was characterized for yield, density, composition, thermal stability and mechanical properties. Efforts have been made to co-relate the properties with processing parameters in order to optimize the parameters to develop high yield and high strength bio-morphic Silicon Carbide. The work incorporated in this thesis has been divided in to seven chapters. First chapter gives brief introduction and scope of present work.

Wood is an excellent example of naturally optimized structural material which combines light weight, highly directed porosity and large specific surface area with high specific strength. In the recent years, biotemplating technology has been developed for conversion of naturally grown plant structures in to biomorphic, highly-porous ceramic with unidirectional pore morphologies in the microstructure range. This technology offers a possibility to use the large variety of natural developments to produce microcellular
ceramics, which are so far difficult to manufacture by conventional techniques. The basic method involves transforming wood into a carbon template having wood structure and carrying out the chemical reduction of this template with silicon.

A wide variety of SiC/Si composites have been fabricated by melt Si-infiltration of wood depending on the type of wood and technology conditions. Bio SiC fabrication technique has several important advantages such as low cost and not requiring high purity starting powders and very high processing temperature and fast fabrication by using open cell porous carbon template. Bio SiC ceramics have outstanding mechanical properties as compared to other porous or siliconized SiC. Bio SiC ceramics have been successfully developed as reinforcement in refractory concrete. These are considered to be promising material for dental and orthopedic implants.

Wood ceramics made from various waste materials, e.g woody papers and wood materials are beneficial for reducing resource usage and for improving environmental protection. The wood ceramics are regarded as environmentally conscious material, but with the relatively poor mechanical properties, highly variable quality and poor oxidation resistance of wood ceramics greatly limits their applications. For these reason, research has been carried out to overcome these shortcomings. Xie et al. reported that the bending strength and elastic modulus of wood ceramics prepared from medium density fiber board could be improved by three to eight times by fabricating wood ceramics/metals composites through high pressure infiltration of Mg alloy in to wood ceramics. Quiao et al. enhanced mechanical properties by infiltrating silicon in to charcoal. While Yano et al. improved the bending strength of wood ceramics by 50% through compressing wood impregnated with phenolic resin. Unfortunately, each of these methods resulted in sharp
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decrease in porosity and correspondingly increases in weight. However, development of novel wood derived ceramics requires control of the transformation of instinctive microstructure features of natural wood at all levels in to pseudomorphous structure of prepared inorganic materials without distortions and fractures.

The experimental methods used for developing silicon carbide from pine wood by three different techniques i.e. silica sol infiltration in to porous carbon template, firing of mixture of wood powder, phenolic powder and silica powder prepared by dry and solution route and their characterization have been given in chapter II. Detailed procedures used have been described. Weight and volume shrinkage of wood, change in density and porosity on pyrolysis and activation have been measured. TGA of carbon materials was carried out on Mettler thermal analysis system with TG50 for getting information about the amount of carbon present in the material and also oxidation behavior of final ceramic material. Reaction and gas evolution during pyrolysis was determined by differential scanning calorimetry (Mettler DSC-50). Surface morphology of pyrolysed wood was studied using scanning electron microscope (SEM Hitachi S-3000N). Surface area of pyrolysed as well as activated pine wood was carried out by BET method (Micromeritics Gemini 2375). Phase analysis of biomaterials was carried out by using X-ray diffractometer (Philips X`pert) model. Raman spectra was taken with Renishaw in via Raman microscope using an argon ion laser at 514nm excitation, using 50x objective where the laser beam was focused in area of 1µm.
Chapter III gives result on pyrolysis of pine wood and its steam activation in to porous carbon. The results show that weight loss of approximately 70±5% and volume shrinkage about 60±5% of pine wood on pyrolysis. After pyrolysis, the percentage axial, radial and tangential shrinkages were found to be 28.5%, 21%, and 12% respectively. Before pyrolysis the density of pine wood was 0.51 g/cm³ which reduce to 0.44 g/cm³ after pyrolysis. Pine wood contains 24.2% carbon and 0.38% ash. Surface morphology of as such pine wood exhibit open as well as closed pores. During pyrolysis, the cellulosic materials got disintegrated to create pore with average pore diameter of 22-37µm. After steam activation, the surface area of 721 m²/g and the average pore diameter of less than two nanometer could be achieved. It means that sample contains micro porosity. Pyrolysed pine wood showed diffraction from the 002 planes (2θ = 22⁰). Overlapping 110 and 004 planes (2θ = 22⁰) shows formation of typical turbostratic carbon. Pyrolysed and activated pine wood were also analyzed by Raman spectroscopy. Raman spectra obtained from the surface of pyrolysed wood show only two broad peaks at 1338.64 cm⁻¹ and 1594.74 cm⁻¹ mainly known as D and G band confirming presence of disorder carbon. ID/IG ratio was found to be 1.61 for pyrolysed pine wood. Raman spectra obtained from activated pine wood was located at 1332 and 1600 cm⁻¹. ID/IG ratio for activated carbon was found to be 1.44. It shows an increase in crystallinity of carbon after activation.

Results of SiC ceramic developed by infiltration of silica sol in to the carbon template are given in fourth chapter. Infiltrated silica-sol- carbon composites were heat treated at 1000⁰C, 1350⁰C and 1650⁰C. Carbothermal reduction was carried out at 1650⁰C and 65% yield of SiC was obtained. The C/SiO₂ composite on heat treatment at
1650°C for 4 hr results in sintering with formation of small initial SiC particles having particle size ~0.75 to 1µm. From SEM observation it was conclude that the SiC forming cell wall material between the cell was highly porous having average pore diameter of ~18µm and thickness of cell wall was ~4-7µm making rapid gas transport through SiC layer. XRD pattern of the composite heat treated at 1350°C exhibit sharp peaks of crystobalite (SiO₂) and small’s one of tridimite (SiO₂).

Fifth chapter gives result of SiC developed by using wood powder as precursor. Fine ground wood and silica powder and liquid phenolic resin were mixed in different composition and casted in to pellets at different temperatures 60°C, 80°C and 110°C followed by drying for 12hrs. Firing was carried out at 1650°C for 4 hr in argon atmosphere. SEM micrograph of resulting SiC material showed highly porous materials with the formation of SiC whiskers. XRD pattern of the composite heat treated at 1650°C for 4hr shows peak at 2θ = 35.60° showing the formation of biomorphic SiC. Raman spectra were also taken with double grating spectrometer DFS-24 at room temperature. 514nm, line of an Ar laser used for excitation. Analysis of Raman spectra supported biomorphic polytypes silicon carbide. Raman spectra gives value of LO and TO at 792 cm⁻¹ and 968 cm⁻¹ respectively.

Sixth chapter comprises the results of formation of biomorphic SiC from pine wood, silica and phenolic powder. Pine wood powder, silica and phenolic resin powder were mixed together in different compositions and grinded in the ball mill for 12hrs for uniform mixing. After ball milling pellets were made by hot pressing at 150kg/cm² pressure and at 150°C for one hr. Casts had cold strength initially as absence of solvent reduce the porosity. On heat treatment at 1650°C, the samples became very fluffy. The
percentage, yield of silicon carbide was 88% and amount of unreacted silica was 12%. These samples had improved mechanical properties. Kerosene porosity was 82%. XRD diffraction pattern shows formation of SiC and quantitative analysis confirm formation of 88% SiC and 12% silica.

Various conclusions drawn from the experimental results are compiled in seventh chapter. Carbothermal reduction leads to formation of biomorphic SiC. Density and the porosity of silicon carbide vary from method to method. Presence of solvents in the mixture yields more porosity and less strength. Formation of SiC whiskers was observed in the sample by SEM. Due to the formation of whiskers mechanical properties of SiC gets decreased. When silica sol was used for infiltration purpose in porous template, after carbothermal reduction at 1650\(^{0}\)C in inert atmosphere, resulting structure was extremely soft and weak. Mechanical properties of biomorphic SiC were enhanced by mixing the carbon and silica precursor through solution and dry route. Solution route resulted in increasing yield of SiC, but samples were very soft and could not be handled for measurement of mechanical properties. Dry route yielded high yield of 88% of SiC. Sample had improved strength and could retain its strength shape and structure. Dry route method provides high yield of silicon carbide on carbothermal reduction and with sufficient cold strength. Hence biomorphic SiC can be prepared by simple single step method by pine wood as template.