**Review Article**

*Pak. J. Sci. Ind. Res. 2004* ***47****(6) 478-481*

# HIGH TEMPERATURE SI-B-C-N CERAMICS

***Shah Alam Khan* and Mahtab Faisal***

*PCSIR Laboratories Complex, Jamrud Road , Peshawar - 25120, Pakistan*

(Received February 21, 2003; accepted October 16, 2004)

The importance of pyrolysis of preceramic organometallic compounds is increasing year by year as a key technology for the synthesis of new inorganic materials. According to this process, preceramic polymers are synthesized from monomer units. After cross-linking of such precursors, the obtained preceramic networks are transformed by pyrolysis into amorphous materials. Further increase of the temperature yields thermodynamically stable crystalline materials. In this paper, the general methods of the synthesis of ceramic materials based on the Si-B-C-N system via thermolysis of preceramic compounds have been reviewed. Bulk materials, coatings and fibers of such materials reveal quite interesting high temperature properties.

***Key words*****:** Pyrolysis, Preceramic compounds, High temperature ceramics.

## Introduction

In the process of the pyrolysis of preceramic compounds (Fig 1) proper monomer units are polymerized and cross-linked into organometallic preceramic networks. The networks are then subsequently pyrolized at elevated temperatures providing inorganic materials of great scientific and technical interest. Since the first proposal of this concept (Popper 1967) several research groups in Germany, USA, Japan and France have been working in this field. The achievements of these groups and the ongoing activities in the exploration of chemical synthesis routes for the production of proper preceramic networks, the controlled decomposition of the preceramics into inorganic materials as well as the characterization and technical aspects of many different materials have been reported in several articles (Laine 1986; Bill and Aldinger 1995; Birot *et al* 1995; Baldus and Jansen 1997) The idea behind the process of the pyrolysis of preceramic compounds is to build up organometallic polymeric chains of structural units of the ceramic materials. The goal is to synthesize the macromolecules at first and then to condense them at relatively low temperatures into inorganic materials.

Several aspects make this technique most attractive for the development of new materials and compounds such as:

I) With this technique one can easily produce amorphous materials with compositions not obtainable with common synthetic routes.

II) Because of the low mobility in predominantly covalent bonded materials the amorphous stage can be thermally stable to very high temperature before transforming into crystalline phases.

III) One can control the thermal activation in the amorphous stage for material transport mechanisms. So the technique kinetically stabilizes the less stable phases and microstructures with morphologies not possible by common synthetic techniques such as melting or sintering.

IV) Taking advantage of the various fabrication capabilities of polymer process engineering, components such as fibers, coatings, infiltration and complex-shaped bulk parts can mostly be produced in an easy manner.

The purpose of this paper is to outline the general methods of the synthesis of ceramic materials via thermolysis of preceramic compounds. This outline will consist of general information taken from the literature.

*Precursor synthesis*. Since the type of the backbone and the functional side chains of precursor molecules substantially influence the ceramic yield, chemical composition, and microstructure of precursor-derived ceramics a variety of different compounds has been investigated as starting materials. Figure 2 shows examples of the polymers which have been synthesized from monomers for the preparation of silicon carbide and silicon nitride-based ceramics.

These polymers are characterized by a direct attachment of silicon to carbon or nitrogen. Boron-containing polycarbosilazanes (Bill *et al* 1995, Riedel *et al* 1996) carbon containing polyborosilazanes and silylated borazine derivatives (Seyferth *et al* 1991) have been shown to be excellent precursor molecules to ceramic materials in the quaternary system Si-B-C-N. In general, these molecules consist of Si-N skeletons, which are more or less cross-linked via B, B-N, B-C or borazine units, carrying different substituents bonded to the silicon centers.

---

*Author for corresesondence

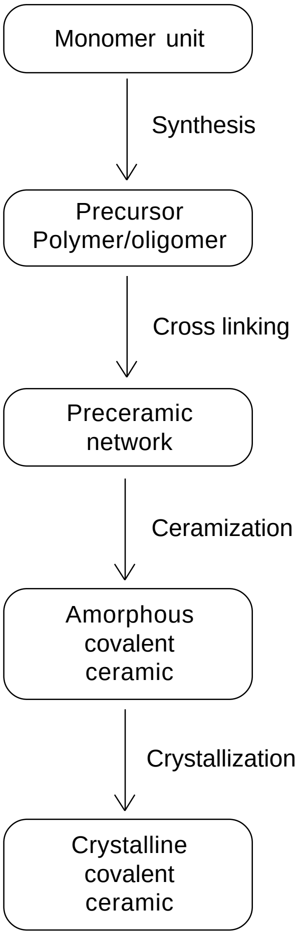

**Fig 1.** Material design by molecular architecture.

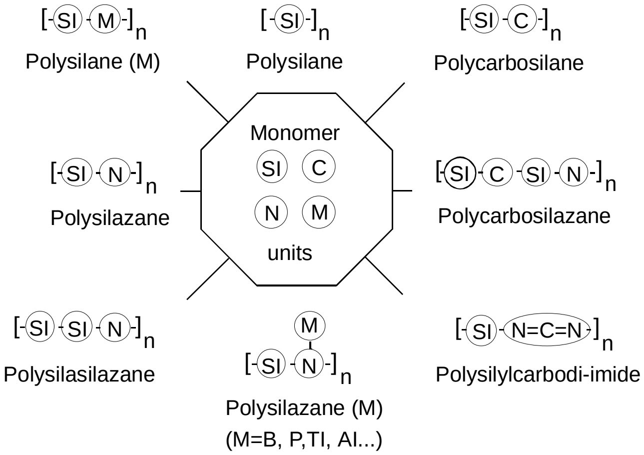

**Fig 2.** Formation of non-oxide organic silicon polymers from monomer units.

Recently, substantial progress has been made by the synthesis of boron-modified polysilazanes and polysilylcarbodiimides (Weinmann *et al* 1999, Bill *et al* 2000) using vinyl groups for the attachment of boron.

*Thermolysis*. The reactions which occur during thermolysis are still not cleared up in detail. Figure 3 describes schematically the formation of ternary $Si_3N_4$/SiC composites from cyclic oligosilazane (Aldinger 2002). NMR studies (Aldinger *et al* 1998, Bill *et al* 1998, Banfeld *et al* 1999) have shown that at temperatures below 500°C cross-linking by reactions like dehydrogenation between N-H and Si-H groups occurs. Between 500°C to 700°C, ceramization takes place and methyl groups split off yielding an amorphous silicon carbonitride. At temperatures higher than 900°C residual hydrogen is removed. 29Si and 13C solid state NMR studies (Aldinger *et al* 1998) were performed on a series of ternary silazanes after thermolysis of a commercial polyhydridomethylsilazane (PHMS, NCP200 of Chiosso Crop., Tokyo, Japan). The results at different temperatures revealed a short range order of the elements consisting mainly of tetrahedral SiCxNy (x + y = 4) units and sp3-hybridized carbon. However, the short range order of silicon carbonitrides is directly correlated with the molecular structure of the polymer. This has been demonstrated in the case of the thermolysis of a commercially available polyvinylsilazane (PVS, VT50, Hoechst AG, Germany)

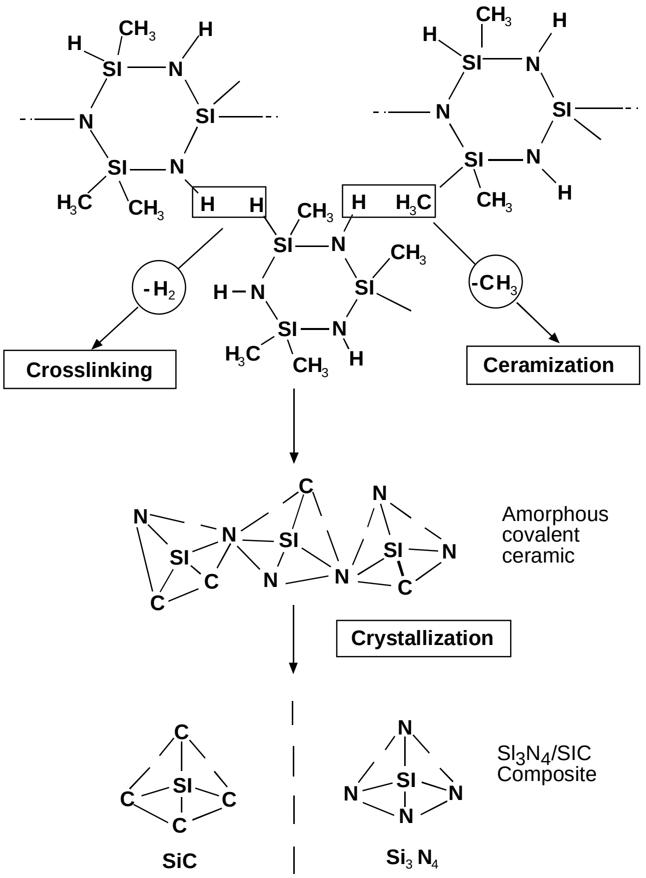

**Fig 3.** Schematical description of the formation of $Si_3N_4$/SiC composites from cyclic oligosilazane.

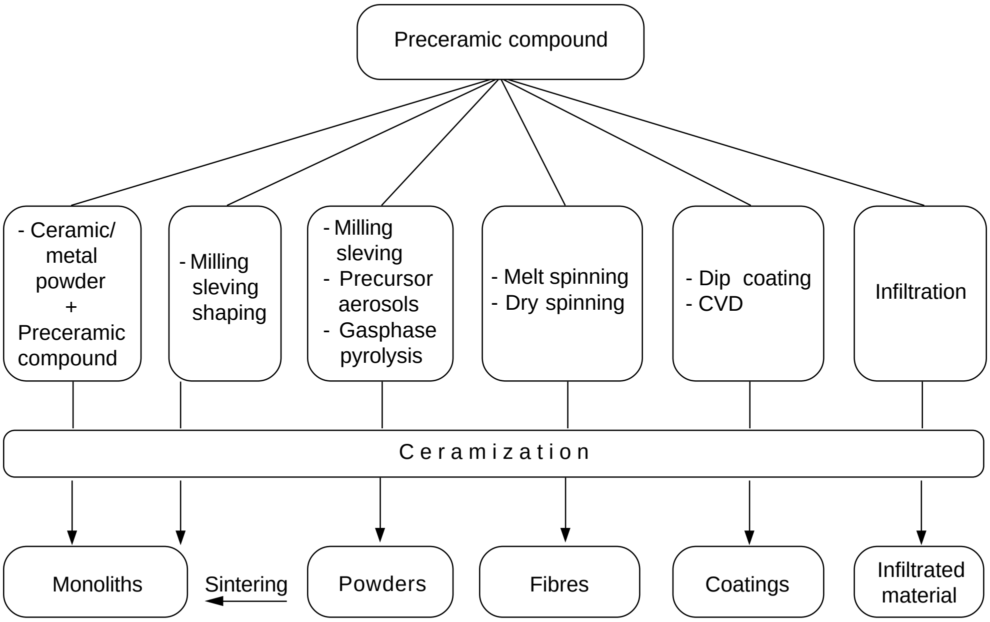

**Fig 4.** Preparation of ceramic materials by precursor processing.

which results in SiN4 tetrahedral units and sp 2-hybridized carbon. Against this, the effect of boron on the reactions during thermolysis is not clearly understood.

*Precursor pyrolysis engineering*. The production of precursor-derived ceramics takes advantage of highly developed polymer process engineering. Powders, fibers, coatings, bulk materials, infiltration and other types of preforms can be produced by techniques well known from polymer process engineering followed by a pyrolysis step (Fig 4) (Ramakrishnan *et al* 2001).

The production of dense bulks material is of special interest. This is not trivial, since the condensation reactions during pyrolysis are combined with the evolution of gases like $H_2$, $NH_3$ and $CH_4$. These species degas easily with the manufacture of fibers or coatings, i.e. with shapes which are thin in at least one dimension (Heimann *et al* 1995, Gadow and Kienzle 1998, Kamphowe *et al* 1998, Weinmann *et al* 1999, Bill *et al* 2000) Coatings have been produced by dip coating substrates into precursor solutes and subsequent conversion into inorganic pyrolysis.

## Conclusion

It has been shown that the preparation of Si-B-C-N ceramic composites from element organic polymers is a suitable methods for the synthesis of high temperature stable materials. The polymer syntheses are realized on different reaction pathways (e.g. dehydrogenation from hydridosilazanes and borazine derivatives or by ammonolysis of suitable boron containing chlorosilanes or chlorosilylaminodichloroborane). A new class of Si-B-C-N precursors are boron containing polysilylcarbodi-imides which can be obtained from a non oxide sol-gel process of bis (trimethylsilyl) carbodi-imide and hydroborated vinylchlorosilanes. The advantage of this non oxide sol-gel process as compared to common methods (e.g. ammonolysis of chlorosilanes) significantly facilitated workup. It has been shown that polymer solutions of boron containing polysilazanes of convenient viscosity are applicable for both, the production of oxygen resistant fibers and coatings. Moreover it has been determined that boron modified polysilylcarbodi-imides are outstanding precursors for the production of dense bulk ceramics. The obtained preceramics are then transformed into amorphous ceramics by subsequent thermolysis. Depending on the structure of the amorphous state, which is still not known in detail, the metastable amorphous ceramics crystallize at higher temperatures into the thermodynamically more stable crystalline materials.

## References

Aldinger F, Weinmann M, Bill J 1998 Precursor-derived Si-B-C-N ceramics. *Pure Appl Chem* **70** (2) 439-448.

Aldinger F 2002 Thermal expansion behaviour of precursor derived amorphous Si-C-N and Si-B-C-N ceramics. *J Mater Sci Technol* **18** (2) 139-142.

Baldus H P, Jansen M 1997 Modeme Hochleistungskeramiken-amorphe anorganische Netzwerke aus molekularen Vorlaufem. *Angew Chem* **109** 338-354.

Banfeld B, Gu H, Bill J, Wakai F, Aldringer F 1999 High temperature deformation of precursor-derived amorphous Si-B-C-N ceramics. *J Eur Ceram Soc* **19** 2797-2814.

Bill J, Aldinger F 1995 Precursor-derived covalent ceramics. *Adv Mater* **7** (9) 775-787.

Bill J, Kienzle A, Sasaki M, Riedel R, Aldinger F 1995 Novel routes for the synthesis of materials in the quaternary system Si-B-C-N and their characterization. In: *Advances Science and Technology 3B Ceramics*: Charting the Future, (ed) Vincenzini P Techna Srl pp 1291-1299.

Bill J, Seitz J, Thurn G, Durr J, Canel J, Janos B Z, Jalowiecki A, Sauter D, Schempp S, Lamparter H P, Mayer J, Aldinger F 1998 Structure analysis and properties of Si-C-N ceramics derived from polysilazanes. *Phys Stat Sol* **166** 269-296.

Bill J, Schuhmacher J, Muller K, Schempp S, Seitz J, Durr J, Lamparter H P, Golezewski J, Peng J, Seifert H J, Aldinger F 2000 Investigation into the structural evolution of amorphous Si-C-N ceramics from precursors. *Z Metallkd* **91** (4) 335-351.

Birot M, Pillot J P, Dunogues J 1995 Comprehensive chemistry of polycarbosilanes,polysilazanes and polycarbosilazanes as precursors of ceramics. *Chem Rev* **95** 1443-1477.

Gadow R, Kienzle A 1998 Development of ceramics via pyrolysis of metal organic polymers. *Mat wiss u Werkstofftech* **29** 371-384.

Heimann D, Bill J, Aldinger F 1995 Development of oxidation protected carbon/carbon. *Z Flugwiss Weltraumforsch* **19** 180-188.

Kamphowe T W, Weinmann M, Bill J, Aldinger F 1998 Preparation of fibre-reinforced Si-B-C-N ceramics by polymer precursor infiltration. *Sil Ind* **63** (11-12) 159-162.

Laine R M 1986 Transformation of organometallics into common and exotic materials: design and activation. In: *Proceedings of the NATO Advanced Research Workshop*, Cap D Agde France.

Popper P 1967 Brit Ceram Res Assn Special Pub location **57** 1.

Ramakrishnan P A, Wang Y T, Balzar D, An L, Haluschka C, Riedel R, Herman A 2001 Si-B-C-N ceramics: A class of high temperature dopable electronic materials. *APL* **78** (20) 3076-3078.

Riedel R, Kienzle A, Dressler W, Rumisch L, Bill J, Aldinger F, 1996 A silicoboron corbonitride ceramic stable to 2000°C. *Nature* **382** 796-798.

Seyferth D, Plenio H, Rees J W S, Buchner K 1991 *Silicon Ceramics with a Dash of Boron in Fronterrs of Organosilicon Chemistry*, The Royal Society of Chemistry, Cambridge, UK.

Weinmann M, Bill J, Aldinger F 1999 *Boron-containing polysilazanes, their manufacture, and manufacture of ceramics and coatings by thermal degradation of the polysilazanes*. Ger Offen DE 19741458.

Weinmann M, Bill J, Aldinger F 1999 *Manufacture of boron, carbon, hydrogen, nitrogen, and silicon containing polymeric precursors for manufacturing ceramics, the precursors, ceramics and coated composites obtained and their use*. Ger Offen DE 19741459.

Weinmann M, Kamphowe T, Bill J, Aldinger F 1999 *Manufacture of boron, carbon, hydrogen, nitrogen, and silicon containing polymeric precursors for manufacturing ceramics, and the precursors, ceramics and coated composites obtained*. Ger Offen DE 19741460.