Production of improved SiC and SiCN ceramics from polycarbosilane and polysilazane composites

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Abstract. With the aim of modifying the composition and microstructure of SiC and SiCN ceramics, we have investigated different reactive additives for polymer derived ceramic (PDC) precursors as well as changes in processing conditions (polymerization conditions, sintering conditions, etc.). Different concentrations of additive were dispersed in commercial carbosilane and silazane resins to give preceramic composites, which were pyrolyzed to ceramics. By adjusting the ratio of additive, the microstructure of resultant ceramics was affected as are the electrical and mechanical properties.

Keywords: Polymer derived ceramics, Nanocomposites, Silicon carbide, Silicon carbonitride

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INTRODUCTION

SiC and SiCN ceramics are known for high thermal and oxidative stability as well as interesting mechanical and electrical properties.[1-3] SiC and SiCN ceramics can be readily synthesized by pyrolysis of carbosilane and silazane precursors under inert atmosphere, where the upper temperature of pyrolysis will have bearing on microscopic structure and material properties.[4] Liquid precursors of polymer derived ceramics (PDCs) are amenable to processing methods including injection molding, extrusion and film casting.[5-7]

A variety of carbosilane and silazane resins are commercial available, with rheological properties and cure kinetics dependent on molecular weight and the presence of specific reactive groups. SMP10 is a popular carbosilane precursor with reactive allyl sidegroups. By comparison, Ceraset PSZ 20 is an attractive silazane precursor with vinyl sidegroups. Both precursors can be thermally crosslinked at temperatures below 100 °C with the addition of peroxide initiators or UV crosslinked with an appropriate photoinitiator (Figure 1).[8-10] Photoreactive siloxane and carbosilane resins have been investigated by other researchers for stereolithography, which uses spatially resolved light to selectively crosslink the polymer and build objects via layer-by-layer fabrication.[11-13] Resultant siloxane or carbosilane green bodies can then be pyrolyzed to give SiCO or SiC ceramics with well-defined geometries.[14, 15] Carbosilanes and silazanes can crosslink via multiple pathways, and polymer architecture can have an effect on the microstructure of resultant ceramics (Figure 1).

Polycarbosilane and silazane resins can be modified with inorganic fillers including SiC, Si₃N₄, TiN and MoSi₂ powders to give composite resins.[16] Pyrolysis of the composite green bodies gives first composite ceramics with filler grains entrapped within an amorphous SiC or SiCN matrix. At higher temperatures, the filler will sinter and in some cases form new crystal phases with Si, C and N. Resultant materials can in some cases have very different properties from the parent compounds. With SiCN ceramics, there is interest in adjusting carbon and nitrogen concentration to modify electrical and mechanical properties. To increase carbon concentration, organic monomers rich in carbon such as styrene and divinylbenzene can be used.[17] Carbon nanotubes have also been tested as reactive additives. One method for increasing nitrogen concentration is to conduct the pyrolysis step in reactive gases including NH₃, N₂/H₂ mixtures and N₂, which becomes reactive at temperatures above 1400 °C. This methodology is limited since the gas reactions proceed from the surface and can require extremely long reaction times to produce dense ceramics with homogenous compositions. Alternatively, inorganic and organic reactive fillers can be used to increase nitrogen content.

FIGURE 1. Crosslinking reactions of carborosilane SMP 10 (left) and silazane Ceraset PSZ 20 (right).

Results and Discussion

Commercial polysilazane (Ceraset PSZ 20) and polycarbosilane (SMP 10) resins have been modified with varying degrees of reactive additives to improve properties of resultant ceramics. In particular, triphenylvinylsilane (TVPS) and divinylbenzene (DVB) have been used to increase carbon content. Generally, graphitic carbon, homogeneously distributed within an amorphous Si/C/N matrix tends to act as a lubricant and can negatively affect mechanical properties. Small molecule additive such as TVPS and DVB, on the other hand, are soluble in the preceramic polymers and form covalent bonds during cross-linking (Figure 1). As a result, most of the added carbon is conserved during pyrolysis, as indicated by TGA (Figure 2), which shows increased ceramic yield compared to pristine polysilazane or polycarbosilane.

FIGURE 2. TGA of nanocomposite resin consisting of polysilazane, polycarbosilane and TVPS (A), polysilazane alone (C), and polycarbosilane alone (D). Image reproduced with permission from ref 5. Copyright Elsevier 2012.

3-Point bending tests revealed a characteristic strength of approximately 700 MPa for the ceramics prepared from Ceraset and from mixtures with SMP-10. Variation in content of SMP-10 in the range of 0 – 45 wt% and pyrolysis

temperature (1130 – 1370 °C) did not affect the strength significantly. Slight differences in measured value have been treated statistically and indicate a relatively low Weibull modulus of 6.1. By comparison, Shah and Raj measured similar strength values and a higher Weibull modulus for non-polished pressure-casted Ceraset ceramics, although strength was significantly improved when the samples were polished prior to pyrolysis ($\sigma = 1.1$ GPa).[18] As is true with many other ceramics, surface finish is a key parameter on the measured mechanical properties.

FIGURE 3. SMP10 thermally crosslinked with increasing content of DVB (SMP10 0 wt%, C40 12 wt%, C50 29 wt%, C60 45 wt% DVB) before (a) and after pyrolysis at 1400 °C. Image reproduced with permission from ref 17. Copyright Elsevier 2014.

Working with carbosilane (SMP 10) without silazane, DVB has been tested as a reactive additive to increase carbon content of SiC ceramics. In these studies, opacity of thermally crosslinked composites gradually increases according to the amount of DVB added (Figure 3). At low concentration, the resin is homogenous and clear. This results, however, in the formation of white bands at high DVB concentration (C60 with 45 wt% DVB). After pyrolysis at 1400 °C, the cracking behavior is different according to the amount of DVB amount used and sample C50 displayed no visible cracks. Since C50 samples had a relatively high concentration of additive and were the most stable, they were used for most comparative testing.

FIGURE 4. XRD diffractograms of samples SMP10 (left) and C50 (right) after different annealing temperatures. Image reproduced with permission from ref 17. Copyright Elsevier 2014.

The crystallization behavior of the carbosilane/ DVB derived ceramics was also investigated. Figure 4 presents XRD for samples SMP10 (formed from carbosilane alone) and C50 (with DVB) pyrolyzed at different temperatures. Some common features are seen for both starting compositions. When pyrolyzed at 800 °C, broad humps centered at 35.5° (111) and 64° are visible, typical of an amorphous and disordered microstructure. Their intensity and sharpness increase according to the temperature and at 1200 °C the formation of two peaks at 60° (220) and 71.5° (311) indicates the formation of β -SiC crystals in the amorphous microstructure. The crystallization progresses with

increasing temperature and results at 1400 °C in the formation of an additional peak at 75.5° (222) also attributed to β -SiC formation. We attribute the SMP10 peak at 41° to β -SiC (200). While most peaks are recognized for both starting compositions, the samples pyrolyzed with DVB do contain some unique peaks as well. In particular, the XRD of C50 shows broad reflections at 26° and 43°, which can be attributed to the formation of free carbon. This starts to form ordered nanodomains at 1000 °C when the peak at 43° is already visible as a small shoulder.

Conductivity of the carbosilane/DVB ceramics was measured as well, where DVB content and pyrolysis temperature were both found to have an influence. For instance, samples SMP10 and C40 pyrolyzed at low temperature (800°C) are insulators with conductivity below 10^{-10} S/cm. These values increase by over 7 orders of magnitude as pyrolysis temperature is increased. When pyrolyzed at 1200°C, the conductivity is 2.5×10^{-4} and 8.5×10^{-3} S/cm for SMP10 and C40 ceramics respectively. At 1400°C the values increase to 2.3×10^{-3} S/cm for both samples. This increase is attributed to formation of a conductive network in the matrix and percolation. Such conductivity values are typical for crystalline SiC and it is assumed that this phase dominates the conductivity behavior with the SMP10 sample. For high carbon content compositions C50-C60, conductivity is already semiconductor like (5.2×10^{-6} and 1.5×10^{-4} S/cm) for samples pyrolyzed at 800°. When pyrolyzed at 1000°C, conductivity increases by 3-4 orders to 7.8×10^{-2} and 1.9×10^{-1} S/cm. Increasing pyrolysis temperature to 1400°C further increases the values to 9.4×10^{-1} and 2.5 S/cm for C50 and C60 respectively.

CONCLUSIONS

Reactive organic additives such as TVPS and DVB have been used with commercial silazane and carbosilane polymer resins to modify the properties of resultant ceramics. The additives can be used to increase ceramic yield and conductivity versus the ceramic precursor alone. An optimal concentration of additive provides first homogenous green bodies and after pyrolysis ceramics with better toughness. These processes and materials are suitable for numerous applications including advanced coatings, MEMS, and sensors.

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