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THE INFLUENCE OF CARBON ON THE STRUCTURE OF PRECERAMIC POLYMER DERIVED SiC

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ABSTRACT

The microstructure of SiC produced from allyl-hydridopolycarbosilane (AHPCS) was studied after thermal treatments at temperatures up to 1600°C. SiC samples were prepared in contact with pyrocarbon, carbon fiber, carbon felt, carbon powder, and graphite. Each of these configurations was examined using optical, scanning electron, and transmission electron microscopy. The resultant microstructure of the SiC in the vicinity of the carbon/graphite source was different for each sample. In some cases the grains were uniform, equiaxed and about the same size as SiC grains derived from neat AHPCS. Other samples exhibited accelerated grain growth in the vicinity of the carbon, and occasionally appeared to mimic the original carbon structure. Understanding and controlling such behavior will facilitate the fabrication of polymer derived stoichiometric SiC, and also has significant implications for the fabrication of SiC/SiC composites with a pyrocarbon interface and polymer derived matrix.

INTRODUCTION

A number of preceramic polymeric SiC precursors have been developed including polycarbosilane, polymethylsilane, polycarbosilazane. The SiC produced from these precursors has been discussed and evaluated in the open literature (1-8). Questions remain, however, about optimization of processing for desired mechanical properties and environmental resistance. Processing variables such as time and temperature of thermal processing, the environment during processing, the chemistry of the precursor, and the presence of additives can affect the final SiC microstructure and ultimately the resultant properties. This project approaches process optimization by studying the effects on microstructure of processing with several additives including pyrocarbon, carbon fiber, carbon felt, carbon powder, and graphite. The reason for these additives was to tailor the microstructure to an optimum grain size for maximum properties (thermal conductivity, creep resistance, radiation resistance and mechanical strength) and to determine whether the polymer reacts with carbon which would affect the fabrication of polymer derived composites with pyrocarbon (PyC) reinforcements. Reported here are the effects on microstructure and reactions with additives for the allyl-hydridopolycarbosilane (AHPCS) SiC precursor.

EXPERIMENTAL

One SiC preceramic polymeric precursor, allyl-hydridopolycarbosilane (AHPCS), was the focus of this study. A "5-20" version of AHPCS (5 w/o allyl and 20 w/o dichloro) polymer obtained from Rensselaer Polytechnic Institute (RPI) was used. This polymer is a viscous liquid which can be infiltrated into preforms or mixed with powders and pyrolyzed to form SiC. There were four types of samples in this study. The first sample type involved the impregnation of AHPCS into a pyrocarbon (PyC) coated

Hi-Nicalon woven preform. The second sample type was made by mixing carbon additives including powders, chopped felt, and chopped fibers with AHPCS polymer into a paste before pyrolysis. The third sample type was prepared by applying just enough polymer to carbon felt or fiber to wet the surfaces and then thermally treating the sample. The fourth sample type was thermally treated polymer as formed on graphite tooling.

The thermal processing was standardized for all samples into three treatments. The first was a cross-linking cure at 400°C for 8 hours in argon to solidify the polymer. Note that when forcing AHPCS polymer into a preform, the cure was carried out in an argon atmosphere pressurized to 600 psi, otherwise atmospheric flowing argon was used. The second treatment was a pyrolysis at 1000°C for 10 hours in flowing argon. The third treatment was a crystallization cycle at 1600°C for 10 hours in flowing argon.

After thermal treatment the samples were visually inspected for voids and uniformity followed by analysis. Many were analyzed by X-ray Diffraction (XRD) followed by metallography and Scanning Electron Microscope (SEM) inspection. All samples were examined with a Transmission Electron Microscope (TEM) and several of the samples were examined using Electron Energy Loss Spectroscopy (EELS) to obtain information about the chemical state. Of these methods, the TEM was the most informative about the polymer derived SiC microstructure because the features are Angstrom sized. Therefore, this report contains mostly TEM data.

RESULTS AND DISCUSSION

Baseline Microstructure of Pure Polymer

AHPCS polymer derived SiC material has a two-phase microstructure consisting of β -SiC grains and about 10-20% amorphous carbon-rich regions which also contain some silicon. EELS analysis determined that the amorphous regions were carbon-rich but little else is known about these areas. Typically these two phases are finely inter-dispersed and have the same grain/region sizes, about 20-500Å, depending on temperature and duration of thermal treatment. This two-phase structure is evident when the polymer is treated above 1400°C for sufficient time. Material treated below 1400°C has an amorphous structure. Figure 1 contains TEM images showing the baseline structure for neat (no additives) polymer treated at 1600°C for 10 hours. As a result of this treatment the grain size is between 20-100Å, and the amorphous carbon-rich areas are uniformly dispersed throughout. The selected area diffraction pattern indicates that the crystalline structure is β -SiC except that an extra line is present. It is interesting to note that this line corresponds to the 4H α -SiC pattern, but no other 4H indications are present. Figure 1 is the baseline microstructure to which all other samples are compared.

The Addition of Pyrocarbon

The addition of pyrocarbon (PyC) is interesting because PyC is used as an interface coating in SiC/SiC composites to improve mechanical properties. In order to replicate this application, PyC coated

Figure 1- Baseline microstructure of AHPCS without additives, treated at 1600°C for 10 hours.

Hi-Nicalon SiC fibers were used in this study. For comparison, samples reinforced with Hi-Nicalon were prepared without PyC and also without both PyC and polyvinyl-alcohol (PVA) sizing.

Hi-Nicalon with PyC: All of these samples came from woven Hi-Nicalon preforms with 0.5-1.5 μm of PyC interface coating. These preforms were infiltrated with AHPCS polymer to form a SiC matrix and then thermally treated. Most samples were examined after 8 infiltration and pyrolysis cycles, but some were examined after 4 and 6 cycles. In general the matrix (region not adjacent to the fibers) exhibited the baseline polymer derived SiC structure except that the β -SiC grains were larger (about 200-1000 $\text{\AA}$). The amorphous carbon-rich regions were evenly distributed and at the smaller end of the grain size range.

The formation of SiC adjacent to the PyC coated fibers is very different from that of the matrix. Instead of the fine two-phase microstructure, large blocky β -SiC grains (about 2000-3500 $\text{\AA}$) formed along the PyC or directly next to the fiber, see Figure 2. Note that the grains in the fiber retained their initial dimensions. The formation of the large SiC grains along the fibers look like a coating and in that sense they mimic the PyC layer. Such a phenomenon may result from heterogeneous nucleation of polymer derived SiC along the PyC, or from an interaction between the PyC and the polymer. To explore this, Hi-Nicalon without PyC was studied and is discussed in the next section.

Whether or not PyC coating is present appears to be a function of the number of polymer infiltrations and thermal treatments above 1500°C. Comparing the structure after 4 infiltrations and 1 cycle at 1600°C with the structure after 6 infiltrations and 2 cycles at 1600°C it was noticed that PyC was present in the 4 infiltration sample and was not in the other. In an attempt to determine whether the dependence is on infiltrations, thermal exposure, or both, samples with 4 infiltrations and 1 cycle at 1600°C were exposed to additional cycles at 1600°C. After 3 cycles at 1600°C, regions with PyC were as frequently observed as after 1 cycle indicating a strong link between the loss of PyC and the number of infiltrations. More is said about this in the discussion on the maximum exposure temperature.

Another observation after 3 cycles at 1600°C was that the interface between the AHPCS and PyC changed, and the fiber grain size coarsened. Figure 3 shows how the interface between the PyC and the AHPCS derived SiC became undulating instead of straight as it was after 1 cycle at 1600°C. This indicates that there must be a diffusion controlled reaction occurring during the additional thermal

Figure 2- TEM image showing large polymer derived β -SiC grains next to PyC coated Hi-Nicalon fibers.

Figure 3- TEM image showing undulations at the PyC/SiC interface which developed after several treatments at 1600°C.

cycles. The Hi-Nicalon fiber coarsened to grain sizes about 200-500Å instead of 20-100Å. Based on the data presented here, it is impossible to determine whether the observed fiber grain growth after multiple 1600°C cycles was related to the changes along the PyC- polymer derived SiC interface or just due to thermally activated coarsening.

The disappearance of PyC may be facilitated by multiple infiltrations as well as the heat treatment, so the effect of the maximum exposure temperature was also studied. In this case, samples with 8 infiltrations and 2 treatments at 1425°C were subsequently exposed to 1 cycle at 1600°C. Comparing the structures before and after the 1600°C cycle, all PyC disappeared and the polymer derived SiC had undergone significant grain growth after the 1600°C exposure. The structure before the 1600°C cycle contained PyC and blocky β -SiC grains (about 200-300Å) next to the PyC. After the 1600°C cycle PyC was not present. However, there were enlarged blocky SiC grains (about 1600-3000Å) where the PyC was, and also a region with baseline polymer derived structure away from the fiber. The formation of blocky SiC grains (not baseline structure) next to the PyC indicates that the presence of PyC affects the formation of SiC from the polymer. Because of the significant structure change with maximum exposure temperature, a thermo-chemical reaction between the polymer derived material and the PyC occurs; however, there may also be a heterogeneous nucleation mechanism. The fact that after a 1600°C cycle the PyC disappears indicates that it may be primarily a chemical mechanism. To determine whether there is a heterogeneous nucleation mechanism due to the presence of an additive as opposed to interaction with PyC, Hi-Nicalon without PyC was studied.

Hi- Nicalon with sizing but without PyC: Instead of using a woven preform in the fabrication of this sample type, Hi-Nicalon tow with PVA sizing (about 0.2- 0.5 μ m) was cut into short lengths ($\approx$ 3mm), mixed with AHPCS polymer and thermally treated to 1600°C. In general, the matrix (region not adjacent to the fibers) exhibited the baseline polymer derived SiC structure except that the β -SiC grains were larger (about 400-800Å). Amorphous carbon-rich regions were difficult to identify; when observed they were small and appeared infrequently. No sizing was seen next to the Hi-Nicalon fibers, however there were large blocky β -SiC grains along the edge of the fiber which averaged about 5000-7000Å with some as large as 1-10 μ m. One explanation for the large SiC grains is that since PVA is a carbon rich polymeric material, thermal processing of sized fibers can leave a carbon film. Such a film may be analogous to the PyC coating and therefore cause the formation of large blocky SiC grains as were observed for the PyC coated fibers. Also note that there is some coarsening of the Hi-Nicalon fiber grain size to 500-1000Å. This coarsening occurred even though there was less total thermal exposure than the sample with 3 cycles at 1600°C, however the PVA derived carbon layer was thinner than the PyC on that sample. If these two examples of coarsening are related, this supports the link between the fiber coarsening and the chemical changes in the carbon layer (PyC or sizing).

Hi-Nicalon without PyC and without sizing: In order to determine if the formation of large blocky β -SiC grains along the fibers is due to the presence of carbon or whether the fiber is merely a heterogeneous nucleation site, Hi-Nicalon without sizing was studied. Preliminary results indicate that few blocky SiC grains form along the uncoated fibers and that coarsened baseline polymer derived SiC microstructure is adjacent to the fibers. These changes reinforce the preceding conclusions about a reaction between a carbon layer and polymer derived SiC, and indicate that uncoated Hi-Nicalon and potentially other SiC additives produce different results from carbon coated additives.

The Addition of Carbon

Since there was a noticeable interaction between the PyC and the AHPCS polymer, the effects of several types of carbon additives were studied including fibers woven into a fabric form, felt, -325

mesh powder, and dense graphite tooling. For most of these cases the presence of carbon affected the growth of polymer derived SiC, resulting in the formation of large SiC grains instead of the baseline structure seen for neat polymer derived material.

Carbon fibers (fabric) and carbon felt: These two additives are discussed together because they produced similar results. There were two configurations for the incorporation of carbon fibers and felt. In one configuration the fibers/felt were cut into short lengths (≈ 2 -5 mm), mixed with the AHPCS polymer, and thermally treated to 1600°C. In the other configuration small amounts of AHPCS polymer were dropped from a pipette onto a square of carbon fabric or felt to just wet the fibers, and then thermally treated to 1600°C. These two processing methods allowed for the observation of how a polymer derived matrix forms at a distance from carbon fibers, and how polymer derived SiC forms directly adjacent to a carbon fiber. In the first configuration, with ample amounts of AHPCS to form a matrix away from the carbon fibers/felt, typical polymer derived microstructure was observed with β -SiC grains about 100-400Å and evenly dispersed amorphous carbon-rich areas about the same size as the SiC grains. Such a structure was not found next to the carbon additives. Most likely this indicates that a reaction occurs locally about the carbon additive so that large β -SiC grains form, depleting the adjacent polymer regions of nuclei from which SiC grains would grow. Since the grain growth of covalently bonded materials like SiC generally is stopped when grains impinge upon each other, less nuclei means fewer grains which will grow bigger before they impinge on another grain. This could explain the coarsened baseline structure.

In the second configuration there was only enough polymer to wet the fibers/felt so that SiC is seen as a coating on the carbon. SEM examination of the fibers before and after the application of AHPCS polymer revealed that the fibers decreased in diameter after infiltration from 8-12 μ m to about 6-9 μ m. TEM examination of the AHPCS coated fibers revealed large β -SiC grains about 2000Å to 2 μ m which formed along the carbon fibers. The baseline structure was not observed in this sample type with fibers. Because of the decrease in fiber diameter, and the absence of baseline structure, there appears to be a chemical reaction between the AHPCS polymer and the carbon fibers, not just heterogeneous nucleation.

Due to the felt being made of fibers, particles and chunks of carbon, even the sparse pipette application of AHPCS polymer in the second configuration resulted in the formation of matrix in some void areas which trapped the polymer. Therefore, the TEM images revealed polymer derived SiC coating carbon surfaces, and baseline structure in void spaces away from the carbon. Next to the carbon, large (2000Å) β -SiC grains were formed and no baseline microstructure was observed. The typical polymer

Figure 4- TEM images of carbon converted into β -SiC. a) Shows a converted carbon particle and b) a converted carbon fiber.

derived structure observed in void areas away from the carbon was larger than the baseline with grains about 200-400Å. Again this indicates a local reaction about the carbon additive so that large β -SiC grains form.

It was interesting to note that there were signs of carbon conversion into SiC. For instance, in the felt samples large ($\approx 1\mu\text{m}$) SiC grains were occasionally observed surrounded by the typical structure, see Figure 4a. Potentially these huge grains resulted from the conversion of a carbon particle into SiC by the polymer. Also carbon fibers converted to β -SiC have been observed in other samples, see Figure 4b. Considering these cases there is a strong indication of a reaction between the carbon and the AHPCS polymer.

Carbon powder: Fine carbon powder (~ 325 mesh) was added to the polymer and thermally treated to 1600°C resulting in a variety of observations. There were small areas with typical polymer derived β -SiC structure which were about 200-700Å with comparably sized amorphous carbon-rich regions. Generally these regions of baseline structure were surrounded by large β -SiC grains (about $3\mu\text{m}$) and not observed adjacent to carbon. However, there were several spots where the baseline was adjacent to carbon particles. In these cases, there was coarsening in the baseline microstructure close to the particle. These observations suggest that the typical polymer derived structure formed in the interstices away from the carbon particles, and that a reaction with the carbon additive occurs so that only large β -SiC grains form adjacent to carbon additives.

Figure 5- TEM images of various structures believed to represent the conversion of carbon powder into SiC. a) Sinewy texture resembling the original condition. b) Ring like carbon grains. c) β -SiC grains formed in a carbon region are marked by arrows.

The study further expanded on the role of the carbon in the formation of SiC through the various carbon structures observed in the fully processed sample. One carbon structure exhibited a sinewy texture which most resembled the original condition of the carbon powder additive (Figure 5a). A second structure observed resembled the amorphous carbon-rich areas seen in typical polymer derived material. A third structure consisted of ring like carbon grains (Figure 5b). The last type of carbon structure observed contained SiC grains about 200-600Å distributed throughout the carbon (Figure 5c). One theory about these different carbon structures is that they depict the progression of the conversion of carbon powder into SiC. If this is the case, given an appropriate thermal exposure (time and temperature), and the appropriate powder to polymer ratio, there would be only SiC in the sample.

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Large graphite pieces: The final carbon and polymer configuration studied was the polymer next to the graphite (AXF-5Q from UNOCAL/POCO). For this, cross-sections were made from polymer derived SiC that was on graphite tooling after thermal treatment (some at 1600°C and one at 1900°C). When considering these samples as a group, it appears that grain size depends on distance from the graphite tooling with large β -SiC grains next to the graphite, and typical polymer derived structure in the center. The large β -SiC grains that formed next to and near the graphite tooling were about 5000Å - 2 μ m in size. The typical structure was about 20-2000Å depending on distance from the tooling and had comparably sized amorphous carbon-rich regions of a uniform dispersion. No measurements to determine if there was consumption of the graphite were possible with these samples, therefore there is no evidence of a carbon-polymer reaction except for the changes in SiC grain size. These results indicate that the use of graphite tooling can affect the resultant SiC microstructure.

CONCLUSIONS

1. Without additives the microstructure of AHPCS polymer derived SiC contains two phases, β -SiC grains with about 10-20% amorphous carbon-rich regions. The SiC grains are 20-500Å while the amorphous carbon-rich regions are comparably sized and uniformly dispersed. The effect of carbon additives was to coarsen this microstructure so that the SiC grains and carbon-rich regions were 100-1000Å.

2. The AHPCS polymer was found to react with carbon additives during the curing process up to 1600°C. This reaction resulted in different microstructures depending on the carbon. Especially interesting was the consumption of PyC interface coating on Hi-Nicalon fibers. Since a weak interface coating such as PyC is needed for the mechanical performance of ceramic composites, the fabrication of SiC composites with polymer derived matrices and PyC coatings must be tailored so that a PyC coating remains after fabrication.

3. In some instances the direct conversion of carbon particles and fibers into β -SiC was observed. This may be a technique for forming large grain sizes resulting in a polymer derived SiC with improved thermal conductivity and radiation resistance compared to the neat AHPCS derived material.

4. For the AHPCS polymer, there are chemically and/or thermally activated mechanisms (e.g. diffusion) that occur around 1425-1600°C. This was evidenced in the loss of PyC interface coating between thermal treatments at 1425°C and 1600°C, and the development of undulations along the polymer derived SiC-PyC interface with prolonged thermal exposure. In order to avoid chemical reactions and fiber coarsening in a composite with PyC coated Hi-Nicalon fibers and an AHPCS polymer derived matrix, the maximum thermal exposure is around 1500°C.

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REFERENCES

1. L.V. Interrante, W.R. Schmidt, P.S. Marchetti and G.E. Maciel, "Pyrolysis of Organometallic Precursors as a Route to Novel Ceramic Materials", Mat. Res. Soc. Symp. Proc. Vol. 249, 31-43 (1992).
2. L.V. Interrante, C.W. Whitmarsh, C-Y. Yang, W.J. Sherwood, W.R. Schmidt, P.S. Marchetti and G.E. Maciel, "Processing of Si-Based Ceramics and Ceramic Composites Using Hydridopolycarbosilane (HPCS)", Silicon Based Structural Ceramics, ed. B.W. Sheldon and S.C. Danforth, Ceramic Transactions Vol. 42, 57-70 (1994).
3. J.M. Schwark and M.J. Sullivan, "Isocyanate-Modified Polysilazanes: Conversion to Ceramic

Materials", Mat. Res. Soc. Symp. Proc. Vol. 271, 807-812 (1992).

4. J.M. Schwark, "Peroxide-Substituted Polysilazane: Self-Thermosetting Ceramic Precursors", Polymer Preprints, Vol. 34 [1] 294-5 (1993).

5. Z-F. Zhang, F. Babonneau, R.M. Laine, Y. Mu, J.F. Harrod and J.A. Rahn, "Poly(methylsilane)- A High Ceramic Yielded Precursor to Silicon Carbide", J. American Ceramic Society, Vol. 74 [3] 670-73 (1991).

6. R.M. Laine, F. Babonneau, K.Y. Blowhowiak, R.A. Kennish, J.A. Rahn, G.J. Exarhos, and K. Waldner, "The Evolutionary Process during Pyrolytic Transformation of Poly(N-methylsilazane) from a Preceramic Polymer into an Amorphous Silicon Nitride/Carbide Composite", J. American Ceramic Society, Vol. 78 [1] 137-45 (1995).

7. S.H. Yu, R.E. Riman, S.C. Danforth, R.Y. Leung and S.T. Gonczy, "Pyrolysis of Poly(siloxane) Preceramic Polymers: Effect of Atmosphere on Product Chemistry", Silicon Based Structural Ceramics, ed. B.W. Sheldon and S.C. Danforth, Ceramic Transactions Vol. 42, 71-79 (1994).

8. E. Bouillon, F. Langlais, R. Paillet, R. Naslain, F. Cruege, P.V. Huong, J.C. Sarthou, A. Delpuech, C. Laffon, P. Lagarde, M. Monthieux, and A. Oberlin, "Conversion Mechanisms of a Polycarbosilane Precursor into an SiC-based Ceramic Material", J. Materials Science, Vol. 26, 1333-45 (1991).