

# Selective Laser Pyrolysis for Solid Free-Form Fabrication of Silicon Carbide

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## Abstract

Selective laser pyrolysis rapidly decomposes a polymeric precursor to form a cohesive ceramic shape. The considerable shrinkage and porosity during pyrolysis of pure precursor can be modified by the addition of either inert or reactive fillers. With polycarbosilane as the polymeric precursor, the process forms shapes of  $\beta$ -SiC and, by using fillers, composites of  $\beta$ -SiC/Al<sub>4</sub>C<sub>3</sub>/Al,  $\beta$ -SiC/TiC/Ti, and  $\beta$ -SiC/ZrC/Zr. The technique offers some potential for ceramic shapes with custom designed composition and microstructure including nanometer grain size.

## Introduction

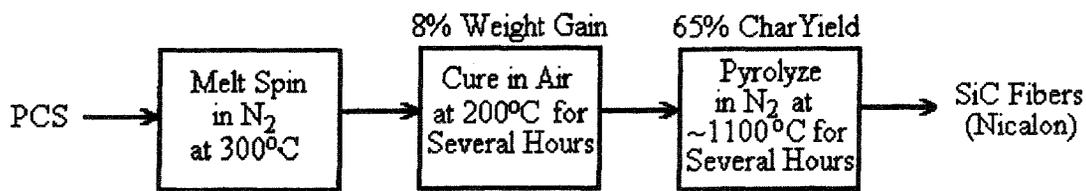
Polymeric precursors provide a means for synthesizing and forming ceramics that reduces the need for high temperature processing. Polymeric ceramic precursors contain an inorganic component such as silicon or titanium in an organic polymer chain. Pyrolyzing the polymer results in a residue in which the inorganic component converts to a ceramic such as silicon carbide (or nitride) or titanium carbide. Several researchers have used this approach to produce nano-powders<sup>1-4</sup>; the commercially available Nicalon (SiC) and Tyranno (SiC-TiC) fibers are also formed from pyrolysis of polymeric precursors.<sup>5</sup>

Selective laser pyrolysis seeks to use the relatively low pyrolysis temperature of polymeric precursors to overcome some of the difficulties seen in direct Selective Laser Sintering of ceramics. Polycarbosilane (PCS), the raw material for Nicalon fibers, provided suitable characteristics for the first laser pyrolysis work. Figure 1 compares conventional and laser pyrolysis of PCS and Figure 2 schematically depicts laser pyrolysis of PCS.

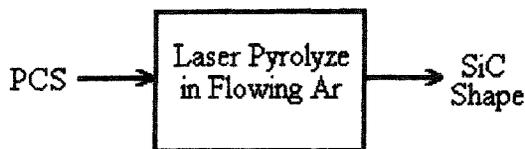
## Experiments and Discussion

The experimental set-up consists of a vacuum chamber mounted on an x-y table and a 25W cw CO<sub>2</sub> laser. The laser is focused through a ZnSe window, and by moving the chamber, the laser scans across a powder bed of the material to be pyrolyzed. The design of the chamber is discussed in detail in reference 6.

Experiments with laser pyrolysis of PCS were divided into three groups: pure PCS, PCS with inert filler, and PCS with reactive filler.<sup>7</sup> All of the experiments involved



a) Conventional Pyrolysis of Polycarbosilane (PCS)



b) Selective Laser Pyrolysis of PCS

Figure 1 Conventional and Selective Laser Pyrolysis of Polycarbosilane

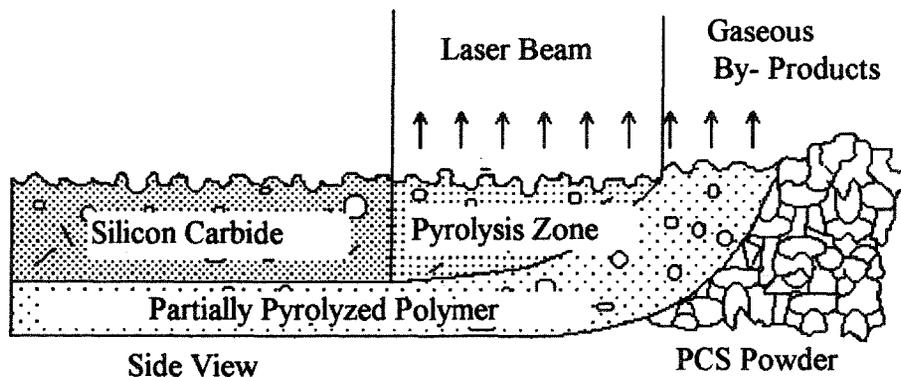


Figure 2 Schematic of Laser Pyrolysis of Polycarbosilane

PCS powder prepared by mortar and pestle grinding. The powder combinations were formed by mechanical mixing.

### Pure PCS

The first group of experiments involved pyrolysis of pure PCS. Shapes formed from pure PCS have rough surfaces and are highly porous, but show good cohesion, including between layers. The pores appear evenly distributed both within and across layers. Significant shrinkage occurs during pyrolysis; the surface of the pyrolyzed region of the powder bed is significantly lower than the surrounding non-pyrolyzed regions.

Figure 3 presents the X-ray diffraction spectrum for pure PCS after laser pyrolysis while Figure 4 shows the grain size / laser power relationship. The grain size, as

determined from X-ray diffraction peak widths and the Scherrer equation, shows poor correlation with total energy, but a strong correlation with laser power. Grain size is expected to be independent of laser power but increase with total energy flux (energy flux is proportional to power, scan speed, and scan spacing). The connection of power and grain size here suggests that pyrolysis occurs very rapidly, in less time than the total laser dwell time on a given area (<10 seconds for the scan speed and spacings examined), and that the laser powers examined are too low to raise the temperature enough to cause grain growth after SiC forms. In addition to increasing grain size, higher power also increases cracking and surface roughness.

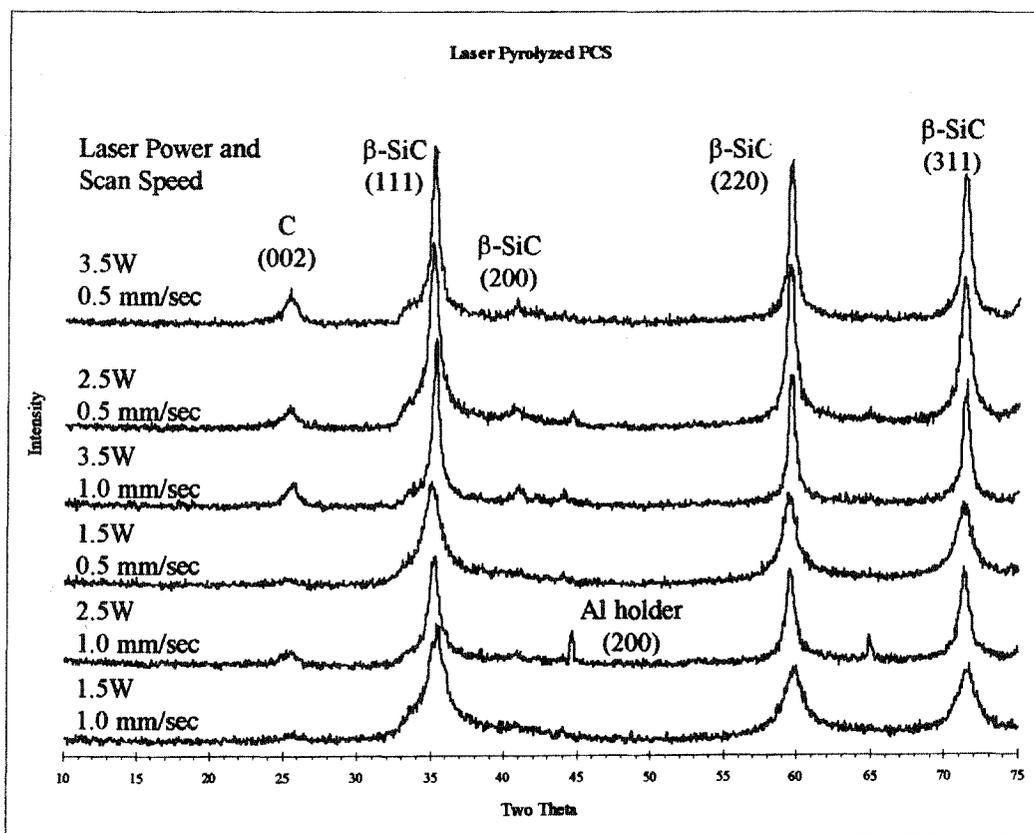


Figure 3 X-Ray Diffraction Spectrum for Laser Pyrolyzed Pure PCS

### PCS with Inert Filler

The second group examined consisted of PCS with an inert filler. The filler reduces the shrinkage and porosity seen during pyrolysis of pure PCS. The inert filler simply decreases the volume of PCS needed and therefore the amount of shrinkage during processing. Both silicon carbide and silicon nitride were examined as inert fillers, but none of the silicon nitride mixtures formed cohesive shapes, possibly because of poor bonding

### Silicon Carbide Grain Size vs. Laser Power for Laser Pyrolyzed Polycarbosilane

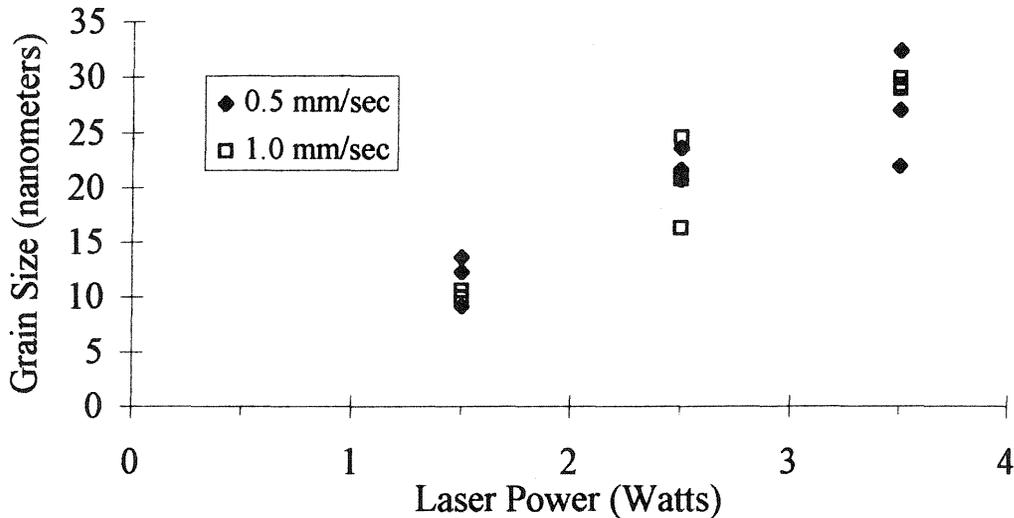


Figure 4 Silicon Grain Size vs. Laser Parameters for Laser Pyrolyzed Polycarbosilane (Grain Size determined from X-ray Diffraction peak widths and the Scherrer Equation).<sup>8</sup>

between the pyrolyzed material and the silicon nitride powder. Silicon carbide filler, however, did show good bonding between pyrolysis product and filler.

#### PCS with Reactive Filler

Reactive fillers (carbide forming metals) decrease shrinkage and boost yield after pyrolysis by consuming carbon normally lost as gaseous by-products. For all reactive fillers, local porosity appears high, but some regions contain large voids which greatly lowers the overall density of the samples. The compositions resulting from laser pyrolysis of reactive mixtures closely parallels that seen in conventional pyrolysis of such mixtures.<sup>9</sup> Table 1 summarizes the results of the various experiments conducted on PCS with and without fillers.

As an example of the effect of reactive fillers, Figure 5 shows a laser pyrolyzed PCS - Ti mixture. After pyrolysis, the mixture contains  $\beta$ -SiC, TiC, and residual titanium. Although the pre-pyrolysis metal to carbon ratio of the mixture was one to one, two factors prevent complete TiC formation: the large titanium powder size (-100 mesh) and some loss of carbon as gaseous by-products. The pyrolyzed PCS-Ti mixture pictured also shows high local density. Overall density, however, remains low because of isolated, large voids caused by inhomogeneities in the original powder mixture.

## Conclusions

Selective laser pyrolysis of polycarbosilane successfully produced shapes composed of nano-crystalline  $\beta$ -SiC. A filler approach showed some success in reducing shrinkage and local porosity while also allowing formation of composite materials. Further study, however, is necessary to further decrease overall porosity to more acceptable levels.

Table 1  
Results of Laser Pyrolysis of Polycarbosilane

Reactants	Metal: Carbon Ratio	Products	Char Yield	% of Theoretical Density
PCS	0.5 : 1	$\beta$ -SiC + C	~ 70%	~ 30%
Inert Filler				
50wt% $\beta$ -SiC (16 $\mu$ m) + 50 wt% PCS	0.7 : 1	$\beta$ -SiC + C	~ 70%	~ 35%
Reactive Filler				
29wt% Si (5 $\mu$ m) + 71wt% PCS	1.0 : 1	$\beta$ -SiC + Si	~ 85%	~ 25%
50wt% Al (-325 mesh) + 50wt% PCS	1.5 : 1	$\beta$ -SiC + Al <sub>4</sub> C <sub>3</sub> + Al + Si	~ 90%	~ 30 %
34wt% Al (-325 mesh) + 66wt% PCS	1.0 : 1	$\beta$ -SiC + Al <sub>4</sub> C <sub>3</sub> + Al + Si	~ 90%	~ 30%
60wt% Ti (-100 mesh) + 40wt% PCS	1.0 : 1	$\beta$ -SiC + TiC + Ti	~ 90%	~ 30%
73wt% Zr (-270 mesh) + 27wt% PCS	1.0: 1	$\beta$ -SiC + ZrC + Zr	~ 90%	~ 30%

## Acknowledgments

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a) Top (Laser Scanned) Surface 100X



b) Top (Laser Scanned) Surface 500X

Figure 5 SEM Photographs of Laser Pyrolyzed Polycarbosilane / Titanium Mixture  
The large nodules are remaining titanium particles (starting size -100 mesh)  
while the smaller nodules seen at higher magnification likely are aggregates  
of TiC and SiC.

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