

# THE PREPARATION PROCESS OF SiCN CERAMIC BY PYROLYSIS OF PSN-1

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## ABSTRACT

After Vinyl poly silazane (PSN-1) precursor was cross-linked and cured at 350 °C, the precursor powders were got by high-energy ball milling. The internal uniformity and relatively compact embryos were prepared by mould pressing, and the SiCN ceramics were obtained by pyrolysis of the embryos at high temperature. By means of TG, XRD, Raman, SEM and other analytical methods, the ceramic preparation process was studied and the regulation of the microstructure changes along with temperature was obtained. The result shows that precursor treated by curing, cold isostatic pressing and low rate pyrolysis will make ceramic yield increase. With the temperature increasing, the SiCN amorphous ceramics are converted into crystalline at 1400 °C. Raman analysis shows that when the pyrolysis temperature is below 1400 °C, D and G peak partially overlap, which indicating that the free carbon is highly disordered; and when the temperature is above 1400 °C, D and G peak are separated from each other, which indicating the crystallization degree of free carbon increase.

## 1 INTRODUCTION

Dantrell and Popper [1] first proposed Polymer Derived Ceramics (PDCs) in 1964. PDCs have many advantages, such as designable ability of molecules, proper technology, good workability, low preparation temperature, excellence high temperature performance. PDCs have become one of the research hotspots [2]. In recent years, many researches have done to focus on SiCN ceramics, which were prepared from organic polysilazane precursor in the protective gas (Ar or N<sub>2</sub>). Polysilazane is one kind of polymer, whose molecular main chain is composed of alternately arranging silicon, carbon, nitrogen atoms. It can be a precursor of SiCN ceramic and can be prepared SiCN ceramics fiber, coatings and block materials and so on [3-4]. SiCN ceramics have excellent structural and functional properties, including high temperature stability [5] and creep resistance [6-7], oxidation/corrosion resistance [8-9], high-temperature semiconductor performance [10-11]. For PDCs-SiCN ceramics, different precursor system results into different structure evolution in the subsequent process of ceramics. In this paper, we focus on the evolution of composition and structure during the preparation of SiCN ceramics by pyrolysis of vinyl poly silazaneas (PSN-1).

## 2 EXPERIMENTAL MATERIALS AND METHODS

### 2.1 Experimental materials

PSN-1, as a precursor, produced by Institute of Chemistry Chinese Academy of Sciences, is transparent viscous liquid, and its chemical formula is  $\text{Si}_{x+y}\text{C}_{3x+y}\text{N}_{x+2y}\text{H}_{7x+5}$ . Its number-average molecular weight is 636g/mol, and its viscosity at 25°C is 8000Pa·s. Dicumyl peroxide (shorted as DCP), bought from Shanghai Shanpu Chemical Company Limited, was used as a crosslink reagent. Its purity is 98%, and its chemical formula is C<sub>18</sub>H<sub>22</sub>O<sub>2</sub>.

## 2.2 Experimental method

An amount of PSN-1 precursor and 1wt% of the cross-linking agent DCP were stirred by use of a magnetic stirrer. The precursor liquid has been heated at 350 °C in the atmosphere of Ar for 10 hours to obtain insoluble and infusible cross-linking products.

After crushing, high-energy ball milling and sieving, the fine powders were compressed into preformed body and then undergo cold isostatic pressing treatment to obtain higher densification. Having put preformed body into a tube furnace in the atmosphere of Ar, we heat it from the room temperature to 1000~1600 °C according to a heating mechanism for 6 hours, then cool down to room temperature to obtain SiCN ceramics.

## 2.3 Analysis test

X-ray diffraction was used to analyse the phase of the product that comes from PSN-1. The D and G peaks of free carbon were measured by Raman spectroscopy. The STA 449C/6/G Thermal Analyser, produced from Germany Netzsch Company, was used to test the relationship between sample mass and temperature. We use XL30E Scanning Electron Microscope (SEM) built by Philips to observe the microstructure of SiCN ceramic.

## 3 RESULT AND DISCUSSION

### 3.1 Preparation of amorphous SiCN ceramics

The preparation of organic-inorganic conversion is the key step in the preparation of SiCN ceramics. In the process of transition from organic to ceramic, the crosslinking and pyrolysis of precursors play an important role in the final properties of the samples. The macroscopic photos of the liquid SiCN precursor, the blocks obtained by crosslinking and curing of PSN-1, and powders got by crushing and ball milling are shown in Figure 1.



Figure 1: Macroscopic photo of the samples  
(a) the liquid SiCN precursor; (b) curing precursor; (c) precursor powders.

We used the experimental method in the 2.2 to prepare samples that are shown in the following figures. Precursor powders are compressed into disk with  $\phi$  20mm tableting mold to get SiCN samples that are shown in Figure 2(a). The preformed body without cold isostatic pressing has pyrolyzed at 1000 °C for 4 hours to obtain the product, shown in Figure 2(b). The performed body with cold isostatic pressing and pyrolysis at the same situation to get the products is shown in Figure 2(c). From Figure 2, it is clear that ceramic samples after pyrolysis have a large degree of volume shrinkage than the precursor body. There are lots of macroscopic and microscopic cracks in the surface of the samples without cold isostatic pressing. The strength of this kind of ceramics is very low and some specimens are even broken. There are no macroscopic cracks in the samples that treated by cold isostatic pressing. The volume shrinkage of this kind of ceramics is less than that kind of ceramics without cold isostatic pressing. And this ceramic's strength has some improved as well.

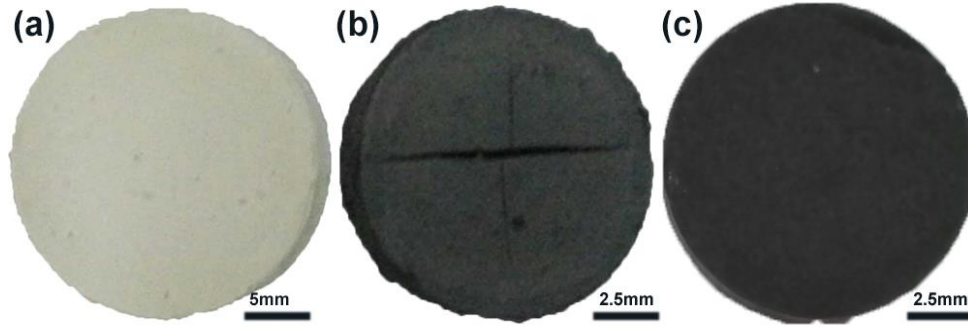


Figure 2: Macroscopic photo of material and after pyrolysis  
(a)non pyrolysis body; (b)compression molding and pyrolysis; (c)cold isostatic pressing and pyrolysis

The microscopic photos of the SiCN samples treated by cold isostatic pressing or not are shown in Figure 3. We can see from the Figure 3(a) that the SiCN ceramic particles are very loose. After cold isostatic pressing, the ceramic particles are more density and uniformity. The results show that the effect of cold isostatic pressing is obvious, and the strength and density of the SiCN ceramics are improved. The shrinkage rate, density and macroscopic morphology of the SiCN samples that treated by different processes are shown in table1.

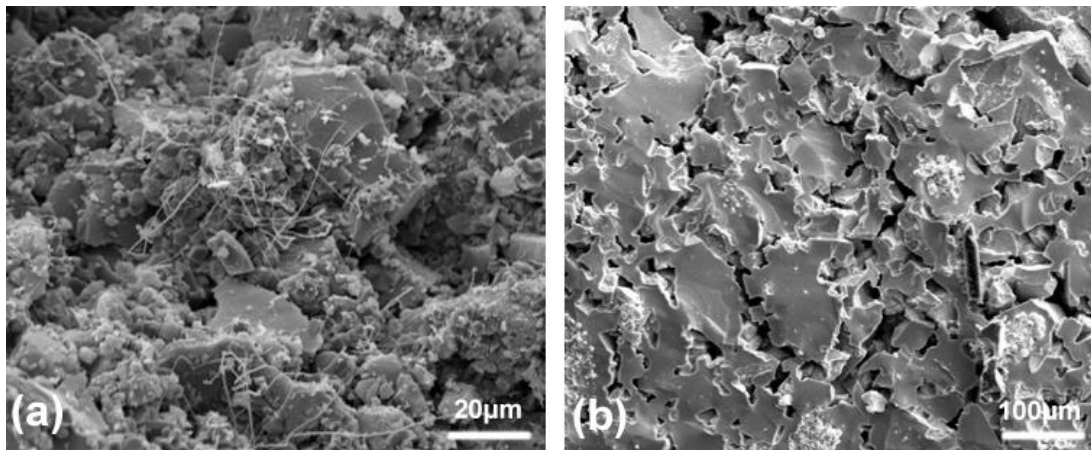


Figure 3: SEM photo of the sintered specimens.  
(a) sectional scanning picture of dry-pressed sintered specimen; (b)sectional scanning picture of dry-pressed and cold isostatic pressing sintered specimen.

Table 1: The shrinkage rate, density and macroscopic morphology of different treatments

Processing technology	Original density [g cm <sup>-3</sup> ]	Diameter [mm]	Shrinkage [%]	Bulk density [g cm <sup>-3</sup> ]	Mass loss rate[%]	Obvious cracks
precursor	1.20	20	—	1.20	—	None
Dry-pressed	1.28	20	22.08	1.72	20.46	Have
Dry-pressed and cold isostatic	1.90	20	10.00	2.30	18.01	None

### 3.2 Analysis of SiCN ceramics yield

In general, there are many factors influence the yield of SiCN ceramics. The pyrolysis rate is an important parameter among them. Figure 4(a) shows the thermo-gravimetric curves of SiCN precursor

at different heating rates in the range of 25~1000 °C, which reflects the effect of heating rate on the pyrolysis products yield in the protective gas (Ar). Decreasing the heating rate can increase the productivity of ceramic. When performed body pyrolysis at 900 °C with heating rate 15 °C/min, the ceramics yield was only about 56.22%. Decreasing the heating rate to 10 °C/min, the ceramic yield can increase to 66.25%. When the rate of heating was reduced to 5 °C/min, the ceramic yield had increased to 71.65%. It can be seen from the Figure 4, with lower heating rate, the sharp weightlessness will start at a higher temperature.

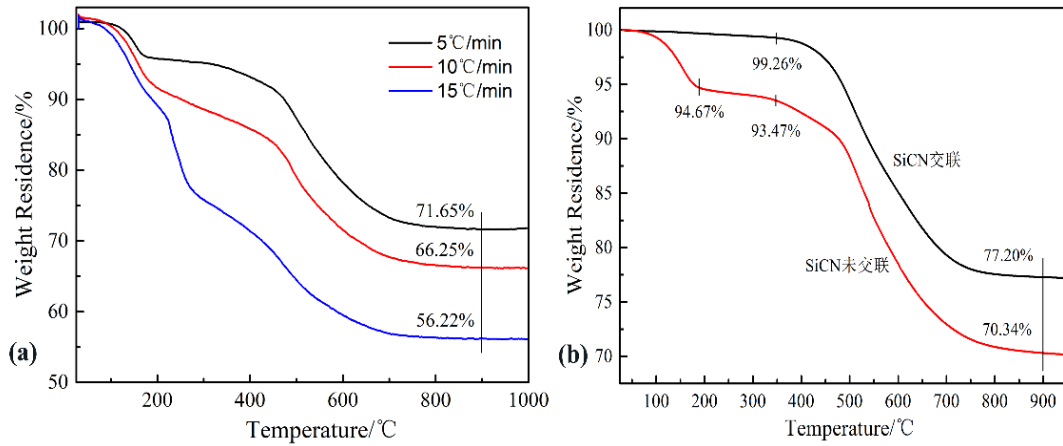


Figure 4: Thermo-gravimetric curves of the SiCN samples  
(a) thermo-gravimetric curves of precursors at different heating rates; (b) thermo-gravimetric curves of cross-linked SiCN and uncross-linked SiCN.

The addition of cross-linking agent is another important factor affecting the yield of SiCN ceramics. TG analysis was exploited on the cross-linked and uncross-linked SiCN precursor and the result is shown in Figure 4(b). It shows thermos-gravimetric curves of uncross-linked SiCN and cross-linked SiCN samples at 25~950 °C and 5 °C/min heating rate. It can be seen from Figure 4(b) that the weight of uncross-linked SiCN decreases drastically with increasing temperature varying from 100 °C to 150 °C, and decreased slowly after 200 °C. At 350 °C, the proportion of the residual mass is about 93.47%. For the cross-linked samples, the sample would decrease drastically at higher temperature (near 400 °C). At 350 °C, the proportion of the residual mass is about 99.26%. At 350 °C, the proportion of the residual mass difference between them is 5.79%. At 900 °C, the residual mass difference between them is 6.86%. By comparison, we can find that with the addition of cross-linking agent there was no escape of small molecular gases in precursor crosslinking. The ceramic yield was increased.

### 3.3 Effect of temperature on SiCN phase evolution

Figure 5 is the XRD spectra of SiCN samples at different pyrolysis temperature. From Figure 5 we can see that, when the pyrolysis temperature below 1450 °C, XRD spectra are smooth curves, in the form of diffuse peaks and no obvious diffraction peak. That means no crystal phase precipitates in the matrix, remaining amorphous state. When the pyrolysis temperature reaches 1450 °C, the diffraction peak appears in the XRD spectrum and the SiCN ceramics start to convert amorphous into crystalline, precipitating  $\text{Si}_3\text{N}_4$  and  $\alpha$ -SiC crystals [12]. With the temperature increases,  $\alpha$ -SiC decreases and  $\beta$ -SiC increases, which is because the  $\beta$ -SiC crystal is more stable than the  $\alpha$ -SiC crystal [13-14].

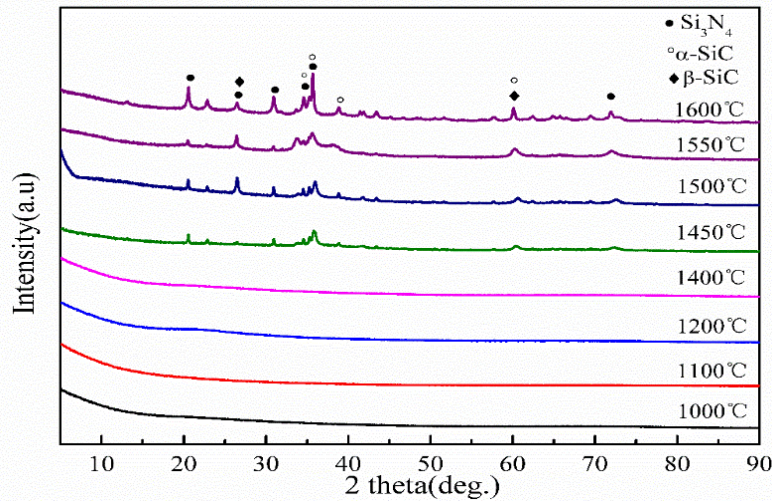


Figure 5: XRD spectra of SiCN samples at different pyrolysis temperature

### 3.4 Effects of temperature on free carbon

Raman spectrum is one of the most effective methods to detect free carbon. The D peak and G peak on the Raman spectrum are characteristic peaks of free carbon. The intensity (I), position ( $\omega$ ), and full width at half-height (FWHM) of the D and G peaks are related to the structure of carbon. The D and G are general located near  $1350\text{cm}^{-1}$  and  $1580\text{cm}^{-1}$ .

Figure 6 is the Raman spectra of SiCN at different pyrolysis temperature. When the temperature is below  $1200\text{ }^{\circ}\text{C}$ , the D and G peaks partially overlap, which indicating that the free carbon is highly disordered. When the pyrolysis temperature is above  $1400\text{ }^{\circ}\text{C}$ , D and G peaks are separated from each other, which indicating the increase of the crystallization degree in free carbon. For further analysis the structure of carbon, the Raman spectra of SiCN ceramics is fitted with Gauss curve and the fitting data is shown in Table 2. From Table 2 we can see that with the increasing of pyrolysis temperature, the intensity ratios of the D and G peak increases, while the peak width decreases. The position of D peak does not change and G peak moves toward the high wavenumber, which means that the free carbon convert the amorphous state into the graphite nanocrystallines [14-15].

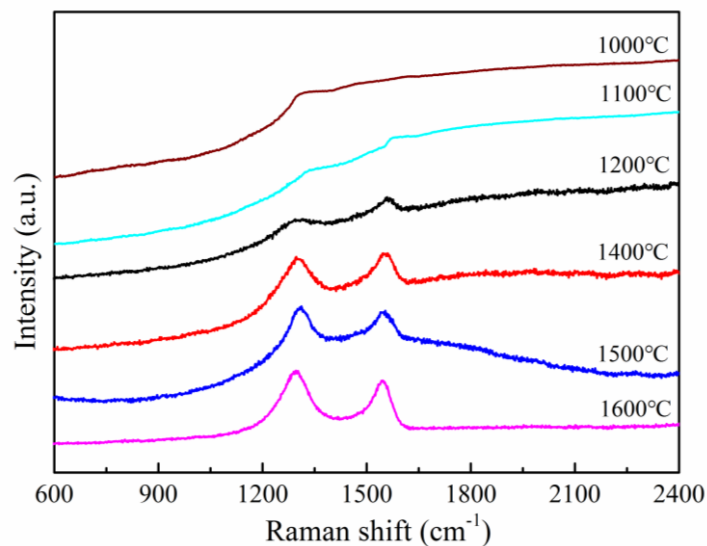


Figure 6: Raman spectra of SiCN samples at different pyrolysis temperature

Table 2: Raman spectra analysis of SiCN Sample at different Pyrolysis Temperatures

Annealing temperature [°C]	G peak position [cm <sup>-1</sup> ]	G peak FWHHG [cm <sup>-1</sup> ]	D peak position [cm <sup>-1</sup> ]	D peak FWHHD [cm <sup>-1</sup> ]	I <sub>D</sub> /I <sub>G</sub>
1100	1572	171	1338	177	1.49
1200	1580	158	11332	9175	11.47
1400	1595	155	11341	1150	11.29
1500	1599	142	11348	120	11.19
1600	1604	87	11355	887	11.09

#### 4 CONCLUSION

The PSN-1 treated by curing and low pyrolysis rate will make SiCN ceramics yield increase. The SiCN ceramic embryo treated by cold isostatic pressing and low pyrolysis rate will increase the strength and density of SiCN ceramics.

When the pyrolysis temperature is above 1400 °C, the amorphous SiCN ceramics are converted into crystalline ceramics. When the pyrolysis temperature is below 1400 °C, the D and G peaks partially overlap, which indicating that the free carbon is highly disordered. While the temperature is above 1400 °C, D and G peak are separated from each other, which indicating the degree of crystallization of free carbon increase.

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