

# Preparation, cross-linking and ceramization of AHPCS/Cp<sub>2</sub>ZrCl<sub>2</sub> hybrid precursors for SiC/ZrC/C composites

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## Abstract

SiC/ZrC/C composites were prepared via pyrolysis of a polymeric precursor, namely AHPCS/Cp<sub>2</sub>ZrCl<sub>2</sub> hybrid precursor prepared by the blend of allylhydridopolycarbosilane (AHPCS) and bis(cyclopentadienyl) zirconium dichloride (Cp<sub>2</sub>ZrCl<sub>2</sub>). The cross-linking and polymer-to-ceramic conversion of as-synthesized AHPCS/Cp<sub>2</sub>ZrCl<sub>2</sub> were characterized by means of FTIR, <sup>13</sup>C NMR, TGA, EDS, Raman spectroscopy and XRD. It is suggested that dehydrocoupling, hydrosilylation and dehydrochlorination are involved in the cross-linking of the hybrid precursor, which is responsible for a relatively high ceramic yield of 75.5% at 1200 °C. The polymer-to-ceramic conversion is complete at 900 °C, and it gives an amorphous ceramic. Further heating at 1350 °C induces partial crystallization, and then the characteristic peaks of β-SiC and cubic ZrC appear at 1600 °C. The effect of the composition of the hybrid precursor is also studied in the work.

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## 1. Introduction

Silicon carbide (SiC) ceramic has been widely applied in high technology fields such as advanced aviation aircraft structure parts, high-temperature engines, turbines, atomic reactor walls, because of its superior physical and mechanical performance such as high intensity, high modulus, high temperature resistant.<sup>1</sup> However, with the development of science and technology, higher requests to the properties of SiC ceramics put forward, and the main method for preparation of high-performance SiC ceramics is the introduction of heterogeneous element to SiC ceramics, which can enhance the comprehensive performance of the SiC ceramics.<sup>2</sup> Zirconium carbide (ZrC) which is similar to SiC is also known as high refractory ceramics with good thermomechanical properties.<sup>3,4</sup> Thus it can be seen if zirconium is introduced to SiC ceramics which can form SiC and ZrC composites, the combination of the passivating character of SiC and the high melting temperature, hardness and thermal

stability of ZrC should generate a kind of high-performance ceramics.<sup>5</sup>

To date, different approaches have been designed to obtain the SiC/ZrC composites, the key point of the approach is the synthesis of precursors containing zirconium. The pyrolysis of an organosilicon polymer in the presence of a metal oxide has been used as a way to obtain Si/C/M (M = Ti, Zr, Al, etc.) multipart ceramics.<sup>6–8</sup> On the other hand, it has also been reported that reaction of polycarbosilane with zirconium (IV) acetylacetonate yields a polyzirconocarbosilane which can be used as the precursor of Si–Zr–C–O ceramic fibers of high tensile strength at high temperatures.<sup>9</sup> However, all of the polymeric precursors mentioned above contain oxygen which would influence the mechanical properties at high temperatures. Recently, Tsirlin et al.<sup>10</sup> chose ZrCl<sub>4</sub>, Cp<sub>2</sub>ZrCl<sub>2</sub>, Zr[N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>, Zr(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> and {[Si(CH<sub>3</sub>)<sub>2</sub>]<sub>x</sub>–[–Si(CH<sub>3</sub>)H–CH<sub>2</sub>–]<sub>y</sub>]<sub>n</sub> (x, y = 1–8, n = 2–6, M = 300–600) as raw materials to obtain non-oxide precursors successfully. Amoros et al.<sup>11</sup> proposed in their work to study the role of bis(cyclopentadienyl)-metal complexes as an alternative source of metal to obtain Si/C/M ceramics. They reported their first results about the reactivity of bis(cyclopentadienyl)-metal dichloride (Cp<sub>2</sub>MCl<sub>2</sub>, M = Ti, Zr, Hf) versus poly(dimethylsilane) PDMS and

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poly(dimethylcarbosilane) (PCS) and their application to synthesis of new ceramics based on Si/C/M (M = Ti, Zr, Hf). It revealed that the metal complex can be incorporated into the PDMS and PCS polymer chains by HCl elimination. However, the ceramic yield of a mixture of  $\text{Cp}_2\text{MCl}_2$  (M = Ti, Zr, Hf) and PCS is only about 30% at 900 °C.

As is well known, liquid hyperbranched PCSs can be regarded as excellent effective precursors especially for a matrix source because of their unique structures and favorable properties, such as lower viscosities, more favorable solubilities, and larger amounts of reactive end-functional groups.<sup>12</sup> In our previous work, we successfully synthesized a series of HBPCSs such as allylhydridopolycarbosilane (AHPCS), ethynylhydridopolycarbosilane (EHPCS) and propargylhydrido-polycarbosilane (PHPCS) by the one-pot synthesis with chlorosilanes and allyl chloride, ethynylmagnesium bromide or propargyl chloride as the starting materials, and the composition of the HBPCSs can be tailored by controlling the amount of the comonomers.<sup>13–16</sup> The polymer-to-ceramic conversion of the HBPCS for SiC ceramics was further studied.<sup>17–19</sup>

Based on the findings that both Si–Si dehydrocoupling (the 1,1-elimination of molecular hydrogen from  $\text{SiH}_n$  groups) and hydrosilylation (a reaction between Si–H and vinyl groups) were effectively improved with bis(cyclopentadienyl)-metal complexes as catalysts,<sup>20–23</sup> we prepared a hybrid precursor of AHPCS/ $\text{Cp}_2\text{ZrCl}_2$  for the first time. On one hand,  $\text{Cp}_2\text{ZrCl}_2$  was used as a new source of Zr to Si/C/Zr ceramic composites. On the other hand, the cross-linking of AHPCS which contains a large amount of C=C groups and Si–H<sub>x</sub> groups could be improved with  $\text{Cp}_2\text{ZrCl}_2$  as a catalyst, involving Si–Si dehydrocoupling and hydrosilylation reactions. Herein, we report our first results about the reactivity of  $\text{Cp}_2\text{ZrCl}_2$  versus AHPCS and their application to the synthesis of new ceramic composites on SiC/ZrC/C composites.

## 2. Experimental

### 2.1. Materials

All manipulations were carried out using standard high-vacuum or insert-atmosphere techniques as described by Shriver and Drezdson.<sup>24</sup> AHPCS with a composition formula  $[\text{SiH}_{1.26}(\text{CH}_3)_{0.60}(\text{CH}_2\text{CH}=\text{CH}_2)_{0.14}\text{CH}_2]_n$  was prepared, as previously described, by a one-pot synthesis with  $\text{Cl}_2\text{Si}(\text{CH}_3)\text{CH}_2\text{Cl}$ ,  $\text{Cl}_3\text{SiCH}_2\text{Cl}$ , and  $\text{CH}_2=\text{CHCH}_2\text{Cl}$  as the starting materials.<sup>13,14</sup> AHPCS used in this work had a number-average molecular weight of ca. 700 and a polydispersity index of 1.96.  $\text{Cp}_2\text{ZrCl}_2$  was purchased from J&K and stored in fridge under 4 °C until use. Chloroform ( $\text{CHCl}_3$ ) was distilled prior to use. Other commercially available reagents were used as received.

### 2.2. Preparation and cross-linking of AHPCS/ $\text{Cp}_2\text{ZrCl}_2$ hybrid precursors

Preparation and cross-linking of AHPCS/ $\text{Cp}_2\text{ZrCl}_2$  hybrid precursors were carried out in a Schlenk flask with a magnetic

stirrer and an argon inlet. One typical synthesis of the hybrid precursor was described as the following procedure. 0.6 g  $\text{Cp}_2\text{ZrCl}_2$  was introduced into a 150 mL Schlenk flask in an argon atmosphere, and then 30 mL  $\text{CHCl}_3$  was added to solve  $\text{Cp}_2\text{ZrCl}_2$  until a clear colorless solution was obtained. Subsequently, 2.4 g AHPCS was introduced into the Schlenk flask with stirring at room temperature, and then a pale yellow solution was obtained. The weight ratio of  $\text{Cp}_2\text{ZrCl}_2$  to AHPCS was 1/4, 1/3 and 1/2, and the samples are abbreviated as AZ-1, AZ-2 and AZ-3, correspondingly. After the  $\text{CHCl}_3$  solvent was stripped off under vacuum at 60 °C to form a yellow AHPCS/ $\text{Cp}_2\text{ZrCl}_2$  slurry in the Schlenk flask. Finally, the Schlenk flask was heated in a 170 °C oil bath. The resultant AHPCS/ $\text{Cp}_2\text{ZrCl}_2$  slurry solidified immediately into a compact, light brown, rubbery solid and was kept at this temperature for 6 h. These cross-linked samples of AZ-1, AZ-2 and AZ-3 were used both for TGA and for a macroscopic pyrolysis.

### 2.3. Pyrolysis of AHPCS/ $\text{Cp}_2\text{ZrCl}_2$ hybrid precursors

With the pyrolysis temperature ( $T_p$ ) of 900 °C, the cross-linked sample was put in an alumina boat and heated in a glass silica tube under an argon flow. The temperature was progressively raised up to  $T_p$  at a rate of 5 °C/min and kept at this value for 2 h. For  $T_p > 900$  °C, the sample (pre-pyrolyzed at 900 °C) was put in a graphite crucible and heated in a tube furnace in argon. The pre-pyrolyzed sample was heated rapidly to  $T_p$  at a rate of 40 °C/min and kept at this temperature for 2 h. After pyrolysis, the resulting ceramic was furnace-cooled to RT.

### 2.4. Characterization

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on Nicolet Avator 360 apparatus (Nicolet, Madison, WI) with KBr plates for liquid samples and KBr discs for solid samples. Nuclear magnetic resonance (NMR) experiments were carried out on a Bruker AV 300 MHz spectrometer (Bruker, Germany) operating at 75.46 MHz for carbon-13 (<sup>1</sup>H-decoupling). The specimen used for <sup>13</sup>C NMR was dissolved in  $\text{CDCl}_3$  solution. The <sup>13</sup>C chemical shifts were referred to tetramethylsilane (TMS) (assigned to 0 ppm). The solid-state <sup>13</sup>C-magic angle spinning (MAS) NMR experiments were also performed on a Bruker AV 300 NMR spectrometer using a 4.0 mm Bruker double resonance MAS probe. The samples were spun at 5.0 kHz. The <sup>13</sup>C isotropic chemical shifts were referenced to the carbonyl carbon of glycine (assigned to 173.2 ppm). Thermal analysis of the samples was performed on a thermal gravimetric analysis (TGA) (Netzsch STA 409EP, Netzsch, Germany) in argon gas with a heating rate of 10 °C/min ranging from room temperature (RT) to 1200 °C. X-ray diffraction (XRD) studies were executed on a PANalytical X'Pert PRO diffractometer (PANalytical, Netherlands) with Cu K $\alpha$  radiation. The specimens were continuously scanned from 10° to 90° (2 $\theta$ ) at a speed of 0.0167° s<sup>-1</sup>. The apparent mean grain size of the  $\beta$ -SiC and cubic ZrC crystalline phase was calculated from the width of the (1 1 1) diffraction peak at mid-height, according to the Scherer equation.<sup>25</sup> The elemental analysis of

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