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Supplementary Information

$SiC/Hf_yTa_{1-y}C_xN_{1-x}/C \ \ ceramic \ \ nanocomposites \ \ with \ \ Hf_yTa_{1-y}C_xN_{1-x}-carbon \ \ core-shell$

nanostructure and influence of the carbon-shell thickness on electrical properties

Qingbo Wen^b, Zhaoju Yu^{a, c*}, Yeping Xu^d, Yan Lu^e, Claudia Fasel^b, Koji Morita^f, Olivier Guillon^g,

Gerd Buntkowsky ^d, Emanuel Ionescu ^b, Ralf Riedel ^{b, c}

^a College of Materials, Key Laboratory of High Performance Ceramic Fibers (Xiamen University),

Ministry of Education, Xiamen 361005, China

^b Technische Universität Darmstadt, Institut für Materialwissenschaft, Otto-Berndt-Straße 3, D-64287,

Darmstadt, Germany

^c College of Materials, Fujian Key Laboratory of Advanced Materials (Xiamen University), Xiamen 361005, China

^d Technische Universität Darmstadt, Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Alarich-Weiss-Straße 4, D-64287, Darmstadt, Germany

^e Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^fNational Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

^g Forschungszentrum Jülich, Institut für Energie- und Klimaforschung 1: Werkstoffsynthese und Herstellungsverfahren, Wilhelm-Johnen-Straße, D-52425, Jülich, Germany

(1) Synthesis of the single-source precursors

Single-source precursors containing Ta

After synthesis, the solid state single-source precursors were collected for FT-IR spectroscopy measurement, and the spectrum of the 30Ta-SMP10 is shown in Figure S1. The spectrum of pure SMP10 at room temperature is also shown for comparison. Compared with pure SMP10, the newly appeared absorption peaks on the spectrum of 30Ta-SMP10 at 945 cm⁻¹ (N-Si stretching on Ta-N-Si unites)¹, 2788 cm⁻¹ (C-H stretching on the NCH₃ groups), 1453 cm⁻¹ (C-H bending on the NCH₃ groups) as well as 1287 cm⁻¹ and 1178 cm⁻¹ (N-C stretching²) prove that the PDMAT can react with SMP10, which is consistent with our previous results based on chemical reaction between SMP10 and Hf(NMe₂)₄.³ Moreover, the increased intensity of alkyl groups at 2956 cm⁻¹, 2882 cm⁻¹, 2922 cm⁻¹ and 2860 cm⁻¹ as well as decreased intensity of Si-H band (2115 cm⁻¹ and 930 cm⁻¹) with respect to the Si-CH₃ band (747cm⁻¹) further confirm the reaction. In addition, absorption bands of the allyl groups (C-H stretching at 3075cm⁻¹ and C=C stretching at 1630 cm⁻¹) disappeared, indicating the occurrence of hydrosilylation.⁴



Figure S1 FT-IR spectra of SMP10 and 30Ta-SMP10.

According to the FT-IR spectra, two reactions are expected to occur during synthesis of the 30Ta-SMP10. The first one involves the hydrosilylation of the allyl groups including α - and β -addition, which explains the disappearance of allyl groups (Figure S1). Normally, the hydrosilylation process of pure SMP10 starts at temperature of ca. 120 °C.^{3, 5} However, the addition of PDMAT into SMP10 induces the disappearance of the allyl groups at 80 °C, which indicates that the PDMAT acts as a catalyst for the hydrosilylation. The second reaction route involves the reaction of PDMAT with the Si-H groups of SMP10. The reaction between the PDMAT and Si-H groups occurs by forming Si-N bonds, which leads to the formation of Si-N-Ta linkages (Figure S1). Based on the two reaction pathways, synthesis of the Ta-incorporated single-source precursor can be described as depicted in Figure S2, which is consistent with our previous work based on Hf-containing single-source precursors synthesized by the reaction between SMP10 and Hf(NMe₂)₄.³



 $X_1, X_2, X_3, X_4 = \{N(CH_3)_2, NSi(CH_2)H_2, NSi(CH_2)(N)H, NSi(CH_2)(N)_2, NSi(CH_2)_2H, NSi(N)(CH_2)_2, NSi(CH_2)_3\}$

Figure S2 Reaction pathways during synthesis of the single-source precursor from SMP10 and PDMAT.

Moreover, the reactions can be further proven by solid state MAS NMR of the 30Ta_SMP10. As shown in Figure S3a, if compared with the ²⁹Si spectrum of pure SMP10, the peaks in the spectrum of 30Ta-SMP10 clearly show that the contents of $C\underline{Si}H_3$ and $\underline{Si}C_2H_2$ units decrease, indicating the consumption of Si-H groups. The ²⁹Si NMR spectrum of pure SMP10 indicates that three kinds of hydrogen-bearing Si sites (hydridosilyl groups) exist as alternating groups of the polymer backbone of SMP10, *i.e.* CSiH₃, SiC₂H₂ and SiC₃H.^{4, 6, 7} Hence, different kinds of Si-N(CH₃)-Ta units including CSiH₂N, CSiHN₂, CSiN₃, SiC₂HN, SiC₂N₂ and SiC₃N can be generated upon reacting the corresponding Si-H groups with PDMAT. On the ²⁹Si MAS NMR spectrum of 30Ta-SMP10, two new signals are detected and assigned to <u>Si</u>C₃N and <u>Si</u>C₂HN units, respectively (Figure S3a). Other signals might be overlapped by the broad signals of the hydridosilyl groups.



Figure S3 NMR spectra of pure SMP10³ and solid state MAS NMR spectra of 30Ta-SMP10: (*a*) ²⁹Si and (*b*) 13 C spectra.

On the ¹³C NMR spectrum of SMP10 (Figure S3b), the chemical shifts of 134.3 ppm and 114.7 ppm are assigned to the carbon sites of \equiv Si–CH₂–<u>C</u>H=CH₂ (d) and \equiv Si–CH₂–CH=<u>C</u>H₂ (e) of the allyl groups, respectively. Multiple chemical shifts in the region from 17.7 to 30.0 ppm are attributed to the \equiv Si–<u>C</u>H₂–CH=CH₂ (c) linkage between silicon and the allyl groups. The signal of the \equiv Si-<u>C</u>H₃ (a) groups is observed around 0 ~ 2.4 ppm, and the chemical shifts from -4.4 to -16.0 ppm are assigned to \equiv Si–<u>C</u>H₂–Si (b) linkages on the polymer chain.⁴ Compared with the ¹³C spectrum of pure SMP10, the allyl-carbon

resonances (d and e) of the 30Ta-SMP10 disappear due to the hydrosilylation process, which is consistent with the FT-IR results. A new broad resonance appears in the region from 16 to 21 ppm, which is assigned to the carbon sites of \equiv Si-CH₂-<u>C</u>H₂-CH₂-Si \equiv units derived from the β-addition product, while the resonance assigned to the methylene carbon of the \equiv Si-CH₂-<u>C</u>H(CH₃)-Si \equiv units derived from the αaddition product is overlapped with those of the \equiv Si-<u>C</u>H₃ (a) units and \equiv Si-<u>C</u>H₂-Si \equiv (b) groups of SMP10.⁶ Concerning the hydrosilylation, the NMR results agree well with the reaction paths shown in Figure S2. The ¹³C spectrum of 30Ta-SMP10 shows one broad additional resonance at around 39.2 ppm, which is assigned to =N-<u>C</u>H₃ groups stemming from the Ta-N<u>C</u>H₃ units of the precursor, thus strongly supporting the reaction between SMP10 and PDMAT.

Single-source precursors containing both Hf and Ta

Based on the reactions between SMP10 and Ta(NMe₂)₅ and previously reported case study between SMP10 and Hf(NMe₂)₄,³ the single-source precursors containing both Hf and Ta can be synthesized successfully as well. FT-IR spectra of the as-synthesized precursors are shown in Figure S4. Compared with the spectrum of pure SMP10, the newly appeared absorption peaks on the spectra of 30Hf2Ta8-SMP10 and 30Hf7Ta3-SMP10 at 945 cm⁻¹ (N-Si stretching on Hf-N-Si and Ta-N-Si unites)^{1, 3}, 2788 cm⁻¹ (C-H stretching on NCH₃ groups), 1453 cm⁻¹ (C-H bending on CH₃ groups), 1372 cm⁻¹ (C-H bending on the -CH₃ of NCH₂CH₃ groups), 1205 cm⁻¹ (C-N bending on NCH₂CH₃ groups) as well as 1287 cm⁻¹ and 1178 cm⁻¹ (N-C stretching²) strongly prove that the SMP10 reacted with both Ta(NMe₂)₅ and Hf(NEt₂)₄ successfully. Furthermore, the highly increased the intensity of alkyl groups at 2960 cm⁻¹, 2922 cm⁻¹ 2885 cm⁻¹ and 2860 cm⁻¹ as well as significantly decreased the intensity of Si-H band (2115 cm⁻¹ and 930 cm⁻¹) with respect to the Si-CH₃ band (747cm⁻¹) further confirm the reactions.



Figure S4 FT-IR spectra of (1) pure SMP10, (2) 30Hf7Ta3-SMP10 and (3) 30Hf2Ta8-SMP10.

(2) Polymer-to-ceramic transformation

Polymer-to-ceramic conversion of the as-synthesized single-source precursors has been investigated using thermogravimetric analysis (TGA) in argon. As shown in Figure S5, the TG and DTG curves (first time derivative of the TG) revealed that there are three main steps during the pyrolysis of 30Ta-SMP10. The first step starts from ambient temperature to approximately 240 °C with the DTG peak at 194.3 °C. During this step, a small mass loss was observed, which should rely on the further reaction between PDMAT and SMP10 (NCH₃/Si-H) with release of CH₄ and SiH₄.³ In the temperature range from 240 to 550 °C (the second step), there is a large mass loss at around 460 °C. This should be contributed by further reaction between the NCH₃ and Si-H groups, decomposition of the organic substituents as well as transamination.³ In the third step, there is a DTG peak at around 590 °C that should result from further decomposition of organic substituent. The ceramization process was found to finish at \approx 900 °C (*i.e.*, beyond this temperature no significant mass loss was observed), leading to a ceramic yield of *ca*. 80 wt.%. Above 1100 °C the weight loss is due to carbothermal reaction with residual oxygen in the system

by the evolution of CO₂ and CO. The TG and DTG curves of 30Hf2Ta8-SMP10 and 30Hf7Ta3-SMP10 (not shown here) are similar to that of the 30Ta-SMP10 and the ceramic yields are ≈ 79 wt.% and ≈ 76 wt.%, respectively.



Figure S5 TG and DTG (first derivative of the TG) curves describing the polymer-to-ceramic transformation of the 30Ta-SMP10.

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