

Note

SYNTHESIS OF ORGANOMETALLIC PRECURSORS FOR Si/Zr/C/N-BASED CERAMICS*

Li-hua Liu, Chun-juan Liu, Shi-yan Yang, Zhi-jie Zhang, Wei Gao and Ze-min Xie**

State Key Laboratory of Engineering Plastics, Center for Molecular Sciences, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080, China

Abstract A new kind of organometallic precursor for Si/Zr/C/N-based ceramics was synthesized from the amine exchange reaction of hexamethylcyclotrisilazane (D_3^N) and tetrakis(diethylamino)zirconium ($Zr[NEt_2]_4$). Pyrolysis was performed under nitrogen at 800 °C in a tube furnace equipped with a temperature program controller. The highest pyrolytic yield was 67.5%.

Key words Si/Zr/C/N-based ceramic precursor, Synthesis, Pyrolysis

Zirconium nitride (ZrN) has excellent properties, such as high hardness, high melting point, corrosion resistance, high electrical conductivity and so on. In recent years, the alloying of ZrN with other covalent refractory materials such as Si_3N_4 or SiC is becoming a research hotspot. According to the literature^[1–3], Si/Zr/C/N-based ceramics were prepared by mixing zirconium/zirconium oxide powders with polymers (polysilazane, polycarbosilazane and polysilane) and pyrolyzing the resultant polymer/metal composite powders. Now, attention has been directed to the pyrolysis of ceramic precursors containing zirconium in their structures. In general, the dispersion of zirconium at the atomic level in the precursors may control the stoichiometry and the microstructure of the resulting ceramics. Chandra^[4] used organohalodisilane to react with $ZrCl_4$ in the presence of a redistribution catalyst under argon and obtained zirconium-containing polysilane, which contained less than 1% zirconium. We have studied the condensation reaction of hexamethylcyclotrisilazane lithium salts (D_3^{NLi}) and zirconium tetrachloride ($ZrCl_4$) to synthesize the polyorganozircosilazane as Si/Zr/C/N-based ceramic precursor^[5]. In this paper, another novel method, the amine exchange reaction of hexamethylcyclotrisilazane (D_3^N) and tetrakis(diethylamino)zirconium ($Zr[NEt_2]_4$), was investigated to obtain Si/Zr/C/N-based ceramic precursors.

EXPERIMENTAL

IR spectra were recorded on a FT-IR spectrometer (PE-80). The content of carbon and hydrogen were measured with a Heraeus CHN-Rapid instrument. The nitrogen content was analyzed by using Coulomb titration^[5]. Silicon and zirconium were determined by inductively coupled plasma emission spectroscopy (ICP; IRIS/AP).

General procedure for the Reaction and Pyrolysis

Polyorganozircosilazane was prepared by the reaction of D_3^N and $Zr[NEt_2]_4$ following the literature procedure^[6–8]. The reaction was performed in a three-necked flask equipped with a thermometer, an inlet for purging the gas and a reflux condenser. D_3^N (0.1 mol) and 60 mL of toluene were introduced into the flask under

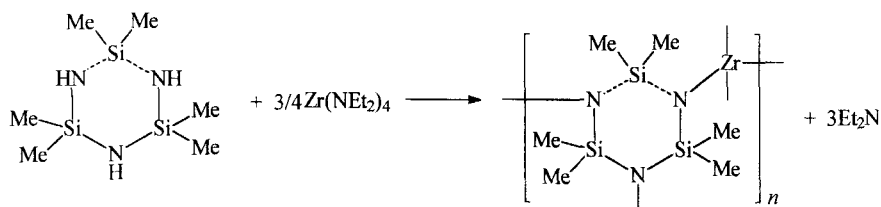
* This work was supported by the National Natural Sciences Foundation of China (No. 50072033).

** Corresponding author: Ze-min Xie (谢择民), E-mail: xiezm@infoc3.icas.ac.cn

Received July 1, 2002; Revised August 15, 2002; Accepted August 20, 2002

nitrogen. To the solution, $\text{Zr}[\text{NEt}_2]_4$ (0.075 mol) was added in a standard glove box at room temperature. The mixture was stirred for 48 h at refluxing temperature. Then the solution was distilled to give precursor (36.86%) as an orange-red solid. The zirconium content of precursor is 32.70%.

Pyrolysis was carried out under nitrogen in an SK2-1-10 tube furnace equipped with a KSW-2-11 temperature controller. The temperature was programmed from ambient temperature to 300°C at 1 K/min, held at 300°C for 1 h, and then was raised from 300°C to 800°C at 2 K/min, and held at 800°C for 2 h. The highest pyrolytic yield was 67.5%.



Scheme 1

Characterization of Precursor

It can be seen from Table 1 that the contents of Si, C, H and Zr are consistent with the theoretical values, but the content of N is somewhat lower. This is because the samples were weighed under air, and the Zr–N bond could be easily broken by water when coulometry was used to determine the N content.

Table 1. Elemental analysis of precursor

Element	Si	C	N	H	Zr
Calcd. (%)	27.20	23.81	13.60	5.83	30.07
Found (%)	28.94	25.90	9.56	5.43	32.70

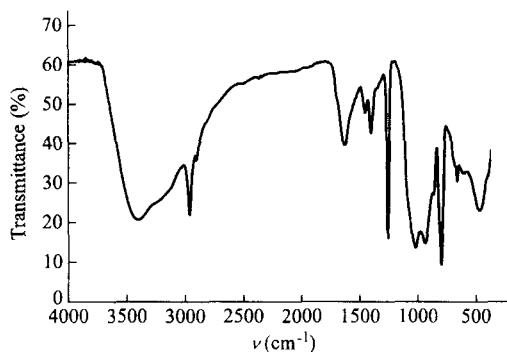


Fig. 1 Infrared spectrum of precursor

From Fig. 1, we can see that the N–H peak (1163 cm^{-1}) in the precursor disappears on comparing with D_3N , and the stretching vibration peak of Si–N–Si shifts from 925 cm^{-1} to 935 cm^{-1} . In addition, new absorption peaks appear at 800, 1023 and 469 cm^{-1} . According to the literature^[9], the peak at 800 cm^{-1} is attributed to the Si–N–Zr absorption, and the peak at 469 cm^{-1} belongs to the Zr–N absorption. The broad peak at 3414 cm^{-1} may result from the absorption of water in air.

REFERENCES

- 1 Seyferth, D. and Lang, H., *J. Inorg. Organometallic Polym.*, 1992, 2(1): 59
- 2 Seyferth, D. and Bryson, N., *J. Am. Ceram. Soc.*, 1991, 74(10): 2687
- 3 Corriu, R. and Gerbier, P., *Adv. Mater.*, 1993, 5(5): 380
- 4 Chandra, G. and Zank, G.A., 1988, U.S. Pat., 4,762,895
- 5 Xie, Z.M. and Wang, Q.Z., *Chin. J. Anal. Chem.*, 1993, 21(2): 206
- 6 Braley, D.C., Thomas, I.M., *J. Chem. Soc.*, 1960: 3857
- 7 Chandra, G. and Lappert, M.F., *J. Chem. Soc. (A)*, 1968: 1940
- 8 Diamound, G.M. and Jordan, R.F., *J. Am. Chem. Soc.*, 1996, 118: 8024
- 9 Perchenek, N., Baldus, H.P., Löffelholz, J. and Jansen, M., 1996, U.S.Pat., 5,567,832