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Journal of the European Ceramic Society 34 (2014) 2163–2167

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Effect of pyrolysis temperature on the electric conductivity of polymer-derived silicoboron carbonitride

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Received 12 January 2014; received in revised form 11 March 2014; accepted 13 March 2014
Available online 31 March 2014

Abstract

The electric conductivity of polymer-derived SiBCNs pyrolyzed at different temperatures was studied. We showed that the boron impeded the graphitization of the free-carbon phase in the SiBCN, leading to a higher characteristic temperature and activation energy as compared to the SiCN. Such an impeding effect is due to the interaction between *h*-BN and graphite phase. We also provided a credible evidence to show that the increase in the electric conductivity of the SiBCN with pyrolysis temperature is likely due to the increase in the conductivity of the free-carbon phase.

Keywords: Precursors-organic; Electric conductivity; Activation energy; Carbon; SiBCN ceramics

1. Introduction

The electric properties of polymer-derived ceramics (PDCs) have attracted extensive attentions in the past years for their promising applications in microelectromechanical systems (MEMS), hash-environmental sensors, and Li-ion batteries.[1–3] It was found that the materials exhibited a set of unique electric properties, such as well-behaved semiconducting behavior up to 1300 °C,[4,5] anomalous piezoresistivity[6] and strong doping effect.[7,8] These unusual properties were attributed to their unique microstructure which was described as a nanodomain structure comprised of amorphous Si-containing phase(s) and highly disordered carbon clusters, namely "free-carbon" phase. The conduction mechanisms of PDCs depend on the concentration and morphology of the free-carbon phase. When the concentration of the free carbon is high enough to form a continue network within the materials, the conduction of the PDCs is analogous to that of glassy carbon.[9] When the free-carbon phase does not form a continue network, two mechanisms are responsible for the conduction of PDCs: tunneling-percolation process when the free-carbon concentration is higher than a threshold, and semiconducting mechanism controlled by the amorphous Si-containing phase(s) when the free-carbon concentration is lower than the threshold.[10]

While the significant progress has been made, there are still many open questions about the conduction of PDCs. One of them is the mechanism responsible for the rapid increase in the conductivity of PDCs with increasing pyrolysis temperature, which was observed in most of PDCs regardless free-carbon concentration.[11] Previous studies vaguely attributed it to the increase in the conductivity of the free-carbon phase.[11] But such an explanation is short of solid evidence, and cannot explain how it is valid for the PDCs without free-carbon network where the conductivity should be controlled by the Si-containing phase(s).[10] Most recently, we have investigated the effect of pyrolysis temperature on the conductivity and structure of the free carbon phase for polymer-derived silicon carbonitride (SiCN); and proved that the increase in the conductivity of the material was indeed due to the increase in the conductivity of its free carbon phase, via a so-called field-concentration effect.[12]

Silicoboron carbonitride (SiBCN) is one of the most notable PDCs with excellent thermal stability and creep resistance,[13,14] thus promising for ultrahigh-temperature applications. Unlike SiCNs, due to the strong interaction of free carbon and disorder

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http://dx.doi.org/10.1016/j.jeurceramsoc.2014.03.012
0955-2219/

BN phases as well as their similarity in atomic arrangement, a turbostratic B-C-N network, instead of pure free carbon, was formed in polymer-derived silicoboron carbonitride (SiBCN).[15,16] Though the location and arrangement of free carbon and BN domains inside the turbostratic B-C-N network are still an open question, it is reasonable to suspect that the behavior of the free-carbon phase in SiBCN could be affected by the existence of B-N; which, in turn, should affect the electric conduction behavior of SiBCN ceramics.

In this study, the effect of pyrolysis temperature on the conductivity of polymer-derived SiBCN ceramics is studied. The result shows that the conductivity of the material exhibits an Arrhenius relation with respect to pyrolysis temperature. The activation energy is calculated and found to be higher than that for SiCN, but similar to that for the crystallization of the free carbon phase in the SiBCN. This suggests that the increase in the conductivity of the SiBCN is also due to the increase in the conductivity of the free-carbon phase; and the presence of B impeded the crystallization of the free carbon phase.

2. Experimental procedure

The SiBCN studied here was prepared by pyrolysis of polyborosilazane, which was synthesized from borane dimethyl sulfide (BDS, BH_3 concentration 1.92 M, purchased from Sigma–Aldrich, USA) and polysilazane (HTT1800, Kion Corp., Columbus, OH), according to the procedure described previously.[17] In brief, a 250 mL three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser was vacuumed and then purged with N_2 gas three times before use. 18.0 g HTT1800 (55.9 mmol) was dissolved in 60 mL toluene (purchased from Sigma–Aldrich, USA) under N_2 protection. 36.4 mL (69.9 mmol) of BDS was added into the mixture at temperature of 0 °C. The solution was gradually heated to 350 °C and refluxed for 24 h. After reducing the temperature to 90 °C, the solvent was removed by vacuum for 10 h. The residue was further dried in vacuum oven at 120 °C for 24 h. Finally, a white odorless solid was obtained. The prepared polyborosilazane was ball-milled to powder of ~1 μm under N_2 protection, and then pressed into disks of 10 mm diameter. These disks were pyrolyzed in a tube furnace at temperatures of 1000, 1100, 1200, 1300, 1400 and 1500 °C for 4 h in flowing ultra-high-purity argon atmosphere to minimize possible oxygen contamination. The SiBCN ceramics such obtained have a Si-to-B ratio of 4:1. The SiCN ceramics without boron were also prepared from HTT1800 at temperatures of 1000, 1100, 1200, 1300 and 1350 °C by following the procedure reported in Ref. 12, to illustrate the effect of boron.

The conductivity of the ceramics was measured on KEITHLEY 2400 (Keithley Instruments, Inc., Cleveland, OH). Before measurement, the surface of the samples was polished to 1 μm finish and then coated with silver paste as electrodes.

X-ray diffraction (XRD) measurement was carried out on a Rigaku D/MAX X-ray Diffractometer (XRD Rigaku, Tokyo, Japan) using a monochromatic Cu-Kα radiation with a wavelength of $\lambda/2 = 154.06$ pm. Thermal gravimetric analysis was performed on a Netzsch STA 409 C/CD apparatus (Selb, Germany) up to 2000 °C at a ramping rate of 10 °C/min under argon protection. Raman spectra were recorded on a Renishaw inVia Raman microscopy (Renishaw Inc., Gloucestershire, UK), equipped with a 532 nm line of silicon-solid laser excitation source and a sensitive Peltier-cooled couple charged device (CCD) detector. The laser beam was focused on the sample through an 50× objective lens purchased from Leica. The size of the laser spot was about 10 μm in diameter and the laser power on the sample was kept below 2.5 mW to avoid decomposition of surface carbon. At least 10 Raman spectra were obtained from each sample for minimizing the measuring error. High resolution solid-state ^{11}B magic angle spinning (MAS) NMR experiments were carried out on Bruker DRX spectrometer at a static magnetic field of 19.6 T (^1H frequency: 830 MHz) using a home-built 4 mm magic angle spinning (MAS) probe. The ^{11}B NMR experiments were performed at 267.4 MHz. ^{11}B NMR spin-echo was recorded at 50 kHz RF field at a pulse length of 3 and 6 μs with a recycle delay of 2 s and a sample rotation frequency of 10 kHz. The spectra were calibrated relative to an aqueous solution of H_3BO_3 ($\delta = 19.6$ ppm) and $BF_3{\cdot}OEt_2$ ($\delta = 0$ ppm).

Table 1
Conductivity of the SiBCN and SiCN ceramics pyrolyzed at different temperatures.

SiBCN		SiCN	
Pyrolysis temperature (°C)	Conductivity (Ohm cm^{-1})	Pyrolysis temperature (°C)	Conductivity (Ohm cm^{-1})
1000	2.53×10^{-10}	1000	1.94×10^{-9}
1100	9.68×10^{-10}	1100	1.34×10^{-8}
1200	1.25×10^{-8}	1200	1.45×10^{-7}
1300	4.37×10^{-7}	1300	7.56×10^{-7}
1400	3.37×10^{-6}	1350	1.65×10^{-6}
1500	1.52×10^{-5}		

3. Results and discussion

The obtained SiBCN and SiCN ceramics were first analyzed using XRD, which suggests that regardless compositions and pyrolysis temperatures all samples are amorphous without detectable crystalline phase. The TGA analysis shows that there is no detectable weight change in the investigated temperature ranges (SiBCN: 1000–1500 °C, SiCN: 1000–1350 °C), revealing that these ceramics are stable against thermal decomposition.

The measured electric conductivity of the ceramics is listed in Table 1. It is seen that the conductivity of the SiBCN increases by five orders of magnitude when the pyrolysis temperature is increased from 1000 to 1500 °C; and the conductivity of the SiCN is increased by three orders of magnitude as the pyrolysis temperature goes up from 1000 to 1350 °C, similar to those reported in Ref. 12. Meanwhile, the data show that the conductivity of the SiBCN is ten times lower than that of the SiCN fabricated at the same pyrolysis temperature, suggesting that boron exhibits a significant impact on the conduction of PDCs.

Further analysis of the conductivity has been done by plotting them in a format of Ln (conductivity) vs. reciprocal of pyrolysis