Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 35 (2015) 1355–1360

www.elsevier.com/locate/jeurceramsoc

Electrical conductivity of dense, bulk silicon-oxycarbide ceramics

Kwang Joo Kim [a], Jung-Hye Eom [b], Young-Wook Kim [b,*], Won-Seon Seo [c]

[a] *Department of Physics, Konkuk University, Seoul 143-701, Republic of Korea*

[b] *Functional Ceramics Laboratory, Department of Materials Science and Engineering, The University of Seoul, 163 Seoulsiripdae-ro, Dongdaemun-ku, Seoul 130-743, Republic of Korea*

[c] *Energy and Environmental Division, Korea Institute of Ceramic Engineering and Technology, Seoul 153-801, Republic of Korea*

Received 22 August 2014; received in revised form 3 December 2014; accepted 6 December 2014

Available online 23 December 2014

Abstract

The effects of sintering temperature on the electrical conductivity of dense, bulk SiOC ceramics were investigated in polysiloxane-derived SiOC ceramics prepared by a conventional ceramic processing route. The electrical conductivity of the SiOC ceramics increased with increasing sintering temperature between 1450 °C and 1650 °C. Raman spectroscopy and high-resolution transmission electron microscopy revealed that the SiOC ceramics contained graphitic species (nanocrystalline graphite/turbostratic carbon) and nano-crystalline SiC grains that were precipitated during the fabrication process. The increase in the electrical conductivity is attributable to an increase in the sp^2 carbon bonding portion within a carbon cluster as the sintering temperature increases. The SiOC ceramics sintered at 1650 °C exhibited an electrical conductivity as high as 7 Ω^{-1} cm^{-1} at room temperature. The electrical conductivity of SiOC ceramics sintered at 1550 °C was ~1.0 Ω^{-1} cm^{-1} at 4 K and ~2.0 Ω^{-1} cm^{-1} at 300 K.

Keywords: Silicon-oxycarbide; Electrical properties; Graphite; Hot-pressing

1. Introduction

Polymer-derived ceramics (PDCs) based on Si-O-C (SiOC) have attracted a variety of interests,[1,2] especially for potential applications in sensors,[3–5] phosphors in LED systems,[6–8] electrode materials in lithium-ion batteries,[9] cost-effective fibers for structural applications,[10,11] micro-parts and patterns in high-temperature microelectromechanical systems (MEMS),[12,13] porous ceramics for thermal insulators and water-treatment membranes,[14–16] precursors for SiC powders,[17] and coatings for metal parts,[18] due to their improved mechanical, thermal, and chemical properties compared to amorphous SiO_2.[19–28]For some applications such as MEMS, pressure sensors using piezoresistivity, and sealant use, control of the electrical conductivity of SiOC ceramics is very important. One way to increase the electrical conductivity is to incorporate conductive phases such as $MoSi_2$, C, and SiC as fillers into the SiOC matrix.[29–31] The conductive fillers form percolation paths through the conductive particles and dramatically increase the electrical conductivity. However, the data on the electrical conductivity of dense, monolithic SiOC ceramics are quite limited. The electrical conductivities of dense monolithic SiOC vary up to 13 orders of magnitude (typically in the range of 10^{-13} to 10^{0} Ω^{-1} cm^{-1}) depending on the composition and temperature. Renlund et al.[32] reported an electrical conductivity of 4×10^{-13} Ω^{-1} cm^{-1} at room temperature (RT) in commercially available polysilioxane-derived SiOC ceramics (SR350, General Electric Silicon Products Division, Waterford, NY, USA) when they had been pyrolyzed at 1100 °C. Cordelair and Greil[2] reported that the electrical conductivities of SiOC ceramics are strongly dependent on the pyrolysis temperature for two different commercially available polysilioxanes-derived SiOC ceramics (poly(phenylmethyl-vinylhydrogensiloxane), H62C, Wacker Chemie, Burghausen, Germany; poly(methylhydrogensiloxane), NH2100, Huels AG, Marl, Germany). The electrical conductivities of H62C- and NH2100-derived SiOC ceramics were ~3×10^{-12} and ~5×10^{-12} Ω^{-1} cm^{-1}, respectively, at

* Corresponding author. Tel.: +82 2 6490 2407; fax: +82 2 6490 2404.
E-mail address: ywkim@uos.ac.kr (Y.-W. Kim).

http://dx.doi.org/10.1016/j.jeurceramsoc.2014.12.007
0955-2219/

300 °C and ~2 and ~$2 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, respectively, at 1400 °C.

In this work, crack-free, dense SiOC ceramics were prepared by a conventional ceramic processing route using a commercially available polysiloxane (YR3370, Momentive Performance Materials Japan Inc., Tokyo, Japan). The polysiloxane was pyrolyzed at 1100 °C and pulverized using planetary milling and hot-pressed at 1450–1650 °C. The electrical conductivity of the hot-pressed SiOC ceramics was measured and the contribution of graphitic carbon clusters to the electrical conduction in the ceramics is discussed.

2. Experimental procedures

Commercially available polysiloxane (YR3370, Momentive Performance Materials Japan Inc., Tokyo, Japan; chemical composition of pyrolysis residue: $SiO_{1.50}C_{0.68}$) was ground using an agate mortar and pyrolyzed at 1100 °C in flowing argon with a heating rate of 1 °C/min and a dwell time of 1 h. The pyrolyzed powders were milled for 48 h using SiC balls and a planetary mill at 250 rpm. The average particle size of the milled powder was 0.39 μm. The milled powder was uniaxially pressed in a cylindrical mold (30 mm in diameter) and subsequently hot-pressed at 1450–1650 °C for 1 h under an applied pressure of 40 MPa in an argon atmosphere. The heating and cooling rates over a temperature range of 1000–1550 °C were 20 °C/min and 30 °C/min, respectively. Discs of 30 mm in diameter and 7 mm in thickness were prepared by this method.

The bulk density of the resulting SiOC ceramics was calculated from the weight-to-volume ratio of the specimens. The open porosity was measured using the Archimedes method. The fracture surfaces were observed by scanning electron microscopy (SEM, S4300, Hitachi Ltd., Hitachi, Japan). SiOC disks (3 mm in diameter) for high-resolution transmission electron microscopy (HRTEM) were prepared using a standard method including slicing, ultrasonic drilling, polishing, and ion milling. HRTEM (400 kV, JEM-4010, JEOL, Tokyo, Japan) was used for observing graphitic species and nano-crystalline SiC grains in an amorphous SiOC matrix. Raman spectra of the specimens were measured using an Ar-ion laser (wavelength = 514 nm) at RT. Electrical conductivity of the SiOC specimens was obtained by Hall measurements at RT under a magnetic field of 1 T. The temperature-dependent resistivity of a selected SiOC specimen was measured in the 4–300 K range using a ^{4}He cryostat equipped with a superconducting magnet (PPMS-9, Quantum Design™, San Diego, CA, USA). At each temperature step, the measurement was made with a current-flip after the temperature had stabilized.

3. Results and discussion

The sintered density of the SiOC specimens increased from 2.341 to 2.465 g/cm^3 as the sintering temperature increased from 1450 °C to 1550 °C, and the density decreased to 2.301 g/cm^3 as the sintering temperature increased to 1650 °C. The open porosity of the bulk SiOC ceramics decreased continuously from 0.4% to 0.2% as the sintering temperature increased from 1450 °C to 1650 °C. The small open porosity suggests that the submicron-sized SiOC starting powder is beneficial in achieving almost full densification by conventional hot-pressing. The decrease of the sintered density at 1650 °C should be related to a carbothermal reduction, which will be discussed using X-ray diffraction patterns of the specimens.

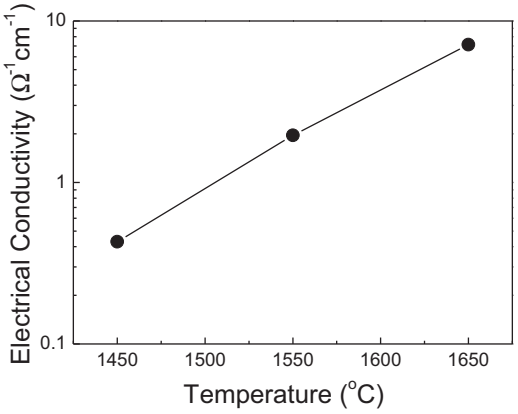

Fig. 1. Electrical conductivities of bulk SiOC ceramics at room temperature.

Fig. 1 exhibits the room-temperature electrical conductivities of SiOC specimens sintered at different temperatures. All of the specimens showed increasing conductivity with increase in the sintering temperature (T_s). For the pure polysiloxane-derived specimen, the conductivity increased by ~17 times between T_s = 1450 °C (0.43 Ω^{-1} cm^{-1}) and 1650 °C (7.1 Ω^{-1} cm^{-1}). The temperature dependence (4–300 K) of the electrical conductivity of the SiOC specimen with T_s = 1550 °C is exhibited in Fig. 2, with the electrical conductivity gradually increasing with increasing temperature. However, the rate of increase in the conductivity with temperature is rather small (~1.0 Ω^{-1} cm^{-1} for 4 K and ~2.0 Ω^{-1} cm^{-1} for 300 K).

The fracture surfaces of all specimens are shown in Fig. 3. As shown, the microstructures consisted of fully dense large domains (2–8 μm), small domains (<1 μm), and residual inter-domain pores. Transgranular fracture behavior was observed in all specimens. There was no remarkable difference in the SEM microstructure between the specimens. Fig. 4 shows a

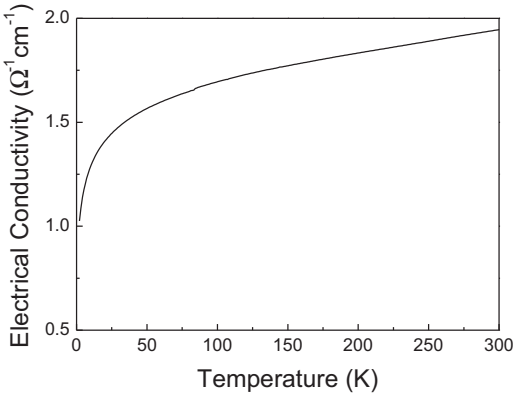

Fig. 2. Temperature dependence (4–300 K) of electrical conductivity of SiOC specimen sintered at 1550 °C.