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# Effects of $SiO_2$-forming additive on polysiloxane derived SiOC ceramics

Donald Erb, Kathy Lu*

*Department of Materials Science and Engineering, Virginia Tech, Blacksburg, VA, 24061, USA*

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## ABSTRACT

Novel ultrahigh surface area materials are highly desired for demanding applications such as high temperature catalysts, electrodes, and harsh environment sensors. In-situ conversion of tetraethyl orthosilicate (TEOS) into $SiO_2$ and its incorporation into silicon oxycarbide (SiOC) ceramics during polysiloxane ceramization are investigated by crosslinking TEOS within a polysiloxane matrix and introducing water vapor during pyrolysis. The effects of the TEOS-derived $SiO_2$ on the thermophysical properties, phase development, and the resulting porous SiOC are investigated. The SiOC with 10 wt% TEOS within the crosslinked polymer creates the highest specific surface area of ~2100 $m^2/g$ with an average pore size of ~2 nm. The specific surface area and pore size distribution are correlated with the theoretical results from Voronoi diagram simulation and an idealized model calculation.

## 1. Introduction

Silicon oxycarbide (SiOC) is a polymer derived ceramic through which polysiloxane polymer precursors undergo thermal decomposition and bond rearrangement, resulting in amorphous or nanocrystalline ceramics (or a mixture of both) with a wide range of tailorable properties, such as high temperature stability, oxidation resistance, and electrical conductivity, depending on the pyrolysis temperature and specific composition [1–3].

In general, porous SiOC can be fabricated with a wide range of pore sizes using several different processing routes before, during, or after pyrolysis, such as by using sacrificial fillers, sacrificial templating, direct foaming, polymer precursor phase separation, and selective removal of phases after pyrolysis [4–7]. However, to create ultrahigh surface areas, only controlled phase separation during pyrolysis and selective phase removal after pyrolysis at the nanocluster level are feasible means, which can create pores with less than 10 nm sizes and very narrow distributions.

Phase separation in an evolving SiOC system can be introduced using two different methods. The first is through phase separation of the polymer precursors during crosslinking. When two or more immiscible polymers co-exist as liquid precursors, they will separate and form two distinct phases after crosslinking. One of the phases can then evaporate after cross-linking or decompose during pyrolysis, leaving behind pores. The SiOC ceramics created with this method have high specific surface areas at temperatures around 600 °C. However, the specific surface area may decrease as the temperature increases due to the sintering of transient pores [4,8]. The second method is by controlling phase evolution within SiOC during pyrolysis. At temperatures above 1100 °C, the amorphous SiOC phase separates into free carbon and amorphous $SiO_2$ nanodomains along with SiOC units of different stoichiometry. Pyrolysis to even higher temperatures, e.g., greater than 1250 °C, leads to further phase separation and thus more carbon and $SiO_2$, as well as nanocrystalline SiC [9,10]. From this point forward, the pyrolysis temperature can significantly influence the phase separation and the separated domain sizes. After pyrolysis, certain ceramic phases can be etched away, such as using hydrofluoric acid (HF) to remove $SiO_2$ nanodomains or chlorine gas to remove SiC nanocrystals, leaving behind single nanometer pores [1,11]. Therefore, nucleation and growth, concentration, and size of different ceramic phases within SiOC are critical factors influencing the final porous SiOC materials.

$SiO_2$ nanodomain sizes in SiOC are related to both system chemistry and processing conditions. From ~1000 °C to ~1250 °C, $SiO_2$ nanoclusters are the main separated phase along with turbostratic carbon. In this temperature range, the $SiO_2$ nanodomains largely remain amorphous but the correspondingly sizes increase with pyrolysis temperature. Saha et al. [12] reported that the size of the $SiO_2$ nanodomains is also dependent on the Si:O elemental ratio of the SiOC, with larger Si:O ratios producing smaller domain sizes. The effect of polymer precursor molecular structure on the resulting $SiO_2$ domain size is shown by comparing a linear polymer, polyhydridomethylsiloxane (PHMS), and a cyclic polymer, 1,3,5,7-tetramethyl-1,3,5,7-tetracyclotetrasiloxane (TMTS), having the same chemical composition. After pyrolysis at 1400 °C, the PHMS sample has only amorphous $SiO_2$,

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* Corresponding author. 213 Holden Hall, Virginia Tech, Blacksburg, VA, 24061, USA.
*E-mail address:* klu@vt.edu (K. Lu).

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while the TMTS sample contains both amorphous and crystalline $SiO_2$ [13,14]. After etching both samples with HF, the PHMS sample has a higher micropore volume compared to the TMTS sample due to the presence of smaller $SiO_2$ domains [13].

$SiO_2$ formation in SiOC can also be influenced by pyrolysis atmosphere, such as by introducing reactive species into the pyrolysis gas, e.g., $H_2$ or $H_2O$ [15–18]. Our previous work demonstrated that injecting water vapor during the temperature range at which precursor bond (chain) breaking occurs results in a dramatic decrease in carbon precipitation and an increase in Si-O-Si bond formation [7,17,18]. The resulting SiOC sample pyrolyzed at 1300 °C after HF etching has a specific surface area of 2391.6 $m^2/g$, much greater than the specific surface area of the sample pyrolyzed in Ar at the same temperature, 630.41 $m^2/g$ [18]. Liang et al. [15] investigated water vapor injection effects on the chemistry and atomic bonding of SiOC from 500 °C to 1000 °C. The samples pyrolyzed in the water vapor atmosphere have only about half the carbon content compared to the samples pyrolyzed in Ar, resulting in a reduction of $SiC_4$ and $SiC_2O_2$ structural units and an increase in $SiO_4$ units.

Additives can be introduced into the polymer precursor to further react with the pyrolysis atmosphere. By adding 10 wt% tetraethylorthosilicate (TEOS), a water reactive molecule, to a commercial polysiloxane and then pyrolyzing in an Ar + $H_2O$ atmosphere, the specific surface area of the SiOC after HF etching increases from 1108.5 $m^2/g$ for the base polysiloxane to 1953.9 $m^2/g$ for the sample with TEOS. Additionally, the average pore size of the 10 wt% TEOS sample is 1.66 nm, less than the 3.03 nm pore size of the polysiloxane sample [19]. However, the evolution of the TEOS during the polymer to ceramic transformation or its effect on the phase separation within SiOC is yet unknown; it is unclear whether the TEOS would interact with the SiOC system to form $SiO_2$ or experience $SiO_2$ nucleation and growth independently.

Understanding and creating highly porous SiOC is of high interest for fundamental understanding, such as addressing the questions related to $SiO_2$ nucleation and growth as well as molecular interactions of different precursors. Porous SiOC also has many exciting applications, e.g., electrodes in lithium ion batteries, catalyst supports, thermal barriers, gas separation membranes, and lightweight components [20–22]. In this work, micro- and meso-porous SiOC ceramics are fabricated through the addition of TEOS to a polysiloxane precursor and then pyrolysis in a water vapor-containing atmosphere. After pyrolysis, $SiO_2$ nanoclusters are etched with a HF solution to create single nanometer pores. The effects of the additive amount and pyrolysis temperature on the resulting thermophysical properties, phase evolution, specific surface area, and pores of the SiOC ceramic are studied.

## 2. Experimental procedures

A commercial polysiloxane (PSO, $[-Si(C_5H_6)_2O-]_3[-Si(CH_3)(H)O-]_2[-Si(CH_3)(CH{=}CH_2)O-]_2$, SPR-684, Starfire Systems, Inc. Gelest Inc. Schenectady, NY) was chosen as the base precursor, tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$, Sigma-Aldrich, St. Louis, MO) was used as the additive, and 2.1–2.4% platinum-divinyltetramethyldisiloxane complex in xylene (Pt catalyst, Gelest Inc. Morrisville, PA) was used as the catalyst.

First, solutions with PSO and either 0, 10, 20, 30, or 40 wt% TEOS were sonicated for 10 min and then mixed in a high energy mill (SPEX 8000M Mixer/Mill, SPEX SamplePrep, Metuchen, NJ) for 10 min to form a homogeneous mixture. Next, the Pt catalyst (1 wt% relative to PSO) was added, the mixtures were mixed again in the high energy ball mill for 5 min, and then poured into aluminum foil molds. The mixtures were placed into a vacuum chamber and vacuumed for 10 min at 200 Torr to remove any bubbles in the solutions. After that, the molds were put in an oven to crosslink at 50 °C for 12 h and then at 120 °C for 6 h. All solutions initially had slightly greater than the listed weight of TEOS added in order to account for the evaporation of the additive during processing, so the actual content of TEOS added was 11, 22, 32, and 43 wt% for the nominal 10, 20, 30, and 40 wt% samples, respectively. The samples were also sealed during the curing process to prevent additional loss of TEOS. The samples designated as 100PSO corresponded to the pure PSO sample; the samples with the additive were labelled as XTEOS, where X was from 10 wt% to 40 wt%, depending on the TEOS amount.

For pyrolysis, the crosslinked materials were first cut and polished into circular pieces roughly 10 mm in diameter and 2 mm in thickness. Next, the samples were placed into a zirconia crucible, covered on both sides with graphite mats in order to reduce friction during shrinkage and prevent warping [23,24], and put into a tube furnace (1730-20 Horizontal Tube Furnace, CM Furnaces Inc. Bloomfield, NJ). With an Ar flow rate of approximately 500 std $cm^3/min$, the samples were heated up to 1100 °C, 1300 °C, or 1400 °C at a rate of 1 °C/min, held for 2 h, cooled to 400 °C with a rate of 1 °C/min, and finally cooled to 50 °C with a rate of 2 °C/min. During heating from 500°C to 700 °C, the Ar gas was bubbled through water at 60 °C, giving a gas flow with a Ar:$H_2O$ molar ratio of approximately 5:1.

Etching of the bulk SiOC samples after pyrolysis was done using a HF solution (20 wt% HF in water). The HF solution was magnetically stirred at room temperature until there was no significant mass loss, taking approximately 4 days (supplement Table S2). The SiOC samples were then rinsed with deionized water and dried at 120 °C. Bulk density of the samples after etching was determined geometrically by dividing the mass after etching by the volume of the samples measured using the image analysis software ImageJ [25].

Ceramic yield was calculated by measuring the mass of the samples before and after the pyrolysis. The apparent density after pyrolysis was measured using the Archimedes method with water as the medium [26]. The phase compositions of the pyrolyzed samples were analyzed in an X'Pert PRO diffractometer (PANalytical B.V. EA Almelo, the Netherlands) with Cu Kα radiation. The JCPDS reference cards used to identify the crystalline phases were 00-039-1425 for $SiO_2$, 00-029-1129 for SiC, and 01-075-1621 for C. The chemical bonding was evaluated using Fourier Transform Infrared Spectroscopy (FT-IR) (Nicolet 8700 with Pike GladiATR attachment, Thermo Scientific, Waltham, MA) between 500 and 4000 $cm^{-1}$ wavenumber with a resolution of 4 $cm^{-1}$ and averaged between 64 scans. The specific surface area, pore size distribution, and specific pore volume of the pyrolyzed samples were evaluated using nitrogen adsorption at 77 K with a Quantachrome Autosorb-1 (Quantachrome Instrumenets, Boynton Beach, FL), and the samples were degassed before testing for 3 h at 300 °C. The relative pressure range used to calculate the specific surface area using the BET method was determined based on the procedure proposed by Rouquerol et al. [27]; the calculated specific surface area should be considered as the "BET-equivalent specific surface area" due to the complications of applying the BET theory to microporous materials. The pore size distribution and specific pore volume were derived by applying the Non Local Density Functional Theory (NLDFT) model for $N_2$ adsorption on carbon with cylindrical pores to the adsorption branch of the data [28]. Assuming cylindrical pores, the average pore size was estimated using $4000V_p/SSA$, where $V_p$ is the specific pore volume, and SSA is the specific surface area [29].

Modeling of the SiOC microstructure after etching was computed using Voronoi software (Rhinoceros 5.0, Robert McNeel and Associates, Seattle, WA). First, a three dimensional Voronoi tessellation model was created, and spheres were then placed within the center of each Voronoi cell to represent pores (or $SiO_2$ nanodomains before etching) within the SiOC matrix. The pore size distributions used in the model were generated by first fitting the experimental pore size distributions from nitrogen adsorption with log-normal distributions (see supplement Fig. S3). Random pore diameters corresponding to the fitted distributions were then generated using Mathematica software (Mathematica 11.0, Wolfram, Champaign, IL). After the generation of the cubes containing the Voronoi cells and corresponding pores, images along the