

Rapid Communication

Accelerated Polymer to SiOC Nanocomposite Conversion

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Abstract

In this work, flash pyrolysis was innovatively used to fabricate polymer derived Silicon Oxycarbide (SiOC) ceramics. Electric field significantly accelerates SiOC microstructure development, creating carbon and SiC phases at ~500°C lower pyrolysis temperatures within the SiOC matrix than the conventional approach. With an electric field, the samples form more SiC and a more ordered carbon phase. The fundamentals can be explained based on the significant phase evolution driving force provided by the electrical field, accompanied by Joule heating. This work provides a novel route to synthesize SiOC nanocomposites at significantly lower temperatures.

Keywords: SiOC; Flash pyrolysis; Ceramic yield; Power density; Microstructure; Phase separation

Abbreviations

SiOC: Silicon Oxycarbide; PMPS: Polyphenylmethylsiloxane; PHMS: polyhydromethylsiloxane; PSO: Polysiloxane

Introduction

Silicon Oxycarbide (SiOC) is a polymer derived system composed of SiOC, SiO₂, carbon, and potentially SiC (at >1300°C pyrolysis temperatures). It was first reported more than 50 years ago [1,2] but has generated great interest in recent years to create intriguing amorphous-crystalline mixed microstructures as well as desirable thermal stability, chemical and oxidation resistance, and functional properties [3-5].

The starting materials for SiOC synthesis are variations of polysiloxanes, with -Si-O- in the polymer backbones. The materials can be easily cross linked into any desirable shapes using the typical polymer cross linking process. Pyrolysis leads to the formation of inorganic materials with pyrolysis temperature and atmosphere dictating the micro structures and compositions [6]. In general, at >1100°C, the SiOC matrix evolves into nano-sized SiO₂ domains and a disordered graphitic phase, which are embedded in an amorphous SiOC matrix [7-9]; at pyrolysis temperatures greater than 1300°C, the SiOC matrix further phase separates, forming SiC nano crystals and additional amorphous SiO₂ and graphitic domains [4,5,10]. Depending on the microstructure, the properties of the SiOC ceramic, such as electrical conductivity and oxidation resistance, can be greatly altered [11-13].

An electrical field-assisted technique, flash pyrolysis, has never been studied even though flash sintering was reported in 2010 [14]. During the flash event, the conductivity of the samples experiences a sharp nonlinear increase, accompanied by a sharp increase in sintering densification. The sharp conductivity increase leads to significant Joule heating, which can heat the samples to several hundred degrees Celsius higher than the furnace temperature [15,16].

In this study, flash pyrolysis has been investigated with two polysiloxanes of different repeating units. Thermo physical changes and SiOC phase evolution are studied along with microstructure

comparison.

Materials and Methods

Vinyl terminated Polyphenylmethylsiloxane (PMPS) and Polyhydromethylsiloxane (PHMS) were chosen as the base precursors to obtain PMPS-15PHMS samples (the PHMS/PMPS weight ratio was 15/85). Polysiloxane (PSO, [-Si(C₅H₉)₂O-]₃[-Si(CH₃)(H)O-]₂[-Si(CH₃)(CH=CH₂)O-]₂, SPR-684) was chosen as the other base polymer. 2.1-2.4% platinum-divinyltetramethyldisiloxane complex in xylene was used as a Pt catalyst. All chemicals were from Gelest Inc. For the PSO polymer, 10 vol% acetone (*vs.* PSO) was used as a solvent. The starting precursors were sonicated for 10 minutes and then mixed in a high energy mill (SPEX 8000M Mixer/Mill, SPEX Sample Prep, Metuchen, NJ) for 10 minutes. Next, the Pt catalyst (1 wt% relative to the base polymer) was added, the mixtures were mixed again for 5 minutes, and then poured into aluminium foil molds. After deairing, the molds were placed in an oven to crosslink at 50°C for 12 hours and then at 120°C for 6 hours to obtain preceramic green bodies.

A silver-palladium paste (conductor type 9627, ESL Electro Science, King of Prussia, PA) was applied to the sample and dried in order to achieve good electrical contact (minimizing contact resistance) on the sample and served as the electrodes. The sample was then placed into a zirconia crucible. The electrical connections of the electrodes to the power supply were made by Pt wires. The samples were put into a tube furnace (1730-20 Horizontal Tube Furnace, CM Furnaces Inc., Bloomfield, NJ) and pyrolyzed in argon with a flow rate of about 70 std cm³/s and a heating rate of 5°C/min to 300°C. The furnace was then heated up to the peaking temperature at 2°C/min. At this point, an electric field was applied to the sample. The limiting current was 2A. The power supply was shut off shortly after the flash occurred. An additional sample was pyrolyzed to 1300°C without an applied electric field with the same heating procedure to serve as a comparison.

The samples were labelled as T-X, where T was the pyrolysis temperature, X was the electric field applied to the sample (30, 40, or 50 V/mm). The ceramic yield of the samples was calculated using

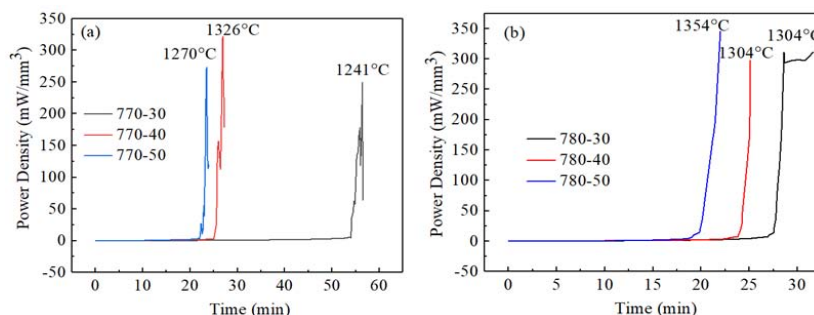


Figure 1: Power density and internal temperature at flash point for (a) PMPS-15PHMS and (b) PSO systems at different electrical field.

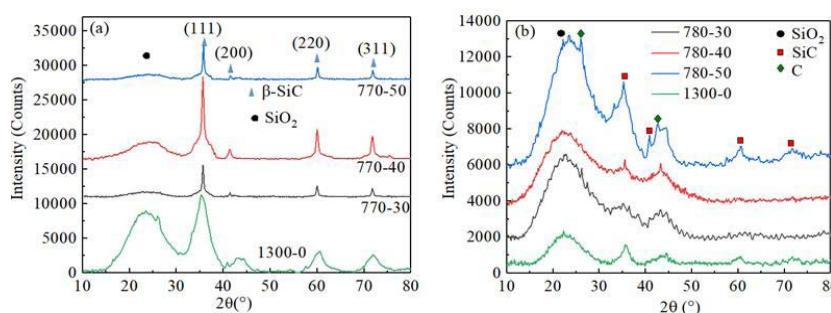


Figure 2: XRD patterns for (a) PMPS-15PHMS and (b) PSO samples at different electrical field.

the mass before and after pyrolysis. The phase compositions of the pyrolyzed samples were analyzed in an X'Pert PRO diffractometer (PANalytical B.V., EA Almelo, the Netherlands) with Cu K α radiation. The microstructures of the pyrolyzed ceramics were studied using a transmission electron microscope (JEOL 2100, Peabody, MA).

Results and Discussion

During flash pyrolysis, the insulating nature of the polymer precursor(s) and decomposed radials create a state that a large amount of Joule heating is generated. Joule heating causes drastic sample temperature increase. The sample temperature during the flash event can be much greater than the furnace temperature. The estimated sample temperature during the flash has been studied based on blackbody radiation [15,17,18]. The temperature of the samples can be estimated using the following equation [15]:

$$T = T_0 \alpha [1 + 1000 W_v (\text{mW mm}^{-3}) / \sigma T_0^4 (\text{V/A (mm)})]^{1/4}$$

where T is the sample temperature in Kelvin, T_0 is the furnace temperature, σ is the Stefan-Boltzmann constant with a value of $5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$, A is the surface area of the sample in mm^2 , V is the sample volume in mm^3 , α is a correction factor to account for emissivity less than that expected for a perfect blackbody, and W_v is the electrical power dissipated in the sample. Approximating α to be 1, the temperature for each of the samples can be calculated as shown in (Figure 1). The internal temperatures of the samples are between 1241–1354°C, which is 470–574°C higher than the displayed values from the furnace. Interesting, the PMPS-15PHMS sample has the highest internal temperature at 40 V/mm electrical field (770-40), at 1326°C. The internal temperature at 50 V/mm electrical field (770-50) is lower due to the smaller current in the sample, at 1270°C. For the

30 V/mm sample (770-30), the incubation time for the flash process more than doubles that of the higher electrical field conditions, at ~55 min, due to the lowest sample internal temperature of 1241°C. For the PSO samples, the internal temperatures are 1304 to 1354°C, the internal temperature change trend is different from that of the PMPS-15PHMS samples due to the precursor difference. The PSO samples also require higher furnace temperature (780°C) than the PMPS-15PHMS samples (770°C) to reach similar internal temperatures. This is because the PMPS-15PHMS samples have more carbon content from the precursors; it is easier to create the flash event in the samples. In addition, the PMPS-15PHMS and PSO samples have very similar incubation time at higher electrical field (40 V/mm and 50 V/mm). However, at lower electric field (30 V/mm), it takes 55 minutes (significantly longer time) for the PMPS-15PHMS sample (770-30) to flash while it only takes 27.5 minutes for the PSO samples to flash at 30 V/mm.

As shown in (Table 1), flash pyrolysis has a tremendous impact on the ceramic yield when compared to the 1300°C pyrolyzed sample without any electrical field. For the PMPS-15PHMS sample, the ceramic yield decreases dramatically, from 78.64% for the 1300°C pyrolyzed sample without any electric field condition to 54.32% at 30 V/mm, 53.37% at 40 V/mm, and 48.14% at 50 V/mm. The percent decrease is 30.93%, 32.13%, and 38.78% respectively when compared to the 1300°C pyrolyzed sample without an electric field. The drastic ceramic yield decrease is a result of the rapid loss of carbon radials under the electrical field. Higher electrical field imposes higher phase evolution driving force and thus causes more weight loss. For the PSO sample, the ceramic yield after 1300°C pyrolysis without any electrical field is 68.43%. Pyrolysis at 780°C under similar equivalent internal temperatures increases the ceramic yield to >72%, opposite to that

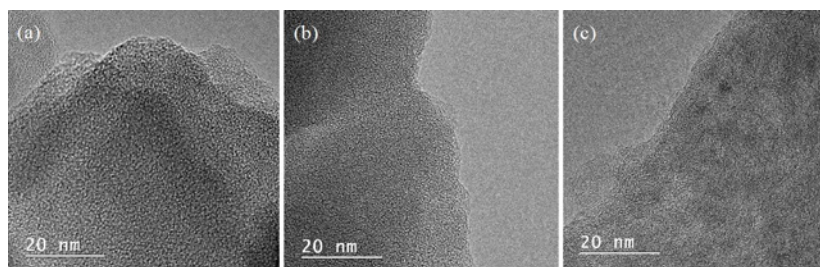


Figure 3: Carbon morphology in the PSO samples pyrolyzed under different electrical field (a) PSO, 780, no electric field, (b) 50V, 0.4A, and (c) 50V, 2A.

Table 1: Ceramic yield results for the PMPS-15PHMS (P-P) and PSO samples under different electric field conditions.

Samples	P-P 770-30	P-P 770-40	P-P 770-50	P-P 1300-0	PSO 780-30	PSO 780-40	PSO 780-50	PSO 1300-0
Ceramic yield (%)	54.32	53.37	48.14	78.64	74.59	72.83	72.32	68.43
Percent Change vs. Conventional Pyrolysis at 1300°C	-30.93%	-32.13%	-38.78%	-	9.0%	6.43%	5.69%	-

of the PMPS-PHMS samples. Higher electrical field leads to lower ceramic yield, changing from 74.59% at 30 V/mm, to 72.83% at 40 V/mm, and 72.32% at 50 V/mm. The ceramic yield increase is 9.0%, 6.43%, and 5.69% respectively, compared to the 1300°C pyrolyzed sample without an electric field. This indicates that the PSO samples have less radial species evaporating out of the system during the electrical field assisted pyrolysis, consistent with the lack of large side groups in its molecular structure.

Figure 2 shows the XRD patterns for the PMPS-15PHMS and PSO samples at different electrical field. For the flash-pyrolyzed samples, all the XRD patterns have an amorphous SiO₂ halo at ~22°, diffraction peaks appear at 35.5°, 41.4°, 60.1°, and 71.9°, corresponding to the (111), (200), (220), and (311) crystallographic planes of β-SiC [19]. This means that the phase separation in the flash-pyrolyzed samples takes place at furnace temperatures of 770°C (for the PMPS-15PHMS) and 780°C (for the PSO samples), which is 474-574°C lower than that of the traditional pyrolysis. Furthermore, the amount of β-SiC in the flash-pyrolyzed samples is proportional to the applied electric field, showing that the SiC crystallization is influenced by the carbon content, which accelerates the onset of the SiC crystallization in SiOC [20]. The results indicate that the PMPS-15PHMS samples from sharper SiC peaks than the PSO samples at the same electrical field. This is because the PMPS-15PHMS samples have more carbon content from the polymer precursors. It is easier to create the flash event in the samples and thus generate more SiC. Furthermore, there is no carbon peak in the PMPS-15PHMS samples, because the electric field accelerates the phase separation and offers the Joule heating to facilitate the SiC formation. Eventually, carbon is consumed in the PMPS-15PHMS samples to form a high amount of SiC.

From the results in (Table 1) on the ceramic yield and (Figure 2) on the phase composition, it is clear that the carbon species has undergone significant changes during the pyrolysis. The TEM images for the PSO samples pyrolyzed at the same condition without any electric field, and with different electric field are shown in (Figure 3). At 780°C pyrolysis condition without any electric field, the carbon phase is totally amorphous and shows no texture. At 50 V/mm electric field with 0.4 A current, the carbon phase remains amorphous even though 1-2 carbon layers start to line up. However, when the current

increases to 2 A, local carbon ordering is evident throughout the samples with 3-5 graphene layers arranged into crystalline structures. This means that the electrical field dictates the carbon species arrangement, consistent with the carbon peak in (Figure 2b).

Conclusion

Flash pyrolysis has been successfully used to produce polymer-derived SiOC ceramics. With the application of an electric field, the samples experience Joule heating and show similar phase evolution at 474-574°C lower pyrolysis temperatures than the traditional process, a remarkable result in light of the high temperatures needed. With both an electric field and significant Joule heating, the formation of SiC is promoted due to the availability of carbon, the amorphous nature of the C- and Si- containing species present. Flash pyrolysis offers a low temperature and highly efficient process for polymer derived SiOC formation.

Acknowledgment

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References

- Ainger FW, Herbert JM. The Preparation of Phosphorus-Nitrogen Compounds as Non-Porous Solids. New York: Academic Press; 1960.
- Chantrell PG, Popper P. Inorganic Polymers and Ceramics. New York: Academic Press; 1965.
- Ionescu E, Kleebe HJ, Riedel R. Silicon-containing Polymer-Derived Ceramic Nanocomposites (PDC-NCs): preparative approaches and properties. Chem Soc Rev. 2012; 41: 5032-5052.
- Colombo P, Mera G, Riedel R, Soraru GD. Polymer-derived ceramics: 40 years of research and innovation in advanced ceramics. J Am Ceram Soc. 2010; 93: 1805-1837.
- Lu K. Porous and high surface area silicon oxycarbide-based materials-A review. Mater Sci Eng R Rep. 2015; 97: 23-49.
- Duan LQ, Ma QS. Effect of pyrolysis temperature on the pore structure evolution of polysiloxane-derived ceramics. Ceram Int. 2012; 38: 2667-2671.
- Brequel H, Parmentier J, Soraru GD, Schifflini L, Enzo S. Study of the phase separation in amorphous silicon oxycarbide glasses under heat treatment. Nanostruct Mater. 1999; 11: 721-731.
- Saha A, Raj R. Crystallization maps for SiCO amorphous ceramics. J Am

- Ceram Soc. 2007; 90: 578-583.
9. Saha A, Raj R, Williamson DL. A model for the nanodomains in polymer-derived SiCO. *J Am Ceram Soc.* 2006; 89: 2188-2195.
 10. Brequel H, Parmentier J, Walter S, Badheka R, Trimmel G, Masse S, et al. Systematic structural characterization of the high-temperature behavior of nearly stoichiometric silicon oxycarbide glasses. *Chem Mater.* 2004; 16: 2585-2598.
 11. Lu K, Erb D, Liu M. Thermal stability and electrical conductivity of carbon-enriched silicon oxycarbide. *Journal of Materials Chemistry C.* 2016; 4: 1829-1837.
 12. Lu K, Erb D, Liu MY. Phase transformation, oxidation stability, and electrical conductivity of TiO₂-polysiloxane derived ceramics. *J Mater Sci.* 2016; 51: 10166-10177.
 13. Cordelair J, Greil P. Electrical conductivity measurements as a microprobe for structure transitions in polysiloxane derived Si-O-C ceramics. *J Eur Ceram Soc.* 2000; 20: 1947-1957.
 14. Cologna M, Rashkova B, Raj R. Flash sintering of nanograin zirconia in < 5 s at 850 degrees C. *J Am Ceram Soc.* 2010; 93: 3556-3559.
 15. Raj R. Joule heating during flash-sintering. *J Eur Ceram Soc.* 2012; 32: 2293-2301.
 16. Raj R. Analysis of the power density at the onset of flash sintering. *J Am Ceram Soc.* 2016; 99: 3226-3232.
 17. Francis JSC, Raj R. Flash-sinterforging of nanograin zirconia: field assisted sintering and superplasticity. *J Am Ceram Soc.* 2012; 95: 138-146.
 18. Yoshida H, Sakka Y, Yamamoto T, Lebrun JM, Raj R. Densification behaviour and microstructural development in undoped yttria prepared by flash-sintering. *J Eur Ceram Soc.* 2014; 34: 991-1000.
 19. Erb D, Lu K. Additive and pyrolysis atmosphere effects on polysiloxane-derived porous SiOC ceramics. *J Eur Ceram Soc.* 2017; 37: 4547-4557.
 20. Lu K, Li JK. Fundamental understanding of water vapor effect on SiOC evolution during pyrolysis. *J Eur Ceram Soc.* 2016; 36: 411-422.