

# Carbon-containing High Temperature Piezoresistive Materials

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## Abstract

Silicon oxycarbide-based ceramics (SiOC) with contents of segregated carbon in the range from 9 to 33 vol% have been synthesized by pyrolysis of polysiloxanes (1100 °C) and subsequent annealing at high temperatures (1400-1600 °C). The samples annealed at 1400 and 1600 °C were found to exhibit piezoresistivity with room temperature gauge factors  $10^2 < k < 3 \times 10^3$ , two to three orders of magnitude higher than those of conventional pressure sensors; whereas the sample synthesized at 1100 °C did not show any piezoresistive effect. X-ray and TEM-analysis of the prepared materials indicate that the piezoresistive behaviour strongly depends on the microstructure of the compounds, most likely on the presence and nature of the segregated carbon phase. The thermal stability and microstructure of the carbon phase has been assessed by means of temperature-dependent Raman spectroscopy ( $25 < T < 600$  °C). Within the investigated temperature range the microstructure of the carbon phase is essentially unaltered, suggesting that the piezoresistive effect seen at RT will persist up to high temperatures, i.e. up to the thermal stability limit of SiOC ( $T \approx 1400$  °C). Due to their other outstanding properties, e.g. thermal and chemical stability as well as excellent creep resistance, the SiOC compounds allow a substantial extension of the operation pressure and temperature range of piezoresistive sensors beyond the current state-of-the-art.

**Key words:** piezoresistive sensor, nanocomposites, nano-carbon, Raman spectroscopy, polymer-derived ceramics (PDCs)

## Introduction

To date resistive, piezoresistive and capacitive measuring principles are predominantly used for industrial pressure sensors, with an increasing need for sensors based on the piezoresistive effect. The main reasons are the high sensitivity, reproducibility, long term stability and robustness of the sensing resistor against interfering factors. Piezoresistive sensors are usually made of doped semiconducting materials or polymer composites [1]. However, these materials are not applicable at elevated temperature or in aggressive environment. On the other hand most of the high-temperature and corrosion stable materials do not exhibit useful piezoresistivity [2]. Polymer derived ceramics (PDCs) are materials which have been intensively studied in the last three decades. They describe a new class of ceramics which can be prepared without any additives by thermal handling of appropriate precursors in inert or reactive atmosphere.

Polymer derived ceramics are amorphous materials and were shown to keep their amorphous nature up to temperatures ranging from 1000 to 1800 °C, depending on their chemical composition and structure. Recently, a topological model for silicon oxycarbides has been proposed, which assumes that SiOC consists of two interpenetrating SiO<sub>2</sub> and C-based networks [3, 4, 5]. In addition, the microstructure of SiOC exhibits a finely dispersed carbon phase. The amount and nature of the segregated carbon within the microstructure of PDCs has a crucial effect on their properties (electrical conductivity, high-temperature creep behavior, devitrification and crystallization behavior).

Polymer-derived ceramics (PDCs) have recently been shown to be promising piezoresistive materials with large gauge factors [6, 7, 8, 9]. As required for high temperature sensor applications, they have excellent stability at elevated temperature and in harsh conditions [10, 11, 12]. However,

PDCs not only exhibit unusual structural properties. A variety of functionalities can be easily introduced, such as electrical conductivity, photo luminescence or magnetic and catalytic properties [10, 11, 12] Furthermore, PDCs have the advantage that they can be processed like thermoplastic materials to obtain complex three-dimensional shapes. The polymer-derived route provides high purity compounds with very good homogeneity as a prerequisite for industrial application. In the following we present experimental evidence that these materials are promising candidates for a new class of pressure sensors showing a strong piezoresistive effect which relies on the formation of a short range-ordered carbon network.

### Experimental

A commercially available poly(methylsilsesquioxane) (PMS MK, Wacker Chemie AG, München, Germany) was used for the preparation of the silicon oxycarbide samples. Zirconium acetylacetonate served as cross-linking agent. A batch of the preceramic polymer was cross-linked at 250 °C for 30 min, ball milled, and finally sieved to a particle size of 100 µm. Subsequently, the ground powder was pyrolyzed in flowing argon at 900 °C for 30 min. The pyrolyzed SiOC powder (denoted as MK\_900) was mixed with the catalytically treated and cross-linked polymer (75 wt% SiOC powder + 25 wt% MK polymer) by ball milling and finally sieved to a particle size of 100 µm. Shaping of the polymer–powder mixture was achieved by uniaxial warm pressing at 25 MPa and 180 °C. Subsequently, the bulk sample was pyrolyzed in a tube furnace up to the pyrolysis temperature of 1100 °C and a 5-h holding time (sample denoted as MK\_1100). Further annealing treatment of the initial MK\_1100 sample was performed at 1400 °C for 5 h under argon atmosphere (sample denoted as MK\_1400) [7].

For the preparation of a carbon-rich sample, the polymer PMS MK was blended with black carbon (83.5 wt% MK polymer + 16.5 wt% carbon black) and subsequently cross-linked at 250 °C and pyrolyzed at 900 °C in argon atmosphere (sample denoted as C\_900).

The ceramic powders MK\_900 and C\_900 were hot pressed in argon at 1600 °C (30 MPa) to dense monoliths denoted as MK\_1600 and C\_1600 (Figure 1) [5, 13].

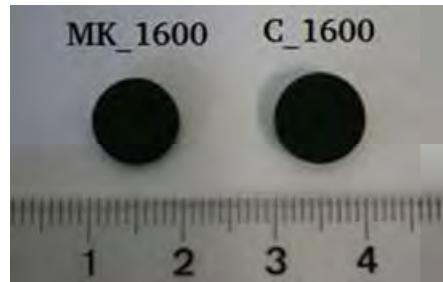


Fig. 1. Photograph of the SiOC samples prepared upon hot-pressing technique [13].

Elemental analysis of the samples was performed by hot gas extraction (Mikrolabor Pascher, Remagen, Germany).

Transmission electron microscopy (TEM) imaging was performed using a CM20STEM instrument (FEI, Eindhoven, The Netherlands) operating at 200 kV on TEM-foils obtained from the bulk samples.

Micro-Raman spectra (10 scans, each scan lasting 3 s) were recorded with a Horiba HR800 micro-Raman spectrometer (Horiba Jobin Yvon, Bensheim, Germany) equipped with an Ar laser (wavelength 514.5 nm). The excitation line has its own interference filter (to filter out the plasma emission) and a Raman notch filter (for laser light rejection). The measurements were performed by using a grating of 1800 gmm<sup>-1</sup> and a confocal microscope (magnification 100×, NA 0.5) with a 100 µm aperture, giving a resolution of 2–4 µm. The laser power (20 mW) was attenuated by using neutral density (ND) filters; thus, the power on the sample was in the range of 2 mW–20 µW.

### Results and discussion

In the following we report on structural and spectroscopic investigations of the SiOC ceramic samples to get further information on the relationship between their microstructure and the piezoresistive behavior. The crystalline phase composition and the microstructure of the samples was studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Furthermore, Raman spectroscopy was chosen to probe the local bonding in the segregated carbon phase.

#### XRD and TEM of piezoresistive SiOC

Fig. 2 presents the XRD spectra of the SiOC compounds synthesized at 1100 < T < 1600 °C. The data indicate that they are X-ray amorphous (independent of the preparation technique and temperature).

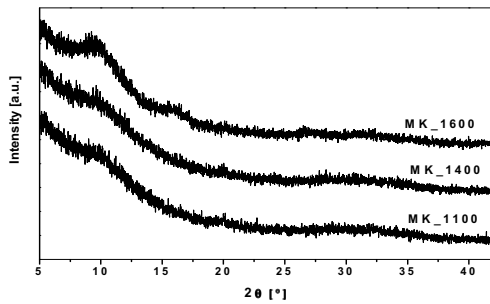


Fig. 2: XRD spectra of SiOC samples prepared at 1100, 1400 and 1600 °C.

TEM measurements provide detailed information on the morphology and microstructure of the SiOC samples. In accord with previous investigations [3, 4, 5], glassy silica nano-domains can be identified as well as amorphous/turbostratic carbon which is introduced within the microstructure of SiOC during the heat treatment of the polysiloxane precursor. The segregated carbon phase is found to partially crystallize within the Si-O-C matrix upon high-temperature treatment and can be described as nano-sized turbostratic graphite particles with  $d \ll 10$  nm. Fig. 3 presents a TEM image of the MK\_1400 sample. The sample is mesoporous and pores are filled with carbon [9]. In contrast to this, no carbon-filled pores were observed in MK\_1100. Hence, both samples differ considerably in their content of highly conductive graphitic domains and in case of the MK\_1100 sample the carbon network appears to be less pronounced. The carbon inside the pores is expected to build up a 3D-network which will render the material conductive beyond the percolation threshold.

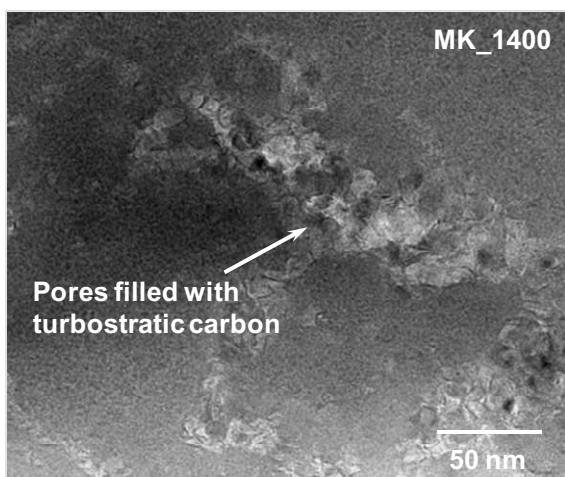


Fig. 3: TEM of SiOC pyrolyzed at 1400 °C. Pores are filled with turbostratic carbon (marked by an arrow) [9] (with permission Wiley-Blackwell).

As shown in Fig. 4 the MK\_1400 sample shows piezoresistive behaviour [7]: the resistivity

dynamically follows the applied stress. The gauge factor defined as

$$k \approx \frac{Y}{R_0} \frac{\Delta R}{\Delta \sigma}$$

has been determined to be 145. Here  $Y$  denotes the Young's modulus (85 GPa for SiOC [7]),  $R_0$  the resistivity of the stress-free sample and  $\Delta R/\Delta \sigma$  the change of the sample resistivity with the applied stress.

Unlike MK\_1400, the MK\_1100 sample does not show any piezoresistivity, suggesting that the piezoresistive effect is intimately connected with a well-established conductive carbon part (or a silica-carbon interface) within the microstructure of SiOC ceramic.

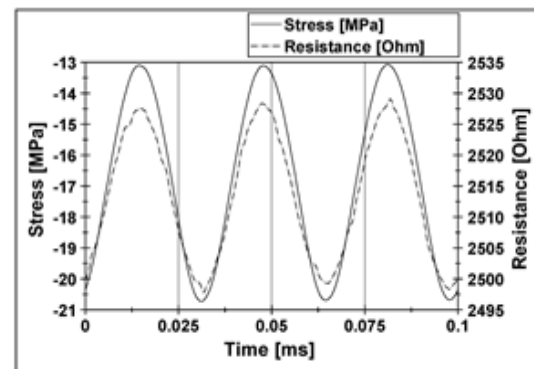


Fig. 4: Room temperature dynamic test of piezoresistivity in the SiOC ceramic MK\_1400 [7] (with permission Wiley-Blackwell).

Apart from dynamic tests, the piezoresistive effect of SiOC compounds has been investigated with the use of an uniaxial hot press modified to allow resistance measurements at a pressure of about 15 MPa. Table 1 lists the resistance  $R_0$  of stress-free samples, the change of  $R$  with applied stress ( $\Delta R$ ,  $\Delta \sigma$ ) and the calculated gauge factor  $k$  for three SiOC samples deliberately chosen to demonstrate the range of achievable  $k$ -values.

Table 1: Electrical resistivity and gauge factors of carbon containing PDCs demonstrating the accessibility of gauge factors  $10^2 < k < 10^3$  (at RT).

Sample	$R_0$ [ $\Omega$ ]	$\Delta R$ [ $\Omega$ ]	$\Delta \sigma$ [MPa]	$k$
MK_1400 [4]	3300	35	8	145
C_1600	35.7	3.64	17	660
MK_1600	548	252	15.7	3230

### Temperature dependent Raman investigations of the carbon phase in SiOC

Raman spectroscopy probes the local structure of a compound and many investigations have been carried out to describe short range ordering in different carbon materials, from structurally not well-defined carbon soots to highly ordered material. In perfectly long range ordered carbon (graphene) only the in-plane stretching mode with  $E_{2g}$  symmetry ("G" mode) and its 2<sup>nd</sup> harmonic ("2D" mode) are raman-active. Looking at the counterpart, disordered (amorphous) carbon, symmetry-forbidden modes like  $A_{1g}$  ("D" mode) become observable and dominate the spectra. In case of the commonly used laser excitation at 514 nm, the D line appears at about  $1350\text{ cm}^{-1}$ . The G mode is non-dispersive and occurs at about  $1580\text{ cm}^{-1}$ , independent of the laser wavelength. The intensity ratio of the D and G mode,  $I_D/I_G$ , can be used for quality control. The lower its value, the better crystallized the material. Fig. 5 presents the Raman spectrum of the sample MK\_1600. Deconvolution of the spectrum reveals a strong D line at  $1350\text{ cm}^{-1}$ , a structured G line (G+D',  $1585$  and  $1620\text{ cm}^{-1}$ ) and weak signals D" ( $1500\text{ cm}^{-1}$ ) and T ( $1200\text{ cm}^{-1}$ ). The latter two signals have been attributed to  $sp^3$ - $sp^2$  carbon bonds and highly disordered graphitic carbon [14]. The D' band at  $1620\text{ cm}^{-1}$  can be assigned to an E mode for a graphite "boundary" layer adjacent to an intercalant layer, not sandwiched between two other graphite planes [15]. As is evident from Fig. 5, the carbon phase in SiOC is highly disordered but cannot be considered as completely amorphous since there exists some degree of order in the basal plane (the G line is pronounced and not negligible).

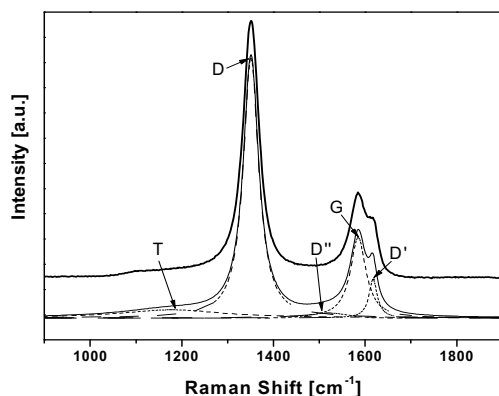


Fig.4: Raman spectrum of MK\_1600 (solid line) and its deconvolution providing evidence for ordered (G+D') and non-crystalline carbon (D,D" and T) – dashed lines [13].

Heating up the SiOC samples in air may cause a strong change in  $I_D/I_G$ . The disordered carbon

is expected to oxidize more easily than the highly ordered graphitic part and consequently, a change in  $I_D/I_G$  will indicate thermal instability. Within the investigated temperature range (i.e.,  $25 < T < 600\text{ }^\circ\text{C}$ ) no major changes of  $I_D/I_G$  occur in all of the samples. The carbon microstructure is essentially unaltered and, consequently, the piezoresistive effect observed at room temperature is expected to persist up to elevated temperature, i.e. up to the thermal stability limit of the materials (approximately  $1400\text{ }^\circ\text{C}$ ). First high temperature experiments confirm this result, as gauge factors in the range of  $10^2$ - $10^3$  (depending on the temperature and applied stress) can be determined at  $800 < T < 1400\text{ }^\circ\text{C}$  [16].

To our knowledge, high temperature piezoresistivity has been observed only in one further carbon-containing compound, i.e. SiCO(N). The published gauge factors ( $k \approx 1000$  at  $800\text{ }^\circ\text{C}$ ) [8] are in good agreement with our values. The piezoresistive effect in SiOC and SiCO(N) should be of comparable size, as seen, because the microstructure of the carbon phase is expected to be rather similar in both systems. However, further systematic work is necessary to establish a profound understanding of the piezoresistive effect in PDCs, notably its possible dependence on local defects in carbon nano-domains.

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