

Electrical Characterization of Polymethylsiloxane/MoSi₂-Derived Composite Ceramics

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High-temperature-resistant ceramics in the system Mo-Si-O-C were prepared from polymethylsiloxanes loaded with MoSi₂ filler. Irreversible structural rearrangement reactions in the polymer-derived Si-O-C matrix phase and at the filler-matrix interface during heat treatment were detected by *in situ* electrical resistance measurements and impedance spectroscopy. At low temperatures a large difference in thermal expansion between the polymer and the filler resulted in an increase of resistance from 0.05 to 560 Ω·cm when the temperature was raised from 20° to 680°C. An increase of filler particle contact distances resulted in a high positive temperature coefficient (PTC_{200°C} = 4.64 K⁻¹). At high temperatures carburization reaction of the filler on the particle surface resulted in contact formation which gave rise to a resistance lower than 10⁻³ Ω·cm above 1000°C.

I. Introduction

POLYMER-DERIVED ceramics are characterized by an amorphous or nanocrystalline microstructure which may be tailored on the molecular scale.^{1–3} Depending on the versatile chemical composition and molecular structures of the preceramic polymer precursors, a wide range of ceramic materials in the system Si-C-N-O-B with additional heteroelements such as Al, Ti, Zr, etc., have been prepared.^{3–9} Extending the polymer precursor route to systems containing inert or reactive particulate fillers, dimensional change upon polymer-to-ceramic conversion, as well as weight loss and porosity generation, may be significantly reduced, and manufacturing of complex-shaped components with improved mechanical properties is facilitated.¹⁰ Depending on the composition of the preceramic polymer and the processing conditions, the electrical properties of the pyrolyzed ceramic material may vary over a wide range of specific electrical resistance. Amorphous Si-C-N and Si-B-C-N pyrolysis products of polysilazanes and borosilazanes were found to behave as semiconductors over a wide temperature range with large polarons representing the major charge carriers in the highly disordered pyrolysis residue.^{11,12}

The electrical conductivity of polysiloxane-derived Si-O-C ceramics was found to be dominated by the precipitation of excessive carbon at temperatures above 800°C (polyphenylsiloxane) and 1400°C (polymethylsiloxane), respectively.¹³ Decomposition of hydrocarbon fragments resulting from the cleavage of the functional groups bonded to silicon (Si-C₆H₅, Si-CH₃) resulted in the precipitation of clusters of turbostratic carbon. With increasing

temperature these carbon clusters grow and may coalesce by edge-to-edge linkage of neighboring basic structural units to form an interconnected, percolating network (cluster size to infinity) of turbostratic carbon ribbons.¹⁴ Above the percolation threshold direct contact of carbon particles allows electron conduction, whereas at lower carbon fractions semiconducting behavior is attributed to thermal-fluctuation-induced tunneling of electrons among evenly distributed charge carrier clusters in the amorphous Si-O-C-H network. General effective media (GEM) theory¹⁵ was used to describe the insulator-conductor transition of the polysiloxanes near the percolation threshold as a function of the carbon content.¹³

Adding filler materials with a high electrical conductivity such as metals or intermetallics offers the possibility of creating polymer-derived ceramic composite materials of low resistance even at low heat treatment temperatures, e.g., in the tunneling regime of the Si-O-C-H matrix material. Polysiloxanes loaded with 40–50 vol% of MoSi₂ filler powder had a specific electrical resistance of less than 10⁻⁴ Ω·cm after pyrolysis at temperatures above 1000°C.¹⁶ The MoSi₂-containing Si-O-C composite ceramics exhibit excellent oxidation stability and creep resistance up to 1500°C and they offer reasonable strength (modulus of rupture ≈ 450 MPa) and toughness (critical stress intensity factor ≈ 4 MPa·m^{1/2}) at a MoSi₂ volume fraction of 40%.^{18,19} These properties make them an interesting material for novel heating devices in the electrical and automotive industries.

The electrical behavior of the polymer/MoSi₂-filler composite is dominated by the intrinsic filler conductivity and the morphology of the filler network, e.g., particle/particle contacts. It is the aim of the present work to analyze the electrical conductivity of MoSi₂-loaded polysiloxane-derived composite ceramics by means of dc-resistance measurements and impedance spectroscopy. The complex nonlinear behavior of conductivity vs temperature will be discussed with respect to microstructural changes.

II. Experimental Procedure

A polymethylsiloxane (NH 2100, Huels AG, Marl, Germany) was used as the preceramic polymer precursor and MoSi₂ (H. C. Starck, Goslar, Germany) as the filler material (Table I). The polymethylsiloxane has 4 wt% of additional silanol groups (Si-OH) which undergo condensation polymerization reaction during thermal-induced curing at temperatures above 150°C. After pyrolysis of the cured polymer in argon atmosphere at 1000–1400°C a Si-O-C residue was obtained which contained SiC (17.1 mol%), SiO₂ (54.3 mol%), and C (free carbon) (28.6 mol%).¹⁹

Polymer/filler mixtures with an initial filler fraction of 50 vol% were prepared by a wet chemical method. The MoSi₂ powder was dispersed in an acetone solution of the polymer (polymer-to-solvent ratio 1:10 by weight). During vigorous stirring in a high-speed ultrathurax mixer for 5 min, water was slowly added up to a fraction of 2/3 water to 1/3 polymer-filler-acetone. After the solvent was removed in a Rotavapor and the residue was dried at 30°C for 12 h under vacuum, the weakly agglomerated polymer/filler powder was sieved (60 mesh) and subsequently warm

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Table I. Properties of Polysiloxane and Filler

	[CH ₃ SiO _{1.5}] _n	MoSi ₂
Composition (wt%)	C: 17 Si: 42 O: 36 H: 4	Mo: 60 Si: 40
Molecular weight (g/mol)	9400, <i>n</i> ≈ 140	152.12
Specific weight (g/cm ³)	1.1–1.3	6.13
Mean particle size (μm)		2
Major impurities (wt%)	[Si–OH]: 4	O: 0.2
Specific electric resistance at RT (Ω·cm) [†]	>10 ¹³	44 × 10 ⁻⁶
Thermal expansion at RT (×10 ⁻⁶ /K)	315	6.5

[†]RT = room temperature.

pressed in a laminate press into rectangular specimens of 100 mm × 50 mm × 10 mm at 250°C with a pressure of 2 MPa. Temperature and pressure were applied for 3 h to achieve complete curing of the polymer and to suppress bubble formation due to release of H₂O from the condensation reaction. The specimens were finally cut into rectangular bars of 3 mm × 4 mm × 50 mm which were used for the impedance measurements. The specimens were pyrolyzed in an electrically heated Al₂O₃ tube furnace under flowing N₂ stream with a flow rate of 2 L/min. The maximum temperature was kept constant for 3 h.

Electrical dc resistance was measured from room temperature up to 1400°C in four-point configuration using a multifunctional resistance analyzer (2010, Keithley, Munich, Germany). Small holes with a diameter of <1 mm were drilled through the specimens to fix molybdenum wires with molybdenum paste. This fastening caused a very small contact resistance. The wires were clamped into a specially designed carbon holder¹⁶ and inserted into the furnace. The measurements were carried out under flowing argon atmosphere with a constant heating rate of 300 K/h. The temperature at the specimen site was controlled using an encapsulated Pt–PtRh thermocouple. Impedance spectra were recorded in air at 20°C in the frequency range from 20 Hz to 1 MHz using an impedance bridge (HP 4284 A, Hewlett-Packard, Munich, Germany). The measurements were taken with triple oversampling.

III. Results and Discussion

Figure 1 shows a typical microstructure of a specimen pyrolyzed at 900°C. The irregularly shaped MoSi₂ particles are uniformly distributed in the Si–O–C matrix. Frequently, direct

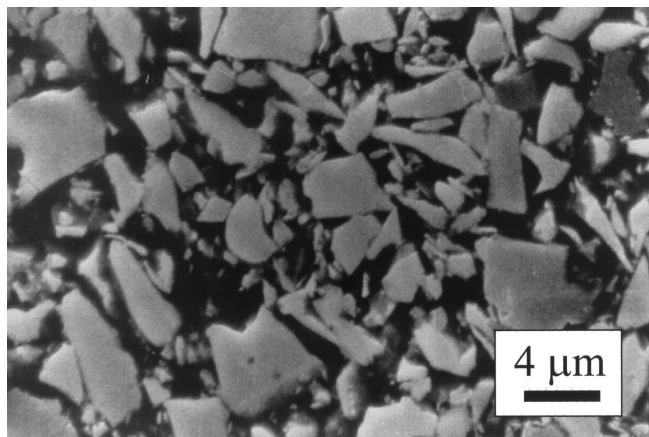


Fig. 1. SEM micrograph of a MoSi₂ (50 vol%) filled polymethylsiloxane after pyrolysis in argon at 900°C for 3 h.

contacts between neighboring filler particles can be observed although the majority of the filler particle surface is covered by the polymer-derived amorphous Si–O–C–H residue.

Figure 2 shows the resistance vs temperature curve during initial pyrolysis heating. As expected, the direct MoSi₂ filler particle contacts give rise to a low resistance of <10⁻¹ Ω·cm at room temperature. The resistance of composite materials containing randomly dispersed conducting filler particles in an insulating polymer matrix has been discussed by taking into account particle percolation theory, quantum-mechanical tunneling, and thermal expansion.²⁰ Microscopic conduction in the composite was attributed to quantum-mechanical tunneling and ohmic conduction through the polymer layer separating the conducting filler particles. With increasing temperature, however, the significantly larger thermal expansion coefficient of the polysiloxane phase ($\alpha_{\text{PMS}} \approx 315 \times 10^{-6}/\text{K}$ near room temperature) compared to that of MoSi₂ ($\alpha_{\text{MoSi}_2} \approx 7.5 \times 10^{-6}/\text{K}$) results in a PTC effect with a resistance increment of approximately 2 orders of magnitude from 200° to 400°C without cracking. On heating, the insulating polymer matrix expands more than the MoSi₂ filler, pulling the filler particles apart and raising the resistance as observed in conducting filler loaded polymers^{20,21} and in graphite-loaded cristobalite composites.²² While the literature data refer to filler contents near the percolation threshold, e.g., between 5 to 20 vol% depending on the filler morphology, the present results were obtained with significantly larger filler fractions. The discrepancy may be associated with the specific wet chemical processing technology applied to the polymer/filler mixture, where each filler particle was coated with a polymer layer. Thus direct contacts between MoSi₂ filler particles are unlikely to occur even at higher filler loadings.

Above 400°C the polymethylsiloxane begins to decompose according to



resulting in a total linear shrinkage of up to 15.9% at 800°C.¹⁶ Assuming the shrinkage to be isotropic, this value corresponds to a volume change $\Delta V/V_0$ of 38.6%, which is supposed to cause reduction of filler interparticle distances resulting in a distinct drop of the resistance by 3–4 orders of magnitude from 600° to 800°C.

Precipitation of carbon and the formation of grain boundaries between the filler particles are likely to occur at elevated temperatures above 700°C. Raman and IR analysis data of MoSi₂-filled polysiloxane mixtures have shown, however, that formation of graphitic carbon with pronounced C–sp²-hybrid orbital bonding could not be observed below 1200°C,¹⁶ suggesting that the carbon precipitation exerts a minor influence on the resistance behavior.

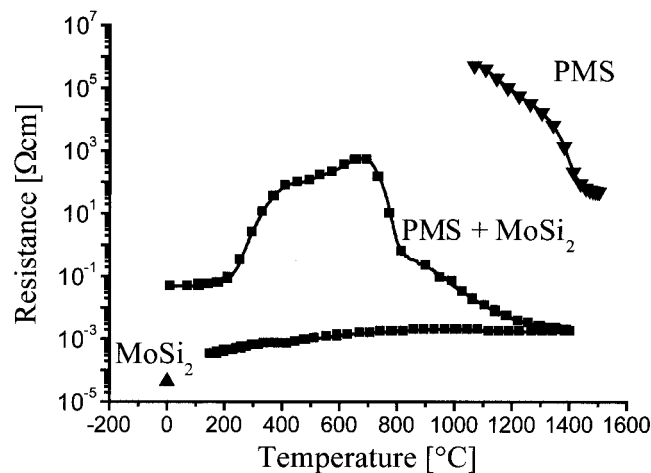
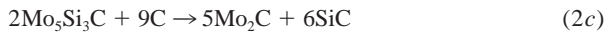


Fig. 2. Electrical dc resistance during heating with a constant rate of 5 K/min in inert atmosphere.

Hence, reaction of the MoSi_2 filler with carbon is supposed to generate conducting bridges between the MoSi_2 particles and the resistance ($<0.1 \Omega\cdot\text{cm}$) follows the behavior of MoSi_2 after reaching a pyrolysis temperature of 1300°C .

MoSi_2 exhibits a high electrical conductivity and provides excellent stability against oxidation at temperatures above 1000°C .^{23,24} Previous work has shown that MoSi_2 needs reaction temperatures of approximately 800°C to undergo carburization reaction with carbon precipitated from the polymer-derived Si-O-C-H residue.¹⁶ As a result of the solid-state reaction between MoSi_2 and carbon, dispersed nanosize SiC , Mo_5Si_3 , $\text{Mo}_5\text{Si}_3\text{C}$, and Mo_2C are formed at the interface:



Thus, for complete carburization of 1 mol of MoSi_2 according to



2.5 mol of C would be necessary. The content of free carbon in the polymer pyrolysis residue is 28.6 mol%, which would be sufficient to convert only approximately 12 vol% of the MoSi_2 into Mo_2C and SiC. Thus, the major part of MoSi_2 is likely to remain unreacted (as confirmed by XRD) and the carburization reaction products are located on the particle surface.

Large differences between the electrical resistance of the filler reaction products ($\approx 10^{-3} \Omega\cdot\text{cm}$) and the polymer-derived Si-O-C-H ceramic ($\approx 10^4 \Omega\cdot\text{cm}$ after heating to 1500°C)¹⁶ suggest that the pronounced decrease of electrical resistance is caused by the formation of a continuous percolation network of MoSi_2 and the filler reaction products. The critical temperature when percolation was reached was 1000°C and further heating resulted in growth of the percolating filler network. At temperatures above 1300°C the resistance followed the behavior of MoSi_2 .

Figure 3 shows a Cole–Cole plot of a specimen pyrolyzed at 900°C . The spectrum can be approximated by two distinct Debye relaxations which are represented by a capacitive and an inductive circuit (Fig. 4). Approximating the microstructure of the MoSi_2 filler containing polymer-derived Si-O-C material by the idealized brick layer model,²⁵ the impedance of a corresponding unit cell, Z_{UC} , can be described by

$$Z_{\text{UC}} = V_{\text{F}}Z_{\text{F}} + \left(\frac{V_{\text{GB}}}{3}\right)Z_{\text{GB}} \quad (4)$$

V_{F} and Z_{F} are the volume fraction and impedance of the conductive filler particle and V_{GB} and Z_{GB} are the corresponding values for the polymer-derived Si-O-C grain boundary phase. For the case where the resistance of the grain boundary phase (Si-O-C) is

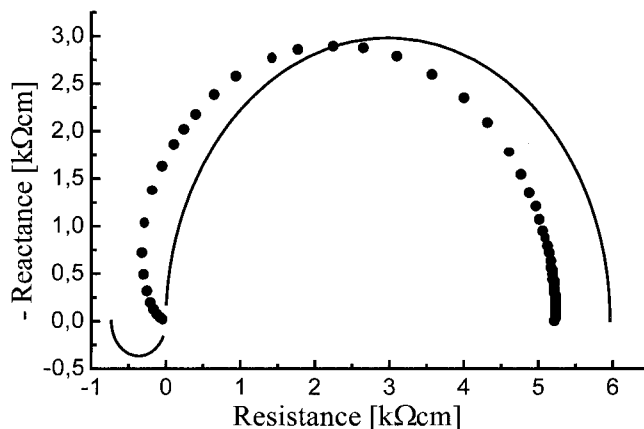


Fig. 3. Cole–Cole plot after pyrolysis at 900°C (dots) and fit functions.

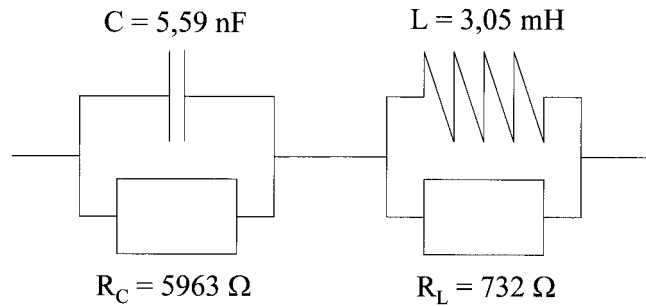


Fig. 4. Equivalent circuit after pyrolysis at 900°C .

substantially higher than that of the filler MoSi_2 , the contribution of the grain in Eq. (4) diminishes and the impedance of a macroscopic body containing n grain boundaries in series can be approximated as a sum of individual RC circuits:

$$Z = \sum_n Z_n = \frac{nR_{\text{GB}}}{1 + i\omega R_{\text{GB}}C_{\text{GB}}} \quad (5)$$

R_{GB} and C_{GB} are the grain boundary resistance and the capacitance of a single grain boundary and ω is the frequency. Expressing the grain boundary resistance and the capacitance by the specific resistance, ρ_{GB} , and the dielectric constant, ϵ_{GB} , of the grain boundary phase

$$R_{\text{GB}} = \left(\frac{\delta}{A}\right)\rho_{\text{GB}} \quad (6)$$

$$C_{\text{GB}} = \frac{\delta_{\text{GB}}A}{\delta} \quad (7)$$

the conductivity behavior of the filler-loaded polymer-derived ceramic may be related to the effective area A and the thickness δ of the grain boundary phase (Si-O-C). Different relaxation times associated with grain boundary relaxation processes will be observed when either A , δ , ϵ_{GB} , or ρ_{GB} changes because of irreversible interface reactions between the MoSi_2 filler particle and the Si-O-C grain boundary phase with increasing temperature.

Based on the system polysiloxane + MoSi_2 filler a variety of low-resistance heating devices are currently being developed in industry for advanced microheating devices. For example, polymethylsiloxane loaded with 50 vol% of MoSi_2 filler with a mean particle size of $2 \mu\text{m}$ and a specific resistance of $4.5 \times 10^{-4} \Omega\cdot\text{cm}$ at room temperature was processed into heating elements which achieved a specific resistance of $10^2 \Omega\cdot\text{cm}$ after heat treatment at 600°C and $10^{-4} \Omega\cdot\text{cm}$ at 1400°C , respectively.¹⁶ Figure 5 shows the specific resistance of a selection of filler-loaded polysiloxanes pyrolyzed above 1200°C . Resistance may be systematically tailored from insulating materials containing inert fillers such as Si_3N_4 ($\rho \approx 10^{14} \Omega\cdot\text{cm}$), Al_2O_3 ($\rho \approx 10^{15} \Omega\cdot\text{cm}$), to conducting materials loaded with CrSi_2 ($\rho \approx 8 \times 10^{-4} \Omega\cdot\text{cm}$), MoSi_2 ($\rho \approx 4.5 \times 10^{-5} \Omega\cdot\text{cm}$).

IV. Conclusions

During heating of a polymethylsiloxane/ MoSi_2 -filler mixture in inert atmosphere a series of irreversible structural rearrangement and interface reactions occur which give rise to a complex, nonlinear behavior of the electrical resistance with temperature. At low temperatures a large difference in thermal expansion between the polymer and the filler results in a PTC-like increase of the resistance due to an increase of filler particle distances. Above 600°C shrinkage of the polymer-derived ceramic residue reduces the distance between the particles, and consequently, the resistance drops. At temperatures above 1000°C shrinkage of the polymer-derived Si-O-C matrix and growth of a continuous filler reaction

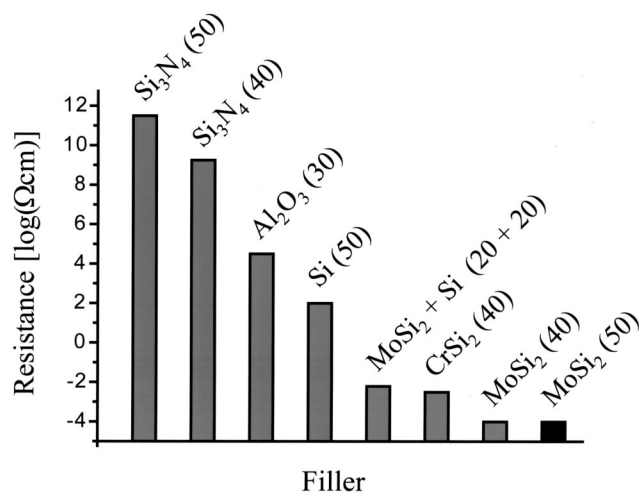


Fig. 5. Specific resistance of polymethylsiloxane–filler derived ceramics pyrolyzed above 1200°C. Numbers in brackets indicate the volume fraction of the filler.

phase network induce the formation of increasing particle contacts, resulting in a percolation transition. Tailoring of grain boundary resistances by changing the filler particle size, the amount of polymer, and the carbon content in the polymer is therefore a key for the development of novel polymer-derived composite materials with high electrical conductivity. Because of the excellent shaping behavior of the low-viscosity polymer phase, such electrical composites may become particularly interesting for advanced heating devices of complex geometrical shape.

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