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Amorphous Si(Al)OC ceramic from polysiloxanes: bulk ceramic processing, crystallization behavior and applications

Rahul Harshe[a], Corneliu Balan[b], Ralf Riedel[a,*]

[a]Institute of Materials Science, Darmstadt University of Technology, Petersenstraße 23, 64287 Darmstadt, Germany
[b]Politehnica University, Hydraulics Department - REOROM Laboratory, Splaiul Independentei 313, 79590, Bucharest, Romania

Abstract

Here we report on bulk Si–Al–O–C ceramics produced by pyrolysis of commercial poly(methylsilsesquioxane) precursors. Prior to the pyrolysis the precursors were cross-linked with a catalyst, or modified by the sol-gel-technique with an Al-containing alkoxide compound, namely alumatrane. This particular procedure yields amorphous ceramics with various compositions ($Si_{1.00}O_{1.60}C_{0.80}$, $Si_{1.00}Al_{0.04}O_{1.70}C_{0.48}$, $Si_{1.00}Al_{0.07}O_{1.80}C_{0.49}$, and $Si_{1.00}Al_{0.11}O_{1.90}C_{0.49}$) after thermal decomposition at 1100 °C in Ar depending on the amount of Al-alkoxide used in the polymer reaction synthesis. The as-produced ceramics are amorphous and remain so up to 1300 °C. Phase separation accompanied by densification (1300–1500 °C) and formation of mullite at $T > 1600$ °C are the stages during heat-treatment. Bulk SiAlOC ceramics are characterized in terms of microstructure and crystallization in the temperature regime ranging from 1100 to 1700 °C. Aluminum-free SiOC forms SiC along with cracking of the bulk compacts. In contrast, the presence of Al in the SiOC matrix forms SiC and mullite and prevents micro cracking at elevated temperatures due to transient viscous sintering. The nano-crystals formed are embedded in an amorphous Si(Al)OC matrix in both cases. Potential application of polysiloxane derived SiOC ceramic in the field of ceramic micro electro mechanical systems (MEMS) is reported.

Keywords: MEMS; Mullite-SiC; Precursors-organic; Si(Al)OC; Siloxanes; Thermal stability

1. Introduction

Enhancement of the thermal and mechanical properties by partial substitution of oxygen in silica glass with carbon or nitrogen has been studied in the past. Initial attempts of oxycarbide glass formation involved conventional glass melting technique.[1] Achievable carbon content was limited by decomposition reactions at melting temperatures between 1600 and 1800 °C. The carbon content of these glasses was below 1 wt.%.

Recently, silicon oxycarbide glasses were fabricated from different sol-gel derived precursors[2–4] or silicone resins.[5–10] The sol-gel precursor is obtained by hydrolysis and condensation reactions of a mixture of triethoxysilane and methyldiethoxysilane. Subsequent pyrolysis in argon yields pure silicon oxycarbide glass. The final Si–C–O composition of the glass is strongly related to the ratio of the above-mentioned silanes. The homogeneous network of the general composition is $SiC_xO_{2(1-x)}$, can be considered as silicon oxycarbide glass. This material consists of Si–O and Si–C bonds, with no Si-Si and C–O bonding. The main advantage is low processing temperature of around 1000 °C and retention of the Si–C bonds in the pyrolyzed stage. The formation of crack free bulk bodies is the main difficulty observed with the sol-gel and siloxane-derived ceramics. However, this fabrication route offers the formation of Si–C bonds in silica based glasses due to the low temperature and non-equilibrium reaction synthesis.

Polyorganosiloxanes are inorganic/organic hybrid compounds comprised of Si–O–Si units as the polymeric backbone. The general formula is $[R_2SiO]_n$ for linear or cyclic polysiloxanes and $[RSiO_{1.5}]_n$ for crosslinked polysilsesquioxanes. The ceramic composition and yield depends to a great extend on the functional group present in the polymer.[5] For example, polysiloxanes containing phenyl groups show lower ceramic yields and higher free carbon contents relative to polysiloxanes where R is methyl, exclusively. Preparation of siliconoxycarbide glass from poly(methylsilsesquioxane) was reported in detail.[6]

Much concentration was given in the last decade on the modification of the SiOC by aluminum and boron.[11–13] Modification was achieved by the reaction

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[*] Corresponding author. Tel.: +49-6151-166347; fax: +49-6151-166346.
E-mail address: riedel@materials.tu-darmstadt.de (R. Riedel).

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of triethoxysilane and methlydiethoxysilane with aluminum or boron containing alkoxides forming a sol-gel process in the presence of a solvent. This method allows incorporation of these elements at the molecular level. After thermolysis the obtained ceramic systems were characterized in terms of composition, structure and crystallization behavior at temperatures beyond the synthesis temperature.

The present work is focused on two processing schemes: (a) cross-linking of a commercially available polysilsesquioxane using a molecular catalyst and (b) aluminum modification of the polymer to form Si(Al)OC ceramics. The preceramic polymers as well as the ceramic produced therefrom were characterized for their thermal stability with respect to decomposition, phase separation and crystallization. Furthermore, the polysiloxanes were processed to dense and crack free bulk ceramics.

2. Experimental procedure

2.1. Mixing of the polymer with catalyst

Commercially available poly(methylsilsesquioxane) (Wacker-Belsil^{TM} PMS, MK), a solid solvent free silicone resin with $(CH_3–SiO_{3/2})_x$ basic structure was used. The polymer is insensitive to air or moisture. Zr-acetylacetonate (referred as cat later) was used for cross-linking. The polymer was dissolved in isopropanol along with the catalyst and the solution was dried under vacuum at moderate temperature (40–50 °C). This method results in homogeneous distribution of the catalyst in the polymer as compared to the mechanical mixing.

2.2. Modification of siloxane by aluminum

Alumatrane (commercial al-alkoxide from ABCR, general formula: $C_6H_{12}NO_3Al$) was used as an aluminum modifier. Alumatrane was dissolved in isopropanol in different mass ratios, namely 9.1, 16.6, and 23.6 wt.% (referred as samples SiAlOC1, SiAlOC2, and SiAlOC3), followed by dissolution of the polymer in isopropanol. A polymer: isopropanol ratio of 4 g:25 ml was kept constant for all the mixtures. A sol-gel transition takes place at room temperature forming a milky white residue. Increasing the alumatrane content changes the color of the polymeric gel from white to faint yellow. The gel time is dependent on the amount of alkoxide present. Gel time of 2, 5, and 11 h is observed for the 9.1, 16.6 and 23.6 wt.% alumatrane mixture, respectively. Very low amount of alumatrane, namely 2.5 wt.% do not transform to a gel state and instead requires temperature of 50 °C for 5 h. All gels were dried at 85 °C in air for 24 h, ball milled and finally sieved to particle size <63 μm.

2.3. Polymer-ceramic bulk body processing

Green bodies formed from catalytically treated polymer were prepared in a cylindrical mold (10 mm diameter) by warm pressing at 50 MPa and 150 °C. The green bodies were transparent and mechanically stable. The samples were sliced by diamond wire saw for maximum thickness of 0.6 mm. Sliced green bodies were pyrolyzed in a quartz tube under flowing argon at 25 °C/h up to 1100 °C forming silicon oxycarbide with the composition $Si_{1.0}O_{1.6}C_{0.8}$ (Fig. 1).

Green bodies of aluminum-modified polymer were obtained by cold pressing of the powder at 80 MPa followed by warm pressing at 90–100 °C and 50 MPa. Polymer to ceramic transformation was performed by pyrolysis in flowing argon atmosphere at 1100 °C in a quartz tube using a heating rate of 30 °C/h up to the final temperature held for 2 h followed by cooling down with 10 °C/min up to room temperature. Crack-free

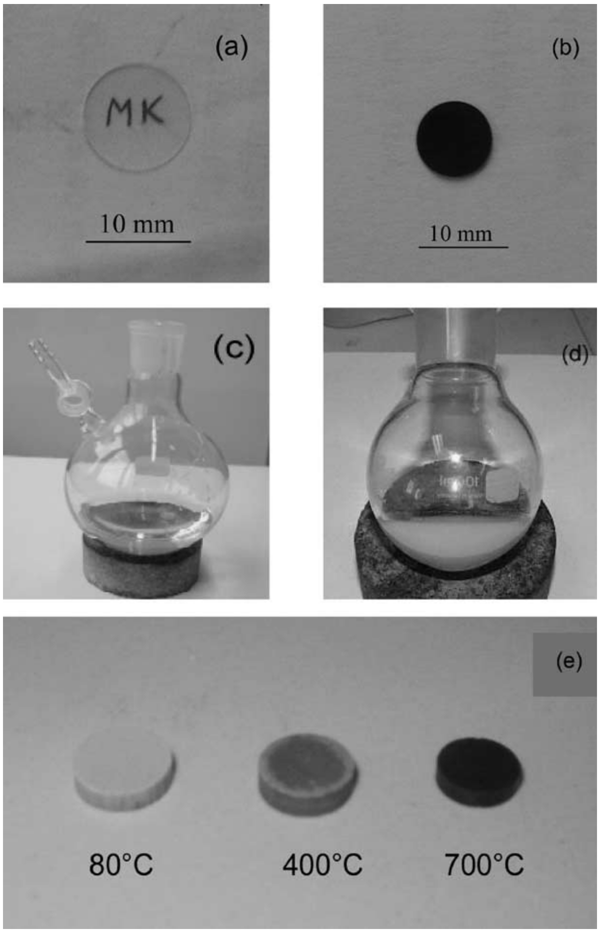

Fig. 1. View of the specimens at various processing steps: (a) SiOC thin green body, (b) SiOC ceramic after pyrolysis at 1100 °C, (c) SiAlOC sol, (d) SiAlOC gel, and (e) SiAlOC green and ceramic bodies obtained at different temperatures.

Table 1
Elemental analysis of the pyrolyzed products

Material	Composition				Empirical formula
	Si	Al	O	C	
SiOC	45.50	–	39.30	14.80	$Si_{1.00}O_{1.60}C_{0.80}$
SiAlOC1	46.05	1.56	42.65	9.02	$Si_{1.00}Al_{0.04}O_{1.70}C_{0.48}$
SiAlOC2	44.35	2.96	42.69	9.01	$Si_{1.00}Al_{0.07}O_{1.80}C_{0.49}$
SiAlOC3	42.05	4.36	44.51	8.59	$Si_{1.00}Al_{0.11}O_{1.90}C_{0.49}$

SiAlOC ceramics (Fig. 1) with different compositions as given in Table 1 were formed.

2.4. Post pyrolysis annealing of Si(Al)OC ceramics (bulk and powder)

Thermal treatments were performed on bulks in closed *h*-BN crucible to analyze the crystallization behavior. These samples were heated between 1300 and 1600 °C in an ASTRO Oven at 10 °C/min in argon atmosphere, and held at the maximum temperature for 5 h. The dimension and mass changes by heat-treatment were measured. Similar heat treatment was performed with powdered samples.

2.5. Rheological investigation

Processing of the ceramic precursors for particular applications requires the rheological characterization of the sample during the phase fluid–solid transition. The control and prediction of rheological properties at different stages of ceramics processing is of great importance in establishing the final quality of products. Each technological process has to be designed for an optimum interval of the magnitude and temperature–time evolution of rheological properties, respectively viscosity and elasticity. In the present work the evolution of viscosity and elasticity of the MK polymer, as function of the catalyst concentration and temperature gradients were investigated. The evolution of viscous and elastic dynamic moduli (G'' and G', respectively) of the samples are measured at constant frequency and constant torque (shear stress amplitude) in a plate and plate configuration, at a constant temperature gradient, see Fig. 2. The established test conditions are the following: frequency—$\omega = 1$ rad/s; shear stress amplitude—$\tau_a = 10$ Pa; temperature gradient—5 °C/min; plates diameter—25 mm, gap between plates—$\delta = 0.6$ mm (Rheometrics RDS 200 controlled stress rheometer). Qualitatively similar results have been obtained for different temperature gradients in the range (1–10 °C/min).

2.6. Thermal analysis

The pyrolytic transformation from the polymer to the glass was studied by differential thermal analysis/thermal gravimetry (DTA/TG) analysis performed with a Netzsch STA 429 equipment operating in argon flow

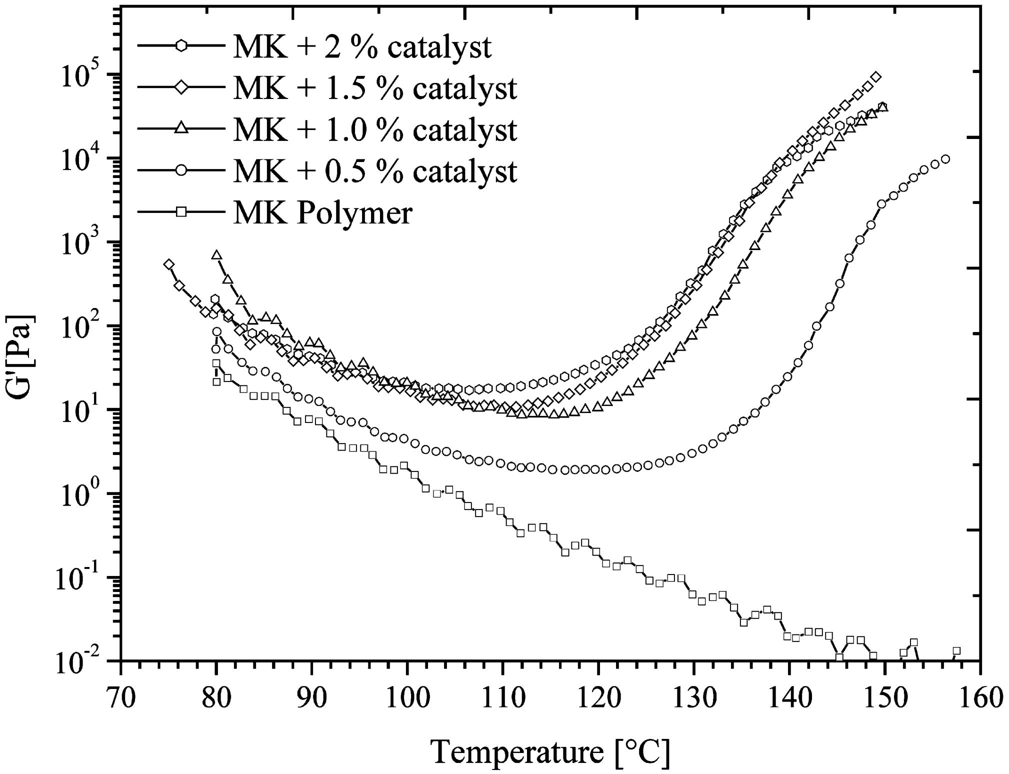

Fig. 2. Evolution of elastic modulus with temperature, as function of catalyst concentration within the MK based polymer.

(5 l/h) using a heating rate of 10 °C/min up to the maximum temperature of 1100 °C. Analysis of the pyrolysis gases was obtained in situ using a quadrapole mass spectrometer (QMA 400, Balzers). Thermal mechanical analysis (TMA) was recorded on a Netzsch Dilatometer 420 under argon atmosphere with a heating rate of 5 °C/min. Thermal dilatometry of the pyrolyzed ceramic bulks was recorded with a horizontal dilatometric system (Model Netzsch 420 S). Alumina plate was used as reference. An argon atmosphere and heating rate of 5 °C/min was used. X-ray diffraction was measured with a Siemens D500 diffractometer with reflection geometry using CuKα radiation and a silicon monochromator.

3. Results and discussion

3.1. Polymer-to-ceramic-transformation of polysiloxane (MK polymer)

Network formation, which gives stability to the green compact, is one of the important steps in polymer pyrolysis processing and was studied by rheology, IR spectroscopy and TG–MS.

From rheological point of view the strength of network is characterized by the magnitude of dynamic elastic moduli. The rheology results prove incapability of the unmodified cat-free MK to visco-elastic behavior necessary for cross-linking, i.e. G' continuously decreases with temperature (see Fig. 2). In contrast, Zr-acetylacetonate (cat) containing polymer shows initial decrease of G' with temperature indicating melting or liquid like behavior. Further heating results in a sharp increase of G' due to network formation by polymer cross-linking (Fig. 2). Enhanced catalyst concentration increases the level of elasticity (i.e. the value of G') and the starting temperature of network formation decreases. Consequently, the minimum of G' is reached at 105 °C with 2 wt.% cat while 120 °C is required for the network formation in the presence of 0.5 wt.% cat. Following the analysis of the rheological tests, the level of catalyst and the most suitable temperature gradient of the process can be precisely adjusted for a particular application.

The infrared spectra of the MK polymer cross-linked with cat at different temperatures are shown in (Fig. 3). The spectra present the typical vibration bands at 1120 (Si–O–Si), 1030 (Si–OR), 770 (assym. ν Si–CH_3), 840-850 (O–Si–CH_3), 1280 (sym. Si–CH_3), 1410 (δ CH_3), 2980 (SiOC–H) and 625–480 (SiOC–H). It is evident that after annealing the sample above 400 °C the C–H vibration band decreases in intensity with increasing temperature. After completed ceramization at 1000 °C no C–H absorption band can be detected.

The polymer to ceramic transformation was investigated by thermal gravimetry and mass spectroscopy. Accordingly, cat-free MK polymer shows three regions of mass losses (Fig. 4, bottom): 200–450 °C (≅ 12%), 450–600 °C (≅ 3%), and 600–800 °C (≅ 8%). The first weight loss step is due to polycondensation resulting in

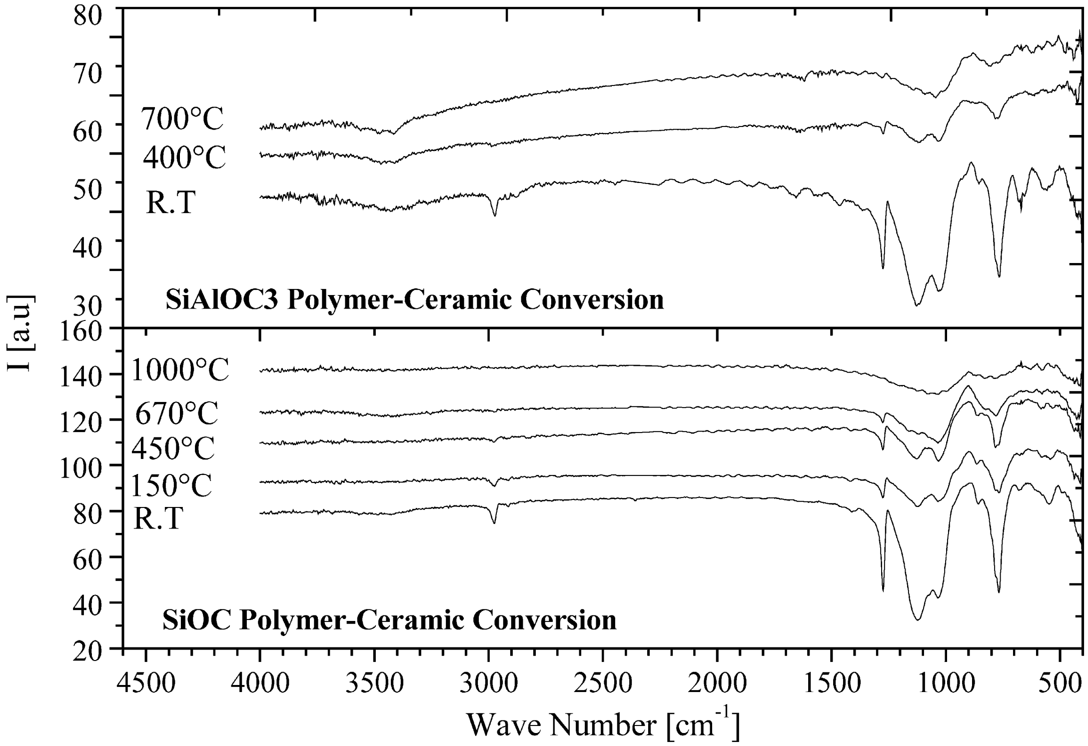

Fig. 3. FTIR of catalyzed and aluminum modified MK polymer heated to different temperatures.

the release of water, ethanol and methanol identified by the masses related to H_2O ($m/z=18$), ethoxy ($-C_2H_5O$, $m/z=45$) and methoxy ($-CH_3O$, $m/z=31$) groups. The further two mass changes correspond to the loss of hydrogen and methane, exclusively.

As can be taken from Fig. 4 (top), addition of 1 wt.% catalyst reduces the weight loss of MK polymer particularly between 100 and 400 °C indicating enhanced cross-linking in this temperature regime. Cross-linking is related to polycondensation shifted to lower temperature compared to the cat-free MK polymer. Again, water, methanol, and ethanol are found to be the outgassing species up to 400 °C.[14] At higher temperatures the decomposition behavior resembles that of cat-free MK polymer.

Cross-linking occurs during warm pressing and results in transparent and dense green bodies. Transparency is lost at 450 °C turning to brown at 600 °C. Crack free bulk SiOC ceramic formation is possible only for thin samples with a section thickness below 0.7 mm and heated with slow heating rate while thicker samples crack due to hindered degassing of the gaseous products evolved. Mass loss and shrinkage of the dense warm pressed samples are listed in Table 2.

3.2. Polymer-to ceramic transformation of aluminum modified polysiloxane

Cross-linking reaction of MK polymer with aluminum alkoxide compounds like alumatrane used in this work proceeds via a sol-gel process at room temperature. The sol-gel transition is found here with isopropanol as the solvent. Sols prepared in acetone, methanol, ethanol, diethyl ether or *n*-hexane do not transform to gel at room temperature. Alumatrane reacts to a gel like state with MK polymer in the

Table 2
Physical changes in bulk Si(Al)OC ceramics during polymer-ceramic transformation

Material	Mass loss[a] (wt.%)	Axial shrinkage[a] (%)	Radial shrinkage[a] (%)	Green density g/cm^3	Pyrolyzed density g/cm^3
SiOC	11.48	16.75	19.54	1.26	2.16
SiAlOC1	20.98	7.63	22.33	1.27	2.17
SiAlOC2	26.02	12.85	24.78	1.26	2.22
SiAlOC3	29.14	15.90	26.49	1.28	2.26

[a] All samples are heated at 30 °C/h. Shrinkages and mass losses are averaged from the measurements on 10 samples each.

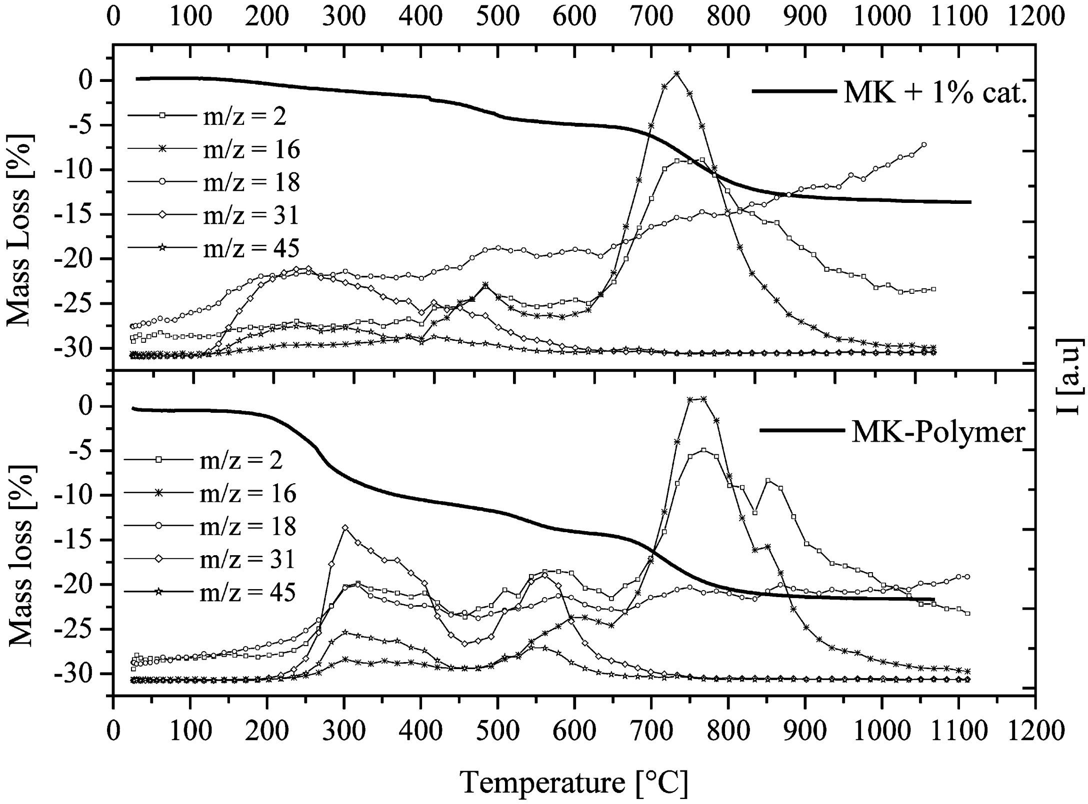

Fig. 4. TG/MS of non-catalyzed and catalyzed MK polymer heated with 10 °C/min in helium atmosphere.

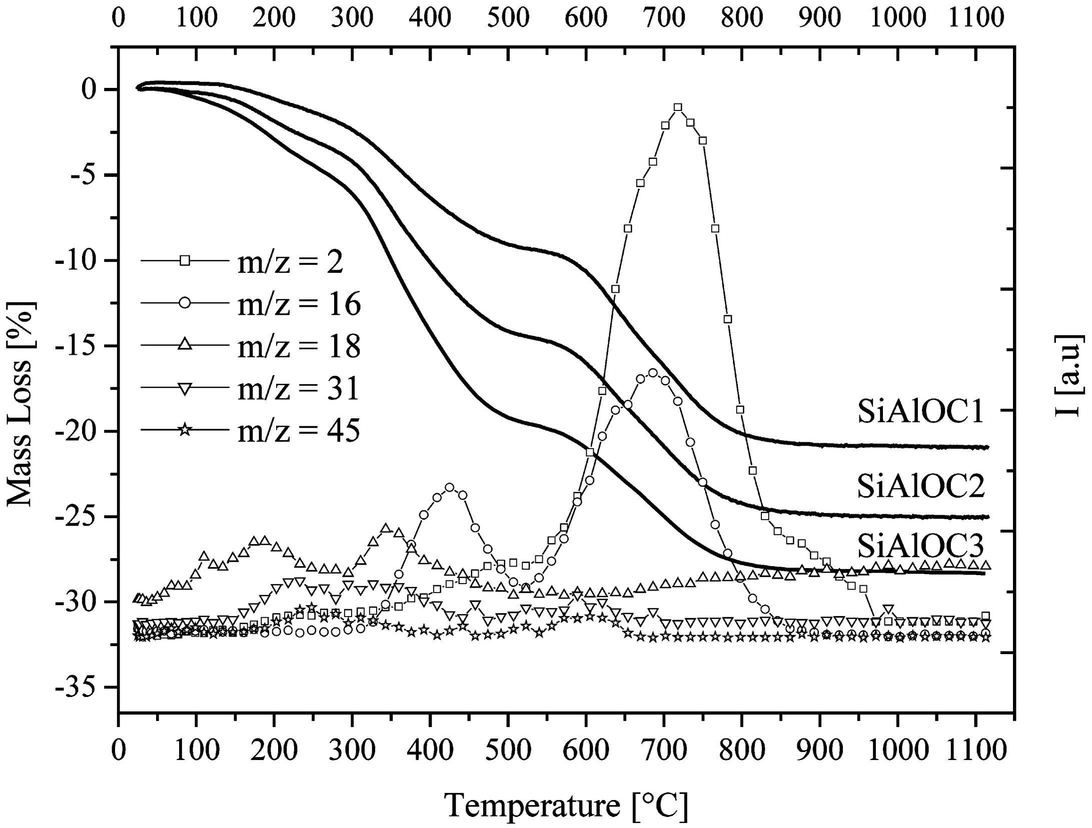

Fig. 5. TG/MS of aluminum modified (SiAlOC) MK polymer heated with 10 °C/min in helium atmosphere.

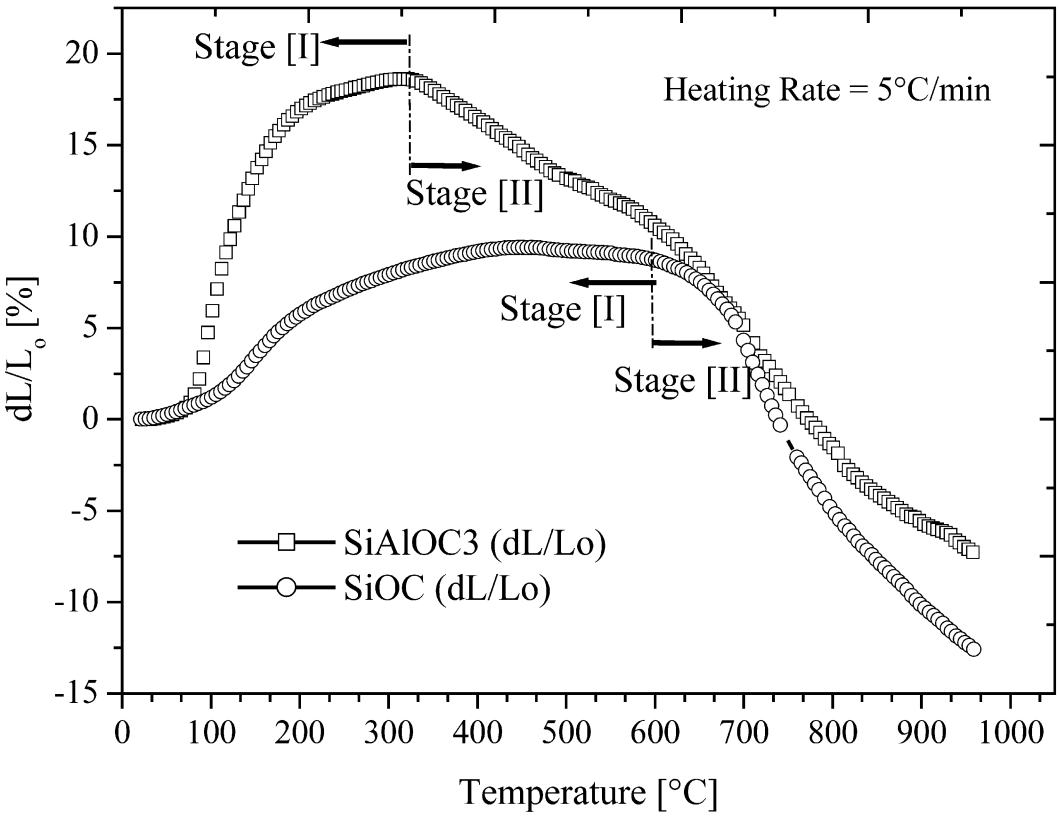

Fig. 6. Thermal mechanical analysis (TMA) of non-modified SiOC and Al-modified SiAlOC ceramics measured with a heating rate of 5 °C/min in argon atmosphere.

presence of non-dried isopropanol by alcoholysis or hydrolysis and subsequent polycondensation. Tetrahedrally and octahedrally coordinated aluminum has been found by ^{27}Al MAS NMR spectroscopy of the as prepared gels, Al(6) being the preferred coordination.[11,13] The thermal gravimetric analyses between room temperature and 1100 °C under argon flow show a total weight loss of 21–29% (Table 2 and Fig. 5). As analyzed by in situ mass spectrometry, between 100 and 400 °C water, methanol and ethanol is evaporated indicating further polycondensation reaction. The masses are identified by $m/z=18$ for H_2O, $m/z=31$ for methoxy (CH_3O) and by $m/z=45$ for ethoxy (C_2H_5O). At higher temperatures, between 550 and 850 °C, methane and hydrogen are released exclusively.

This result coincides nicely with that of the IR spectroscopic investigation. As can be taken from Fig. 3 (top), after annealing of the polymer between 400 and 700 °C the relative intensities of the C–H absorption bands at 2960–2890 cm^{-1} and that at 1260 cm^{-1} are remarkably decreased. The mineralization process involves the cleavage of Si–C and C–H bonds and leads to the evolution of methane and hydrogen.[8]

3.3. Bulk sample formation

Crack free bulk sample formation depends on the viscoelastic behavior of the cross-linked polymer during warm pressing. In the case of MK polymer with cat dense green bodies are formed due to viscoelasticity whereas the aluminum modified polymer had a porous network after warm pressing (confirmed by microstructure analysis). Along with the out-gassing of the organic matter, shrinkage is observed during polymer-to-ceramic transformation. Accordingly, evolution of gases and shrinkage are responsible for the cracking of the compacts during pyrolysis.[3] Therefore, the formation of transient porosity is required to obtain crack free samples. This behavior is exactly observed in the Si(Al)OC system. Additionally, isotropic shrinkage is found during pyrolysis for SiOC ceramic. In contrast SiAlOC ceramic shrinks non-isotropically with higher shrinkage in radial direction than in the axial one as shown in Table 2. During uniaxial warm pressing of SiAlOC material the green body density in axial direction is higher than in radial direction. Such variation is not observed for SiOC green bodies because the polymer melts during warm pressing and maintains pressure homogeneity. Modification of the polysiloxane with alumatrane promotes cross-linking and prevents melting during warm pressing. As a consequence, non-isotropic compaction of the polymer powder occurs during green body formation resulting in an anisotropic shrinkage during polymer to ceramic transformation.

Thermal mechanical analysis (TMA) reveals considerable differences in the dimensional changes for both SiOC and SiAlOC systems. Fig. 6 presents the representative length changes versus temperature (dL/L_0 vs T) using a heating rate of 5 °C/min. For the SiOC system the dimensional changes take place in two different stages. In the first stage I the material expands with temperature up to 600 °C as can be seen from the curve in Fig. 6. At $T > 600$ °C, the shrinkage of the sample coincides with the decomposition process as shown in Fig. 4 (top). The sharp decay in the length change vs. temperature found between 600 and 1000 °C in stage II is discussed to be responsible for the cracking of bulk samples. However, thin (<0.6 mm) SiOC ceramics can be obtained completely dense and do not show any residual porosity as can be seen from the microstructural view in Fig. 7a.

For the aluminum-modified material the thermal expansion in the initial stage I is significantly higher compared to that of the SiOC ceramic (Fig. 6). The material starts to shrink at $T > 300$ °C. Despite of this large dimensional change throughout the polymer-to-ceramic transformation process along with the degassing period the Al containing samples do not crack. This behavior is explained by the enhanced expansion of the material resulting in a transient porous network formed in stage I as confirmed by SEM analysis. Transient porosity allows degassing without producing cracks in stage II. This behavior is supported by microstructural investigation of the surface which reveals crack-free SiAlCO matrix after pyrolysis at 1100 °C (Fig. 7b). A low open porosity of 3–4 vol% was measured by mercury pressure porosimetry for the three pyrolyzed SiAlCO ceramics.

3.4. Crystallization and thermal behavior of Si(Al)OC bulk ceramics

The crystallization behavior and the phase separation of SiOC ceramics are reported in the literature.[4,15,16] Few reports are available on aluminum containing SiOC ceramics.[11,13] Researchers noticed that the distribution of silicon, oxygen, and carbon atoms might not be as random as commonly expected for such materials. Based on Rietveld refinement studies, those researchers proposed the presence of local Si–C and Si–O environments in SiOC glass. From microstructural point of view, such SiOC glasses can be described as a mixture of amorphous SiO_2 and crystalline SiC at temperatures exceeding 1000 °C thus implying that phase separation has occurred.

Kleebe et. al. reported that cristobalite, which usually forms at temperature $\geqslant 1200$ °C, was not seen at high temperature in SiOC systems.[15] This behavior is related to the presence of carbon (either as free C or residual carbon bonded in form of SiC) in the amorphous SiO_2 network. Excess free C is assumed to prevent nucleation of cristobalite, because short-range diffusion is strongly impeded by the incorporation of carbon into the SiO_2 network. A similar phenomenon is explained by Soraru et al. for Al_2O_3+SiOC system.[17] When annealing is conducted in air, the formation of mullite plus cristobalite was observed, whereas annealing in argon revealed the formation of SiC and mullite, no cristobalite was found. Heat-treatment in air burns out the residual carbon in the glass structure, which in turn, promotes nucleation and growth of cristobalite. The above-mentioned ceramics were produced from a mixture of alumina and methyltriethoxysilane. Similar materials could be synthesized using the sol-gel process from methyltriethoxysilane and Al-tri-sec-butoxide.[13] Cristobalite along with SiC and mullite were reported to be formed by heat-treatment in argon.

SiOC and SiAlOC ceramics are X-ray amorphous up to the pyrolysis temperature (Fig. 8). In particular, the thermal stability of the synthesized Si(Al)OC ceramics is investigated by mass loss, X-ray diffraction, density measurement and surface morphology studied by SEM (see Table 3 and Figs. 8 and 9). SiOC ceramic bulks (produced from catalyzed MK-polymer) crystallize to β-SiC and free carbon at temperatures beyond 1300 °C. The density increases from 2.2 to 2.4 g/cm^3 for the pyrolyzed (1100 °C) and heat-treated (1500 °C) material, respectively. The observed weight loss of ~2.15 wt.% observed up to 1500 °C results in cracking of bulks as shown in Fig. 9a.

In contrast the SiAlOC ceramic remains amorphous/nano-crystalline up to 1400–1500 °C. Phase separation into cristobalite, β-SiC and mullite takes place for the silicon rich glass (SiAlOC1). Increasing the amount of aluminum alters the phase separation process. Aluminum rich compositions SiAlOC2 and SiAlOC3 form nano-crystalline mullite and SiC along with an amorphous SiOC phase and no cristobalite up to 1500 °C is analyzed. Past studies on borosilicate glasses which undergoes devitrification have shown that addition of alumina, aluminum nitride, cordierite and mullite can suppress the formation of cristobalite.[18,19] This finding coincides with our results supporting a strong influence of Al-cations on the crystallization of silica. Moreover, the literature data indicate that mullite most effectively suppresses the formation of cristobalite. Accordingly, crystallization of cristobalite depends on the volume and the particle size of mullite. The lower the particle size the lower the amount of mullite required for complete suppression of cristobalite formation.

In the course of our study we found that mullite formed between 1500 and 1600 °C in SiAlOC2 and SiAlOC3 as nano-particles in the glass matrix also prevents partitioning of cristobalite. In general, aluminum in SiOC ceramics clearly inhibits devitrification of the amorphous matrix at higher temperatures. The nano-crystallites formed are embedded in the remaining amorphous matrix with 10–20 nm in size as confirmed by TEM.

Table 3
Evolution of physical properties with temperature for Si(Al)OC ceramics

Material	Density (g/cm^3)			Mass loss (wt.%)			Axial shrinkage (%)
	1500 °C	1600 °C	1700 °C	1500 °C	1600 °C	1700 °C	1700 °C
SiOC	2.39	n.d	n.d.	2.15	n.d	n.d	n.d
SiAlOC1	2.31	2.26	1.80	1.90	2.41	10.13	−5.23
SiAlOC2	2.32	2.24	1.85	1.34	2.44	10.42	−7.93
SiAlOC3	2.31	2.27	1.89	1.11	1.80	6.82	−14.68

n.d: not determined.

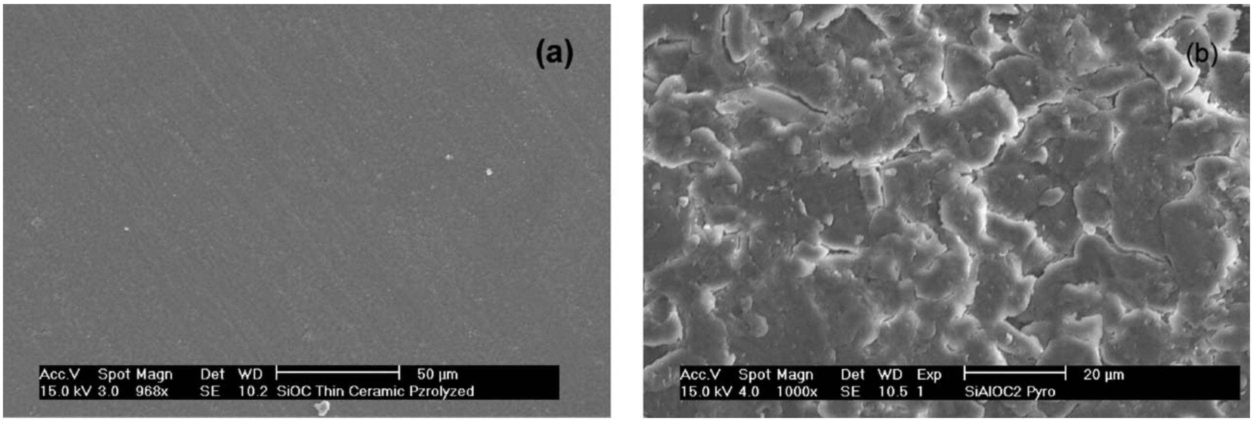

Fig. 7. SEM micrograph of the surface of (a) a thin (<0.6 mm) SiOC bulk ceramic and (b) bulk SiAlOC2 ceramic after pyrolysis at 1100 °C in argon.

The high temperature amorphous SiAlCO-phase is thermally stable at 1300–1500 °C and supports densification. The densification process between 1200–1600 °C is well explained in literature for the low temperature production of high-density mullite ceramics.[20] In short, when Al_2O_3 and SiO_2 are used to form mullite, densification is promoted when the temperature is held where SiO_2 first becomes viscous and then, after initial densification via (transient) viscous sintering, the reaction between Al_2O_3 and SiO_2 to form mullite is initiated simply by raising the temperature (commonly above 1600 °C). In Si(Al)OC system one simply has to perform phase separation followed by densification via viscous sintering. Thus there is rise in the density up to 1400 °C. Mass loss (~1.1–1.9 wt.%) along with 2.0–3.0% axial shrinkage for all SiAlOC ceramics also suggests densification (see Table 3, Figs. 9b and 10). Linear thermal expansion was observed from room temperature to

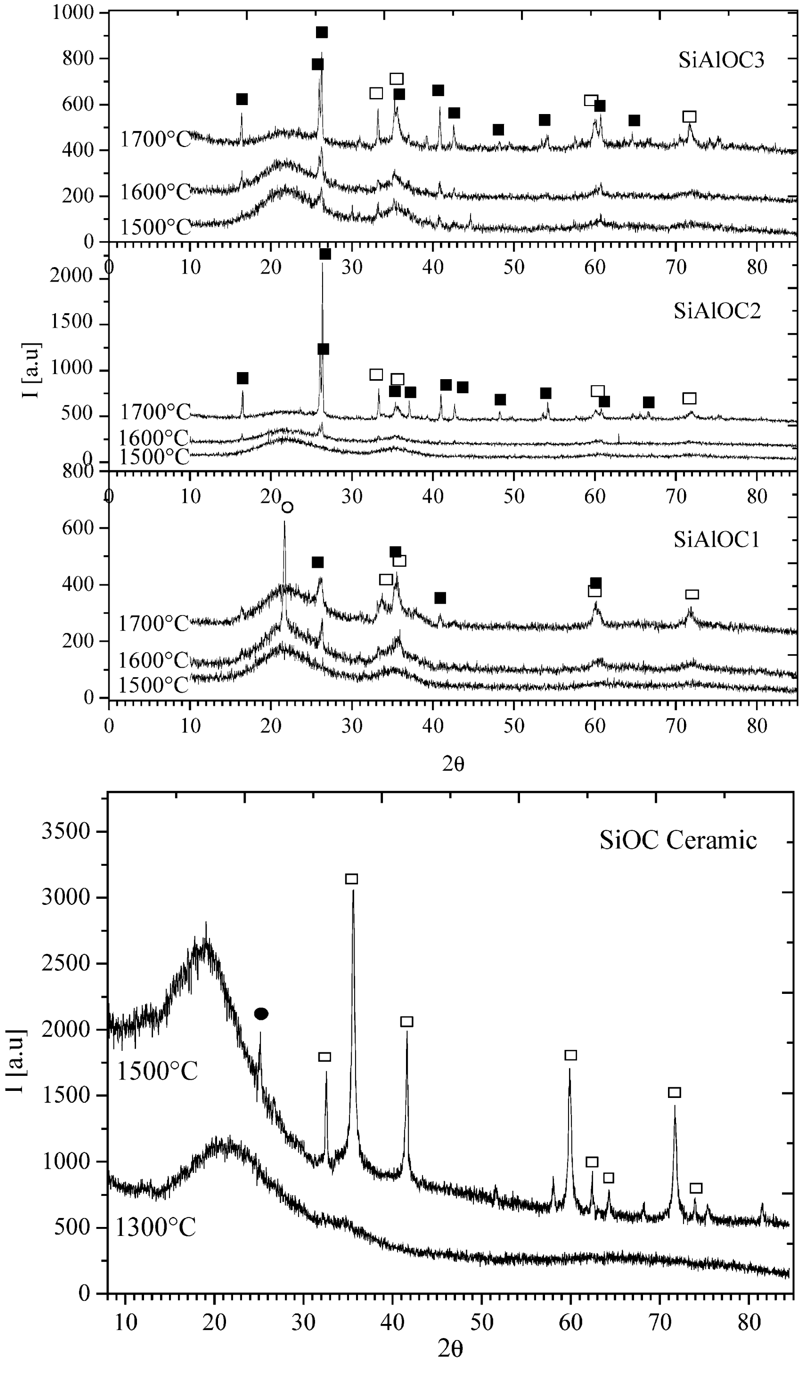

Fig. 8. Evolution of the X-ray powder diffractogram recorded on the Si(Al)OC ceramic at various pyrolysis temperature in argon atmosphere. □ mullite, ■ β-SiC, ○ cristobalite and • carbon.

1100 °C (Fig. 10). The linear CTE between room temperature and 1100 °C is measured to be 6.6×10^{-6} (1/°C). Densification as indicated by shrinkage is initiated above 1100 °C. The SiAlOC1 material continues to densify up to 1600 °C. Increasing the temperature further promotes mullitization along with high mass loss. The mullite formation temperature decreases with the aluminum content (Fig. 8). It is also evident from Fig. 10 that the SiAlOC glasses densify up to 1500 °C. Densification is also confirmed by the sintering of pyrolzed SiAlOC powders which shrink to bulk materials upon heating between 1200 and 1600 °C, while Al free SiOC powder cannot be densified and remains in powder form. Between 1500 and 1700 °C the shrinkage process stops in the case of SiAlOC2. Mass and density loss is observed in this temperature range (see Table 3 and Fig. 10). Dilatometric measurement could not be performed at higher temperature (>1600 °C) because of instrumental limitation. Geometrical measurements of the dimensional changes after annealing at 1700 °C indicate negative shrinkage in the amount of −5.23, −7.93 and −14.68 for SiAlOC1, SiAlOC2 and SiAlOC3 ceramics, respectively as can be taken from Table 3. Increase of the aluminum content reduces the amount of silicon and carbon, reflecting the lower mass loss measured for all annealing temperatures as quantified in

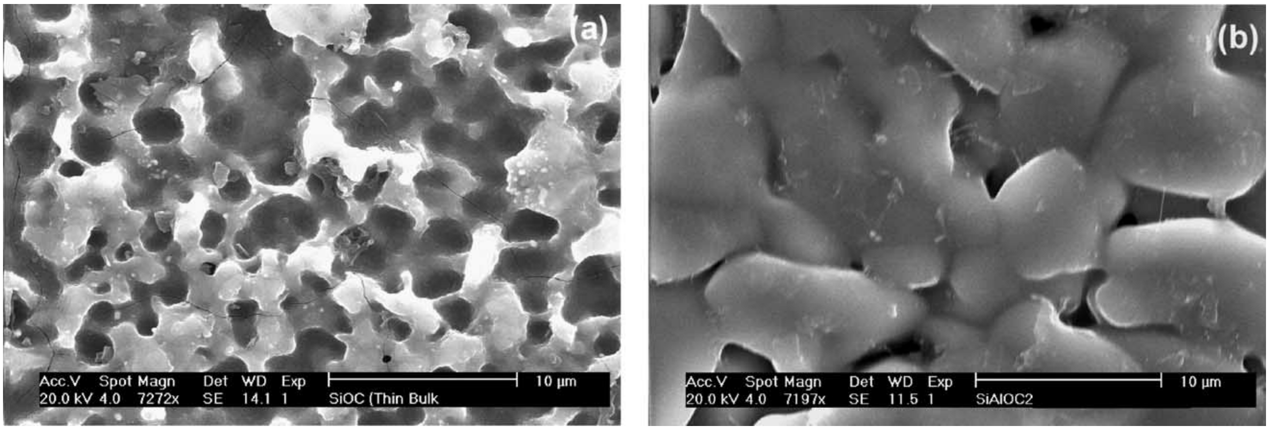

Fig. 9. SEM micrograph of the surface morphology of (a) SiOC and (b) SiAlOC2 after heat treatment in argon at 1500 °C.

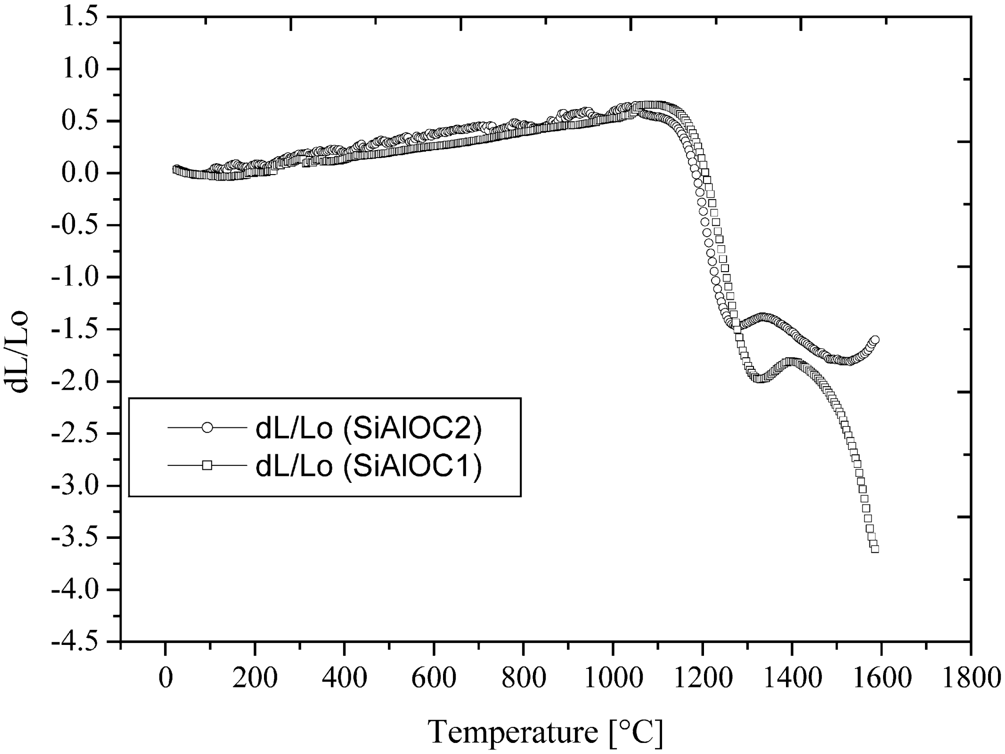

Fig. 10. Dilatometrical evolution of dimensional changes with temperature in argon at 5 °C/min for SiAlOC bulk samples.

Tables 1 and 3. A density decrease with corresponding increase in porosity is observed after annealing at 1700 °C due to the decomposition of the Si(Al)OC matrix phase which leads to the formation for volatile species such as SiO and CO.

4. Application

Major applications of polymer-derived ceramics are seen in the field of flexible processing of ceramic matrix composites. Various active (Ti, TiH_2, Al etc) and passive (SiC, Al_2O_3, TiB_2) fillers are mixed with the preceramic polymers and subsequently converted to ceramics after pyrolysis in various atmospheres.[21,22] According to our study, the commercially available silicone, MK polymer, can be used to produce ceramic matrix composites with suitable mechanical and high temperature properties.

Further applications could be developed in the field of ceramic micro-electro-mechanical-systems (MEMS). For this particular application, the silicon-based polymer should have the following requirements:

- Sufficient wetting of the micro mold by the polymer used to produce a component like the micro gear investigated in this study.
- Solidification of the polymer e.g. by chemical or thermal cross-linking after complete filling of the mold to retain the shape of the mold cavity.
- Easy demolding of the green micro component.

A rheological investigation confirms the aforementioned requirements as shown by the visco-elastic behavior of the MK polymer, which is represented in Fig. 2. In the present study a steel mold with micro gear cavities was used [see Fig. 11 (a)]. Silicone oil spray was used as a lubricating agent for easy release of the green compact. The mold is inserted in a press cavity and the polymer powder (MK + 1% catalyst) is added. The press cavity is heated at 10 °C/min up to 150 °C, held at this temperature for 15 min and subsequently cooled to room temperature. Mechanically stable green compacts with micro gears are formed. Green compact thickness is controlled to 0.6–0.7 mm by optimizing the initial polymer mass. Bulk SiOC ceramic gears were obtained after pyrolysis of the green compact in argon atmosphere with 25 °C/h up to 1100 °C as can be seen in Fig. 11(b). Higher magnification reveals crack-free and dense ceramic micro-gears [Fig. 11(c)].

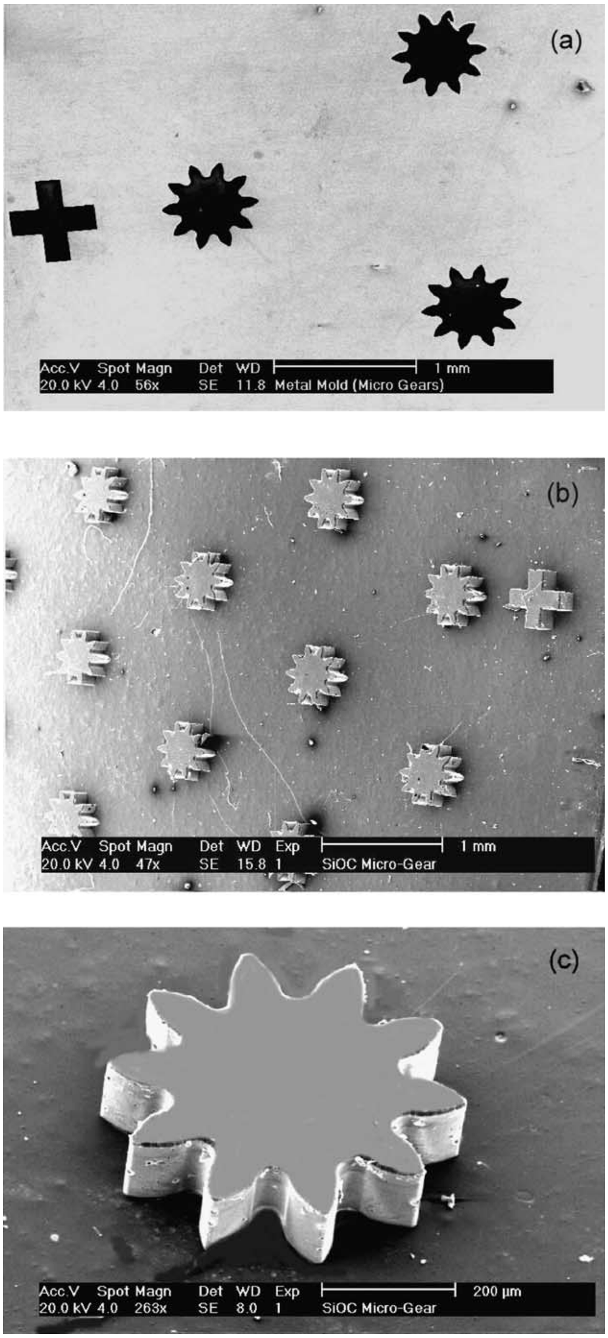

Fig. 11. SiOC ceramic micro-gear: (a) metal mold, (b) SiOC-gear after pyrolzsis of the demolded polymeric green body and (c) SiOC gear at higher magnification of (b).

5. Conclusions

Dense crack free Si(Al)OC ceramics could be produced from easily accessible commercial polysiloxane. Rheology is used as a tool to identify the cross-linking conditions for catalyst initiation reaction, which is an important parameter for the processing of precursor-derived bulk ceramics. The typical visco-elastic behavior enables fabrication of micro-component ceramics, namely MEMS.

The commercial polysiloxane could be chemically modified to form SiAlOC ceramics after pyrolysis. Al-alkoxide alumatrane used as modifier produces homogeneous starting materials in comparison to the filler technique. Modification of the polysiloxane by alumatrane forms SiAlOC ceramics with improved high temperature stability as compared to Al-free SiOC compositions. . The formation of mullite nano particles acts as cristobalite divitrification inhibitor during high temperature annealing. Unlike bulk SiOC ceramic, SiAlOC ceramic remains crack-free after high temperature annealing at 1400 and up to 1700 °C. Moreover, SiAlOC ceramics undergo phase separation followed by densification via viscous sintering at elevated temperatures.

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