Synthesis and high-temperature creep behavior of a SiLuOC-based glass-ceramic

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In this work, a lutetium-modified silicon oxycarbide (SiOC) glass ceramic was prepared from a single-source precursor via pyrolysis and subsequent hot pressing. It is shown that the main crystalline phase in the hot-pressed SiLuOC is Lu2Si2O7. The high-temperature (HT) creep behavior of SiLuOC was assessed by compression creep experiments performed between 1100 and 1300°C at constant true stresses between 25 and 75 MPa. The calculated viscosity values of SiLuOC were found to be significantly higher as compared to those of SiRE(Al,Mg)ON glasses (RE = rare earth elements). Thus, the presented SiLuOC-based glasses might be used as alternative sintering aids for the liquid-phase sintering of HT creep resistant Si3N4 monolithic samples.

Key-words: Silicon oxycarbides, SiLuOC glass ceramics, High-temperature creep behavior, Polymer-derived ceramics

1. Introduction

The fabrication of dense Si3N4 is typically realized by liquid-phase sintering upon the use of sintering additives. Common sintering additives for Si3N4 are MgO, Y2O3, Al2O3, rare-earth oxides (i.e., RE2O3) and combinations thereof.1 During the sintering process, they form a liquid phase with the SiO2 phase being present on the surface of the Si3N4 grains, wetting the Si3N4 grains and thus facilitating the compaction via particle rearrangement. α-Si3N4 grains subsequently dissolve in the formed melt and re-precipitate as β-Si3N4 whiskers which are responsible for the high fracture toughness of the liquid-phase sintered Si3N4 monoliths. Upon cooling, the melt usually forms an amorphous or partially crystallized grain-boundary phase. The viscosity of the glassy phase at the sintering temperature determines on the one hand the densification of Si3N4 during sintering; however, it limits on the other hand its high-temperature (HT) mechanical properties.1 Therefore, grain-boundary glassy phases with improved creep resistance or transient grain-boundary phases which crystallize during the sintering process are necessary in order to provide Si3N4-based monoliths with improved HT creep behavior. If compared to silicate-based glasses, polymer-derived SiOC glasses and glass ceramics exhibit improved HT creep resistance.2 Moreover, SiOC-based materials exhibit improved mechanical properties such as higher hardness and Young’s Moduli (E) as compared to vitreous silica.3,4 SiOC glasses and glass ceramics are typically prepared via pyrolysis of polysiloxanes at temperatures of 1000–1200°C. The as-prepared silicon oxycarbides are X-ray amorphous5 and consist of a glassy single-phase SiOC matrix in which segregated carbon is finely dispersed.6,7 At temperatures exceeding 1250°C, silicon oxycarbides phase-separate and convert into multi-phase amorphous systems comprising of β-SiC nanoparticles homogeneously dispersed within an amorphous SiO2 matrix.8,9

There is rather scarce information available in the literature concerning the use of silicon oxycarbide-based sintering aids for the preparation of dense Si3N4 monoliths. In a case study, Plachký et al. successfully prepared dense Si3N4 ceramics via hot-pressing using aluminum-modified SiOC glass (SiAlOC) as sintering additive. First creep tests showed a promising creep resistance of the obtained Si3N4 sample. Moreover, it has been demonstrated that in this case dense monolithic Si3N4 samples can be obtained at shorter sintering times and lower temperatures (i.e., 30 min at 1600°C) as compared to the conditions commonly used to prepare dense Si3N4 using alumina as sintering additive (1–2 h at 1750–1800°C).10 In the SiAlOC/SiN4 system, the densification was shown to be promoted via liquid-phase sintering, whereas at higher temperatures the melt reacts with Si3N4 upon the formation of O-SiAION, the latter being responsible for the improved HT creep behavior of the samples.

The goal of the present study was to investigate the potential of lutetium-modified SiOC (SiLuOC) as a sintering additive for the preparation of dense and HT creep resistant Si3N4 monoliths. It is known that lutetium provides among the rare-earth metal ions the highest viscosity in Si-RE-Me oxynitride grain-boundary melts.11,12 Moreover, lutetium is known to promote the α-Si3N4-to-β-Si3N4 phase transformation rate, as RE ions with small ionic radius show the fastest transformation rate;11,13,14 thus, the use of SiLuOC might contribute to an improved fracture toughness of the resulting Si3N4 samples with elongated β-Si3N4 grains.

In this study, Lu-containing silicon oxycarbide glasses were prepared upon pyrolysis of a suitable single-source precursor and the evolution of their chemical and phase composition with temperature was carefully analyzed. Furthermore, SiLuOC-based monoliths were prepared via hot-pressing of SiLuOC glass powders and their HT creep behavior was studied. The results
obtained within the present study indicate that SiLuOC glass powder is a suitable sintering aid for the preparation of dense Si₃N₄ monoliths with improved HT creep resistance.

2. Experimental procedure

A commercially available polymethylsilsesquioxane (PMS Belsil MK, Wacker) was mixed with lutetium acetate hydrate (15 wt.%) at room temperature. Thus, lutetium acetate hydrate [Lu(III)AcH₃] was added upon stirring to PMS MK which was previously dissolved in acetone. After 2 h of stirring, a milky white suspension was obtained and subsequently dried in a rotary evaporator. The resulting polysilsesquioxane-based powder was pyrolyzed in argon or nitrogen atmosphere at 1100°C. The thermal conversion of the single-source precursor into SiLuOC glass was investigated using thermogravimetric analysis (TGA) coupled with evolved gas analysis (EGA; i.e. in situ mass spectrometry). TGA/EGA was carried out with a thermal analysis device (STA 449C Jupiter, Netzsch, Germany) coupled with a quadrupole mass spectrometer (QMS 403C Aëolos, Netzsch, Germany). The TGA/EGA experiment was performed upon heating under flowing argon up to 1450°C by using a heating rate of 5°C/min. FTIR spectra were collected using a Bruker Vertex 70 FT-IR instrument (Bruker, USA) in attenuated total reflectance (ATR) geometry. For the elemental analysis, a carbon analyzer Leco-200 (Leco Corporation, USA) was used to determine the carbon content, and an N/O analyzer Leco TC-436 (Leco Corporation, USA) to determine the oxygen content. The Lutetium and silicon content was estimated under the assumption that no lutetium is released during pyrolysis. The silicon fraction was calculated as the difference to 100 wt.% of the sum of the wt.% values of carbon, oxygen, nitrogen and lutetium, assuming no other elements being present in the samples.

The HT evolution of the amorphous SiLuOC glass synthesized upon pyrolysis at 1100°C in argon atmosphere was studied by annealing for 5 h at different temperatures in argon or nitrogen atmosphere using a HT graphite furnace (GT Advanced Technologies, USA). Additionally, pressure-assisted annealing was performed in argon or nitrogen atmosphere using a uniaxial pressure of 30 MPa. The microstructural evolution of the samples annealed at 1100°C and upon hot press at 1600°C in argon was studied by transmission electron microscopy (TEM), utilizing a Jeol 2100F instrument (Jeol, Tokyo, Japan) operated at 200 keV. The received powder samples were finely dispersed on a lacy carbon grid and mildly carbon coated to minimize charging under the incident electron beam.

For the investigation of the HT creep behavior of the SiLuOC-based glass-ceramic, monolithic samples were prepared via hot-pressing of SiLuOC glass powder in nitrogen atmosphere at 1600°C for 30 min, using a uniaxial pressure of 30 MPa. Powder XRD measurements of the annealed samples were performed in flat-sample transmission geometry on a diffractometer from STOE company (STOE STADI P) equipped with a Mo X-ray tube, a Germanium (111) monochromator and a position sensitive detector with a 6° aperture. XRD measurements of the hot-pressed pellet used for creep experiments were performed on a Bruker D8 diffractometer equipped with a Cu X-ray tube and a Sol-X detector [Si(Li)] solid-state detector; Bruker AXS).

The HT creep experiments where performed on a Zwick universal testing device equipped with a Maytec vacuum furnace (<10⁻⁴ Pa). The samples were ground to be plane parallel with respect to the creep loaded surfaces and rectangular in shape with dimensions of 3 × 3 × 5 mm³. The creep behavior was studied in the temperature range between 1100 and 1300°C using a constant true stress of 75 MPa. Additionally, measurements were performed at a constant temperature of 1200°C but with true stresses ranging between 25 and 75 MPa. True strain and true stress were calculated from the continuously monitored compression and load, respectively, according to the procedure described in Ref. 15 and 16. At the beginning of each experiment the zero-point of strain was determined inductively via the extensometer. During the experiment, the difference between the piston and extensometer was continuously followed. The strain rates were computed after reaching the steady-state creep stage being defined when a constant strain rate was observed after a minimum of 2% plastic true strain.

3. Results and discussion

Figure 1 shows the IR spectra of the unmodified PMS MK polymer and the Lu-modified PMS MK in comparison. The bands assignment (Fig. 1) was done according to Ref. 17 and 18. As can be seen in Fig. 1, there are no major differences between the FTIR spectra of the PMS MK and the Lu-modified sample. However bands between 1550 and 1450 cm⁻¹ corresponding to asymmetric stretching vibrations of acetate COO⁻, and to asymmetric deformation vibrations of O–CO–CH₃ bonds respectively, are present in the Lu-modified sample. Additionally, the FTIR spectrum of the Lu-modified precursor shows the presence of an absorption band at ca. 950 cm⁻¹ [Fig. 1(b)], which

![Figure 1](image-url)
has been assigned to Si–O–Lu and thus indicates that the Lu(III) acetate hydrate reacts with the polysilsesquioxane.

The conversion of the single-source precursor into SiLuOC glass was followed by thermogravimetric analysis coupled with mass spectrometry given in Fig. 2. Selected mass spectra of the Lutetium-modified PMS MK are depicted in Fig. 3. PMS MK decomposes showing three main weight losses up to 800°C; whereas the pyrolysis of the Lutetium-modified PMS MK can be divided into 4 stages: (i) from room temperature to 150°C, (ii) from 150 to 450°C, (iii) from 480 to 650°C and (iv) from 650 to 800°C. In the first stage, mainly the used solvent (acetone) and water evaporate. During the second stage the outgassing of ethanol and hydrogen can be identified, indicating that cross-linking of the polymeric precursor is occurring. Additionally, the outgassing of acetate ions can be observed. The stages (iii) and (iv) correspond to the second and third weight loss of the unmodified PMS MK and are mainly identical. At 480°C, remaining acetate but mainly ethanol or ethylene and hydrogen are evaporated marking the beginning of the ceramicization process. The last stage is mainly due to the evaporation of methane and hydrogen marking the end of the ceramicization process. The modification with lutetium leads to an increased weight loss of about 10 wt. % up to 800°C in comparison to the unmodified PMS MK due to the evaporation of acetate. From 800 to 1200°C no further weight loss can be detected. At 1200°C a small weight loss was detected for both precursors where the lutetium-modified precursor exhibits a slightly higher weight loss.

The SiLuOC glass material obtained upon pyrolysis of the Lutetium-modified polysilsesquioxane precursor was annealed at high temperature in order to assess its crystallization behavior. SiLuOC glass samples were annealed in argon or nitrogen atmosphere at temperatures ranging from 1100 to 1600°C. As can be seen in Fig. 4 the annealing atmosphere has no significant influence on the crystallization behavior and the phase composition of the SiLuOC-based samples. At 1100°C, the only detectable crystalline phase is monoclinic Lu$_2$Si$_2$O$_7$. However, the samples prepared at 1100°C were mainly amorphous. The presence of Lu$_2$Si$_2$O$_7$ was already reported in highly creep-resistant Si$_3$N$_4$ with Lu$_2$O$_3$ as sintering additive and is reported to have a beneficial impact on the oxidation resistance. The XRD patterns of the samples annealed at 1300°C show the presence of nano-sized β-SiC in addition to monoclinic Lu$_2$Si$_2$O$_7$. The samples annealed at 1500 and 1600°C show both phases, i.e. β-SiC and Lu$_2$Si$_2$O$_7$, with enhanced crystallization. No additional crystalline phase was detected. Even at 1600°C after 5 h of annealing both samples show an amorphous hump with its maximum at a 2θ value of 10° corresponding to amorphous silica, proving that the sample is still partially amorphous. However, it can be clearly seen that an increase in temperature leads to an enhanced crystallization, which will be beneficial for the mechanical prop-
erties of Si$_3$N$_4$ if SiLuOC will be used as a sintering additive.

TEM analysis of the microstructural evolution of the samples revealed in both samples, (i) annealed at 1100°C (Fig. 5) and (ii) upon hot pressing at 1600°C (Fig. 6), the crystallization of small Lu$_2$Si$_2$O$_7$ particles, identified by energy-dispersive X-ray spectroscopy (EDS) in addition to electron-diffraction data analysis, embedded in the SiOC-based matrix. This finding is consistent with the XRD results given in Fig. 4. While the sample processed at low temperature showed a homogeneous amorphous SiOC matrix with Lu$_2$Si$_2$O$_7$ crystallites ranging from 5–20 nm in size (Fig. 5), the HT sample revealed a marked change in microstructure.

Here, a coarsening of the well crystallized Lu$_2$Si$_2$O$_7$ particles was observed. In this case, the crystal size varied between 20 and 300 nm (Fig. 6). Moreover, the initially fully amorphous SiOC matrix now showed a high volume fraction of turbostratic carbon [Fig. 6(a)] in addition to the crystallization of nanosized SiC crystallites (b). The inset in (b) reveals an enlarged Fourier-filtered image of a SiC crystallite. Moreover, this sample showed a coarsening of the Lu$_2$Si$_2$O$_7$ crystallites, ranging from 20–300 nm. The inset in (d) depicts an enlarged Fourier-filtered image of the well crystallized region of the Lu$_2$Si$_2$O$_7$ (boxed area).

For the assessment of the HT creep behavior, SiLuOC-based monoliths were prepared upon hot-pressing of glassy SiLuOC powders at 1600°C in nitrogen atmosphere. Its estimated elemental analysis is shown in Table 1. As the amount of incorporated lutetium is low, only 3.8 vol.% Lu$_2$Si$_2$O$_7$ is present and the chemical and phase composition is changed only slightly in comparison to the ternary system.

The XRD pattern of the hot-pressed monolithic SiLuOC sample used for the creep experiments is shown in Fig. 7. The main crystalline phase is monoclinic Lu$_2$Si$_2$O$_7$.

In order to assess the deformation behavior of SiLuOC, HT creep experiments at constant applied compressive stress between 25 and 75 MPa were performed and the steady-state creep rates at different temperatures between 1100 and 1300°C and pressures were evaluated from the recorded plastic strain (Table 2). The corresponding creep curves in true compressive strain vs. time are shown in Fig. 8. It has to be noted that long loading
times of nearly up to 100 h were necessary to obtain steady-state conditions.

In the steady-state creep regime Norton’s power law equation is valid [Eq. (1)], where $\dot{\varepsilon}$ is the steady-state strain rate, $B$ is a material-dependent constant, $\sigma$ is the applied stress and $Q$ is the activation energy. Hence, the apparent activation energy for creep can be obtained from the slope of an Arrhenius plot [Fig. 9(a)] whereas the stress exponent $n$ can be evaluated from the slope of a Norton plot (log($\dot{\varepsilon}$) vs. log($\sigma$) [Fig. 9(b)].

$$\dot{\varepsilon} = B\sigma^n e^{-\frac{Q}{RT}}$$ (1)

An apparent activation energy of 520 kJ/mol was determined for SiLuOC. This is significantly lower in comparison to the value of 712 kJ/mol reported for vitreous silica.\(^{24}\) It is however considerably higher than the value of a SiOC sample containing approximately 0.5 vol.% segregated carbon (i.e., 296 kJ/mol).\(^{25}\) These SiOC samples were however prepared at 1100°C and can therefore be regarded as single-phase materials in comparison to the phase-separated sample investigated in this study.

The stress exponent is indicative for the mechanism responsible for the creep. In the present study, a value of 2.1 was determined for SiLuOC. It is generally expected that glasses loaded at lower stresses exhibit a linear dependence of the strain rate on the stress (i.e., the stress exponent $n = 1$),\(^{26}\) which correlates to a Newtonian viscous flow behavior. The rather unexpected stress exponent of approximately 2 determined for SiLuOC, is not yet fully understood, however, similar values were already observed in a glassy SiOC system without segregated carbon.\(^{26}\) As a stress exponent of 2 correlates to grain-boundary sliding in superplastic materials,\(^{27,28}\) a viscous contribution of the silica matrix and a sliding contribution from the nano-crystalline part, [Fig. 6(a)], is proposed here. However, it was already reported for bulk metallic glasses that stress exponents $> 1$ can be as well regarded as a transition from linear to non-linear behavior according to transition state theory.\(^{27,28}\) Additionally, it was observed that this transition occurs at lower stresses with decreasing temperature below $T_g$. As the creep tests in this study were performed below and close to $T_g$ of SiLuOC, the possibility of a transition cannot be ruled out.

The shear viscosity of SiLuOC was calculated from the steady-state creep rates using [Eq. (2)], where $\eta$ is the actual viscosity, $\sigma$ is the applied stress, $\nu$ is the Poisson ratio and $\dot{\varepsilon}$ is the steady-state creep rate. This equation is only valid in the measured temperature and pressure regime as it implies Newtonian viscous flow behavior. The Poisson ratio of SiOC was determined to be 0.11 by Moysan et al.;\(^{23}\) this value was used also for the SiLuOC system.

Table 1. Chemical composition of hot-pressed SiOC and SiLuOC samples and calculated phase composition of the assumed phases present. Volume fractions are calculated assuming the following densities: $\rho$(SiO$_2$) = 2.2 g/cm$^3$\(^{20}\), $\rho$(β-SiC) = 3.22 g/cm$^3$ (ICSD-# 164974), $\rho$(C) = 1.82 g/cm$^3$ (Graphitized Mesoporous Carbons GMC, Sigma-Aldrich, CAS-# 1333-86-4), $\rho$(Lu$_2$Si$_2$O$_7$ mon.) = 6.21 g/cm$^3$ (PDF 00-034-0509)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition</th>
<th>SiO$_2$ [vol.%]</th>
<th>SiC [vol.%]</th>
<th>free C [vol.%]</th>
<th>Lu$_2$Si$_2$O$_7$ [vol.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOC</td>
<td>SiO$<em>{1.44}$C$</em>{0.28}$+C$_{0.42}$</td>
<td>75.9</td>
<td>13.4</td>
<td>10.8</td>
<td>—</td>
</tr>
<tr>
<td>SiLuOC</td>
<td>SiO$<em>{1.46}$C$</em>{0.29}$Lu$<em>{0.02}$+C$</em>{0.36}$</td>
<td>72.8</td>
<td>14.1</td>
<td>9.3</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Fig. 7. XRD pattern of the hot-pressed SiLuOC sample used for the creep experiments.

Table 2. As-determined steady-state creep rates of hot-pressed SiLuOC at different temperatures and stresses

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>25 MPa applied stress</th>
<th>50 MPa applied stress</th>
<th>75 MPa applied stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>—</td>
<td>—</td>
<td>3.5·10$^{-8}$ s$^{-1}$</td>
</tr>
<tr>
<td>1200</td>
<td>5.9·10$^{-8}$ s$^{-1}$</td>
<td>2.5·10$^{-7}$ s$^{-1}$</td>
<td>6.2·10$^{-7}$ s$^{-1}$</td>
</tr>
<tr>
<td>1300</td>
<td>—</td>
<td>—</td>
<td>1.2·10$^{-7}$ s$^{-1}$</td>
</tr>
</tbody>
</table>

Fig. 8. True creep strain plotted vs. time of SiLuOC (continuous curves) (a) at constant temperature of 1200°C and true stresses of 25, 50 and 75 MPa (dashed); (b) at a true stress of 75 MPa and two temperatures, i.e. 1100 and 1300°C (dashed).
SiLuOC was found to be higher than for the single-phasic ternary systems starting at around 1250°C and due to an enhanced crystallization of the Lu₂Si₂O₇ secondary phase.

From the calculated viscosity data the glass-transition temperature \( T_g \) of SiLuOC (defined as the temperature at which the viscosity is 10¹² Pa·s) is estimated to be 1291°C. The viscosity of SiLuOC was found to be higher than for the single-phasic ternary system with 0.5 wt.% segregated carbon and even higher than that of SiAlOC, which was already used by Plachky et al. as sintering additive for Si₃N₄.

As already mentioned, common sintering additives for Si₃N₄ are MgO, Y₂O₃, Al₂O₃, RE₂O₃ and combinations thereof. Consequently, depending on the type of additive, SiYaION or SiRE(Al,Mg)ION glasses can be expected to be present as grain-boundary phases in common Si₃N₄ materials produced by liquid-phase sintering. The viscosity of this glassy phase at the sintering temperature determines on the one hand the densification during sintering and on the other hand the HT performance of the resulting ceramic. Becher et al. investigated the viscosity of silicon-based oxynitride glasses. From their results, the glass-transition temperature of SiYaION glasses (56Si28Y16Al oxyxnitride glasses) was found to be in the range of 870 to 950°C, depending on their nitrogen content. In the system 56.5Si44La0.5Y20N80O a maximum glass-transition temperature of around 1020°C was determined. This is significantly lower than the glass-transition temperature for SiLuOC (1291°C) determined here, which will have an impact on the densification behavior of Si₃N₄ powders and consequently an external pressure during the sintering process should be necessary. A high viscosity of the liquid melt during sintering however provides \( \beta \)-Si₃N₄ particles with high aspect-ratio and improved fracture toughness of the resulting ceramic.

4. Conclusion

SiLuOC glass ceramics exhibit promising behavior for the use as sintering additive for Si₃N₄. The phase composition is independent of the processing atmosphere yielding mainly amorphous materials containing low volume fractions of Lu₂Si₂O₇ as main crystalline phase in all cases. The calculated viscosity of SiLuOC is significantly higher as compared to SiRE(Al,Mg)ION glasses used in typical liquid-phase sintering of Si₃N₄. Furthermore, SiLuOC can partially be crystallized with increasing temperature due to the intrinsic phase-separation common for all SiO₂ systems starting at around 1250°C and due to an enhanced crystallization of the Lu₂Si₂O₇ secondary phase.

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