Polysilsesquioxane derived ceramic foams with gradient porosity

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Abstract

Ceramic foams with a gradient porosity were manufactured using a self foaming process of a Si/SiC filled silicone resin in the temperature range of 220–270 °C. Subsequent pyrolysis at 1000 °C resulted in Si–O–C micro composite foams with a pronounced structural anisotropy. The porosity gradient in the foam was controlled by adjusting the polymer melt viscosity during foaming via temperature. The porosity varied from 40% to 90% within 35 mm. The gradient of the porosity caused variations of the connectivity density, structure model index and surface-to-volume ratio and influenced the gas permeability and fracture strength.

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1. Introduction

Ceramic foams can be characterized as linked networks of irregularly shaped open or closed cell polyhedrons, with a low fractional density ranging from 0.05 to 0.50 [1]. The foam formation, however, is a complex process which involves bubble nucleation, bubble growth and pore coalescence [2]. The cellular foam structure offers a high mechanical stability and non catastrophic localized fracture behaviour at low density [3]. Fabrication of ceramic foams with an isotropic cell structure has been well established for more than four decades. Taking advantage of their high gas and liquid permeability [4,5] and high thermal resistance [6,7], ceramic foams are currently applied in various fields including metal melt filters [8], heating elements in porous gas burners [9], filters, membranes and catalyst carriers, supports in bio reactors [10–14] and sensor elements. Porous ceramics are fabricated most commonly by replica techniques which involve dip coating of a poly urethane foam or natural sponge, removing the excessive slurry and subsequent burn-out of the preform [15]. Other techniques include space holder methods where a salt compact is infiltrated, dried and where the salt is finally removed by dissolution [16,17]. Gel casting [18–20], powder processing [21] and gas bubble formation techniques [22] are other commonly used manufacturing routes. Recently, polysilsesiquoxanes and poly silanes have attracted increased interest for the fabrication of ceramic foams [23–25]. Poly silsesquioxane was foamed with the help of poly urethane acting as foaming agent. The foam cell size and overall porosity were adjusted by adding surfactants to the silicone resin [26]. Average pore sizes ranged from 200 to 400 μm and open porosities of 80–90% at densities of 0.1–0.3 g/cm³ were obtained.

For special applications, however, ceramics with a graded pore structure are desired. Pore gradient
ceramics offer an interesting potential for being used as biocompatible implants [27], preforms for liquid metal infiltration [28–30], thermal barrier coatings [31] and thermal shock resistant structures [32]. The fabrication of porous ceramics with graded porosity is more sophisticated as compared to isotropic ceramic foams and usually requires multiple manufacturing steps [33]. Graded ceramic foams were produced by compacting ceramic powders with varying amounts of porosity generating additives [33] such as polymers or carbon [34], using 3D printing techniques [28], electrophoretic deposition [30], stacking of tapes with different porosity [29] or by packing ceramic powders, fibres or woven preforms to the desired structure and partially sintering of the scaffolds [34]. Recently, a method for the fabrication of ceramic foams with graded porosity by foaming a silicone resin was reported [35].

A novel manufacturing approach facilitates the fabrication of ceramic foams with both isotropic and/or partially sintered scaffolds [34]. Recently, a method for the fabrication of ceramic foams with graded porosity by foaming a silicone resin was reported [35].

2. Experimental

2.1. Foam preparation

A methyl phenyl poly (silsesquioxane) \( [(\text{C}_6\text{H}_5\text{Si})_{0.62} - (\text{CH}_3)_{0.31} \text{R}_{0.07} \text{SiO}_{1.5}]_n \) with \( n \sim 20, \text{R} = [-\text{OH}] \) and \([-\text{OC}_2\text{H}_5\text{]}\) (Silres H44, Wacker Chemie, Burghausen, Germany) was used as preceramic polymer. The polymer is solid at room temperature, has a melting interval of 60–120 °C and exhibits a density of 1.1 g/cm³. A blend of Si (Silgrain, \( d_{50} = 7.6 \mu m \), Elkem, Meerbusch, Germany) and SiC (F500B, \( d_{50} = 16 \mu m \), H.C. Starck, Selb, Germany) was added to the polymer in a polymer:Si:SiC weight ratio of 35:12:53 which corresponds to a volume ratio of 59:7:34. Si and SiC act as inert fillers when fired below 1000 °C and were selected to tailor the foam morphology, to adjust the desired porosity and to increase the strength and structure stability of the foam [38].

The polymer/filler blend was dry mixed in a ball mill for 2 h. The polymer/filler mixture was filled in an aluminium tray and foamed at 245 °C for 2 h in air. The thermoset foam was cut into cylinders (\( r = 15 \text{ mm} \), \( h = 35 \text{ mm} \)) and bars (\( l = 120 \text{ mm} \), \( w = 20 \text{ mm} \), \( h = 35 \text{ mm} \)). The foams were fired in nitrogen atmosphere applying a heating rate of 3 °C/min to 500°C and a hold for 2 h. Subsequently, the foams were further heated by 5 °C/min to 1000 °C with a holding time of 4 h. The cooling rate to room temperature was set to 5 °C/min.

2.2. Viscosity and sedimentation measurements

Thin discs (\( r = 10 \text{ mm} \), \( h = 1 \text{ mm} \)) were uniaxially pressed from each 1.5 g of the polymer/Si/SiC blend. The discs were used for shear viscosity measurements at constant temperatures of 200–300 °C and with increasing temperature, from the melting temperature of the polymer to 320 °C. A heating rate of 5 °C/min was applied. A rotational rheometer setup with a 1 Hz oscillating punch was used (Rheometer UDS 200, Physica Messtechnik GmbH, Ostfildern, Germany). The complex shear viscosity \( \eta \) was calculated from the storage modulus \( G' \) and loss modulus \( G'' \).

Sedimentation of the filler powder particles above the polymer melting temperature was examined using an optical analyser (Turbiscan Lab Expert, Formulaction, L’Union, France) that quantifies the transmittance and the backscattering intensity of an introduced laser beam with a wave length of 880 nm. Using evaluation methods based on the Mie scattering theory a mean sedimentation velocity \( v_s \) of the filler particles in the polymer melt was calculated. As the maximum measurement temperature of Turbiscan is 60 °C, a 1:1 wt% mixture of Silres H44 and of the methyltriethoxysilane (MTES) \( \text{C}_3\text{H}_18\text{O}_3\text{Si} \), which acts as a solvent was prepared. At 60 °C the mixture has the same viscosity as plain Silres H44.
H44 at 220 °C. A H44:MTES:SiC mixture with a weight
to a wave length of 0.024 nm. The
calculated from the three-dimensional tomography data.

defined by triangulating the surface of a specific VOI with

2.3. Structure characterization

The cellular microstructure of the foam was exam-
ined using an X-ray microtomograph (μCT40, Scanco
Medical AG, Bassersdorf, Switzerland). The X-ray tube
was equipped with a tungsten target and operated at
50 kV and 80 μA at a wave length of 0.024 nm. The
specimens were scanned in a near isotropic resolution
of 37×37×38 μm³. A CCD line array was used to
detect the transmitted intensity through the sample.
X-ray source and detector were covered with slit collim-
ators. The object was rotated through 360° with one
step per degree and the raw data were recorded as sinu-
grams. Generally, various approaches for the 2D recon-
struction of CT data are known that are mathematically
identical but differ in image quality [39]. In this case,
two-dimensional reconstructions of the slices were cal-
culated from the sinugrams by Radon back transforma-
tion using a Compaq DC10 Alpha workstation. From
the 2D images the fractional density 𝑝𝑓 was calculated as the
ratio of transmitted material in the measured slice
to the complete slice. The subsequent image analysis of
multiple slices facilitated the determination of a porosity
gradient in the examined volume of interest (VOI).

The morphometric structure model index (SMI) was
calculated from the three-dimensional tomography data.
The SMI was introduced for quantification of bone micro
architecture and can be used for foam structure analysis to
characterize the shape and anisotropy of cellular materi-
als as well [40]. The SMI was calculated according to

\[
SMI = 6 \cdot \frac{V \cdot (dS/dr)}{S^2},
\]

where \( S \) is the strut surface in a volume \( V \) and \( dS/dr \) is
the surface area derivative. The foam surface area is ren-
dered by triangulating the surface of a specific VOI with
the Marching Cubes method and the volume is defined
by setting up polyhedrons inside the VOI that match
the bounding surface triangles [41]. A SMI value of 4 de-
scribes spherical pores, any deviation of the spherical
cell geometry results in lower values. A rod cell structure
is characterized by a SMI value of 3 and plate pores
have a SMI of 0. Negative SMI values result from cells
with concave surface areas which is common when coa-
lescence of pores takes place.

The surface/volume ratio, the mean cell size and strut
thickness were calculated using the distance transforma-
tion (DT) method as described in [42]. The connectivity
density \( CD \) was computed from CT data using the
Conn-Euler principle as explained in detail in [43];
reconstructed 2D CT data images of two neighboured
slices are compared by the Boolean Exclusive-Or oper-
tor. The result is superimposed to the original pictures
and analyzed. All new bridges \( B \) (new connections),
holes \( H \) and islands \( I \) are counted and CD is calculated:

\[
CD = \frac{- \sum H + \sum I - \sum B}{2h \cdot A},
\]

where \( h \) is the distance of the two slices (\( h = 38 \mu m \)) and
\( A \) the examined image area. In the case of determining
the CD of the pores, \( B \) and \( I \) denote cell windows and
cells, respectively. \( H \), which is isolated strut material
completely surrounded by pores, is unlikely to occur.
The value is identical if \( CD \) is calculated for the strut
material, where \( B \) denotes new struts, \( H \) equal cells
and \( I \) isolated struts.

2.4. Gas permeability

The gas permeability of 5 mm thick slices (\( r = 15 \mu m \))
was measured using a self made gas flow meter device.
The slices were sealed in an Al crucible that allows only
one directional gas flow along the cylindrical axis of the
specimen. The air mass flow \( q = \Delta m/\Delta t \) through the
sample was adjusted by a digital mass flow controller
(Bronkhorst MFC-F201-AC-AAB-33-V, Bronkhorst
Hi-Tec, AK Ruurlo, Netherlands). The pressure drop
\( \Delta p \) through the sample was measured with a differential
gas pressure sensor (Bronkhorst DP-P506-AAB-33-V,
Bronkhorst Hi-Tec, AK Ruurlo, Netherlands). According
to Darcy’s law

\[
\kappa = \frac{\eta \cdot L}{A \cdot \Delta p},
\]

the permeability \( \kappa \) was determined from the \( q/\Delta p \) ratio. \( L \)
is the distance of the forced gas flow which corresponds
to the sample thickness (5 mm), \( A \) is the cross-section of
the foam (706 mm²) and \( \eta \) denotes the viscosity (air,
25 °C, \( \eta = 1.83 \times 10^{-5} \) Pa s). \( \kappa \), which has the unit m²,
is mostly specified in Darcy (1 D = 0.97 × 10^{-15} m²).
The mass flow rate was set to 2.0 m³/h to ensure a lami-
nar Darcian flow through the foam and to minimize gas
slippage and Klinkenberg effects [44].

2.5. Compression and bending strength

The compression strength was measured at room
temperature for at least 10 cylindrical samples (\( r = 10 \mu m \)). Specimens with graded porosity were cut from the
top coplanarly to a sample height \( h \) ranging from
10 to 35 mm, respectively. The foams were loaded in a
universal testing machine (Instron 4202, Instron Corp.,
Canton, MA, USA). A constant crosshead speed of
0.5 mm/min was applied. From the maximum stress
after elastic deformation the crushing strength of the
foam was derived.
The bending strength was measured in a four-point setup (support roller distance: 100 mm, load roller distance: 50 mm) using the same testing device at a constant crosshead speed of 0.5 mm/min at room temperature. Bars with a geometry of $120 \times 20 \times 30$ mm$^3$ (length, width, height) were tested. The samples were loaded as fired with the low fractional density part of the specimens on the bottom (tensile stress) as well as with the high fractional density part on the bottom side.

3. Results and discussion

3.1. Foaming

Foam formation by in situ blowing reactions requires control of viscosity behaviour of the polymer melt. The dependence of the viscosity of a polymer melt generally follows an Arrhenius type relation [45]

$$\eta(T) = \eta_0 \cdot \exp \left( \frac{E_a}{R \cdot T} \right),$$

(6)

where $\eta_0$ is an empirical constant and $E_a$ is the activation energy for viscous flow. $R$ is the gas constant and $T$ the absolute temperature. As shown in Fig. 1, the viscosity decreases with rising temperature. Heating by 5 °C/min, the polymer is molten completely at 120 °C. The influence of the crosslinking becomes dominant at temperatures above 250 °C. In the temperature range of 120–200 °C the curve of Fig. 1 can be used to describe the temperature dependence of the viscosity of the Silres H44 melt. The numerical fit of Eq. (6) to the measured data results in

$$\eta(T) = 0.01 \cdot \exp \left( \frac{32 \text{ kJ/mol}}{R \cdot T} \right).$$

(7)

The activation energy of viscous flow of 32 kJ/mol is comparable to that of other silicone melts which depending on the molecular structure typically show activation energies of 10–100 kJ/mol in the temperature range below 300 °C [46].

At temperatures above 200 °C, a dependence on time is superimposed to Eq. (7) due to the curing of the polymer melt, Fig. 2. The reaction rate of the curing reactions of the poly silsesquioxane during heating was expressed by the general approach of Borchardt and Daniel [47]:

$$\frac{dx}{dt} = k^*(T) \cdot (1 - x)^n.$$

(8)

Here, $dx/dt$ is the curing reaction rate with $x$ denoting the degree of curing which may attain values between 0 and 1. The degree of curing was derived from experimental data based on a thermo-barometrical analysis of the gaseous condensation products which evolve during the curing reactions [48]. The exponent $n$ describes the reaction order and $k^*(T)$ the specific conversion rate at the temperature $T$ which follows an Arrhenius type equation

$$k^*(T) = k_0 \cdot \exp \left( \frac{-E_a}{R \cdot T} \right).$$

(9)

Here, $k_0$ is a material dependent constant and $E_a$ is the activation energy of the curing reaction. For the curing reaction rate the following parameters were calculated according to Eq. (8): $n = 1.78$, $E_a = 32.7$ kJ/mol and $k_0 = 0.246$. Previous results obtained from Silres H44 showed a reaction order ranging between $n = 1$ and 2.5 in the temperature interval of 200–300 °C [49]. Si/SiC filled Silres H44 has shown a very similar curing behaviour as compared to the unfilled poly silsesquioxane.

Combining the time dependence and temperature dependence of the polymer melt viscosity was carried out by applying a modification of Mooney’s functional analysis which is an extension of Einstein’s viscosity equation for an infinitely dilute suspension [50]:
\[ \eta(t, T) = \eta(T) \cdot \left(1 - \frac{\eta(T)}{\eta_0}\right)^{-p}, \]  
where \( \eta_0 \) is the degree of curing where no more viscous flow occurs and was set to 0.8. Applying Eq. (8) and numerically fitting the experimental data of Fig. 2, \( p \) was calculated to 2.2 ± 0.4 which is in good agreement with the Einstein coefficient \( p = 2.5 \) [51]. Eq. (10) is valid for viscosities up to \( 10^6 \) Pas. Fig. 3 (a) shows the calculated values of the viscosity as a function of time and temperature in a smoothed 3D plot. Values of \( \eta(T, t) > 10^6 \) Pas were set to \( 10^6 \) Pas. In Fig. 3 (b), the region of controlled foaming is displayed in the contour plot of Fig. 3(a).

Heating the polymer to temperatures above 220 °C caused foam bubbles to be generated. Water, ethanol and traces of benzene were released upon condensation reactions of the hydroxy and ethoxy groups of the polystyrene methyl (silsesquioxane). Foam formation is governed by the time and temperature dependence of bubble nucleation, bubble growth and rise and concurring crosslinking reactions. While bubble formation requires a low viscosity of the polymer melt, stabilization of the foam structure is caused by viscosity increase. In the presence of filler particles, heterogeneous nucleation is assumed to be the governing bubble formation mechanism [52].

Once bubbles are nucleated, increase of bubble size due to cell growth will occur. Various theoretical approaches have been carried out to estimate the bubble growth dynamics [53–55]. Generally, bubble growth in viscoelastic liquids is based on diffusion mechanisms that do not follow Fick’s law. Complex models using several approximations (IDS, infinitely dilute solute; TBL, thin layer boundary) have been studied. A detailed description is given in [54]. However, experimental data from Han and Yoo [56] on gas charged molten polymers could be well described by an empirical approach. Neglecting the solubility of individual gas molecules in the polymer melt, the bubble radius \( r \) tends to be a function of time \( t \) at a temperature \( T \) according to [54]:

\[ r(T, t) = \beta \cdot \sqrt{D(T, t) \cdot t}, \]  
where \( \beta \) is a dimensionless empirical constant. \( D(T, t) \) is the effective diffusion coefficient of the gaseous species through the polymer melt into the growing bubble that is related to the viscosity by the Stokes–Einstein relation:

\[ D(T, t) = \frac{k_B \cdot T}{6 \cdot \pi \cdot \eta(T, t) \cdot r_g}. \]  
Here, \( k_B \) is Boltzmann’s constant and \( r_g \) is the radius of the gas molecules (for water and ethanol \( r_g = 1.39 \) and 2.89 Å, respectively). Inserting Eqs. (10) and (12) in Eq. (11) and numerically integrating over the time finally resulted in the calculation of the maximum bubble size as a function of time, Fig. 4. The calculations were performed for 220 and 270 °C using the numerical solver of Maple V 7 (Maplesoft Inc., Waterloo, ON, CA). A constant water/ethanol ratio of the gases diffusing into the bubbles and a constant gas pressure within the bubble were assumed. A critical bubble nucleus size of 0.2 μm was taken in accordance to literature data [54].

The maximum bubble size radius \( r_{\text{max}}(x = 1) \) used for normalization was determined experimentally from μCT analysis. Values for \( r_{\text{max}}(x = 1) \) of 3.7 and 3.1 mm were derived when foaming was carried out at 220 and 270 °C, respectively. When a degree of curing of \( x = 0.8 \) and thus the end of viscous flow is reached, the bubble growth rate is supposed to significantly slow down as indicated by the kink of the 270 °C curve.

A schematic illustration of the various foaming stages is given in Fig. 5. A filler containing foam thermoset with a homogeneous structure is obtained when heated at 270 °C. The rapid viscosity increase up to 1000 Pas/s of the
polymer at temperatures above 260 °C prevents the rise of the gas bubbles and the fractional density remains nearly constant over the cross-section of the foam. Curing temperatures of 270–300 °C lead to foams with isotropic structure. At 260 °C, a slight gradient is noticeable, Fig. 6. However, if the foaming temperature is set below 260 °C, curing reactions proceed significantly slower and the initial low viscosity makes bubble rise evident. The foam bubbles (1.0–1.5 mm in diameter) rise by several mm/h at a viscosity of less than 100 Pa. Curing temperatures between 220 and 260 °C lead to graded porosity in the foam thermoset. At 220 °C, a linear increase of the fractional density ranging from 0.1 at the top to 0.6 at the bottom of the foam thermoset was obtained, Fig. 6. Bubble nucleation, bubble growth and bubble rise take place simultaneously during the initial stages of foaming (step II in Fig. 5(b)) leading to an accumulation of pores at the foam surface, step III.

Polymer derived ceramic foams with a gradient pore structure were also obtained by Colombo and Hellmann [35] by blowing a mixture of a poly siloxane and a liquid physical blowing agent. During foaming the viscosity remained constant which gave rise for accelerated movement of large pores to the top. Thus, a pronounced pore size gradient with large pores at the top and significantly smaller pores at the bottom developed. In contrast, the foaming process in our work is characterized by a distinctive increase of viscosity over time due to concurrent curing reactions taking place during bubble formation and bubble ascent.

When the bubbles accumulate at the top coalescence by strut rupture might occur resulting in reduction of bubble number and increase of mean bubble size [57]. For coalescence to take place, however, a strut thickness below 0.1 μm and a significantly lower viscosity as given in the poly silsesquioxane system were reported to be necessary [58,59]. Hence, it may well be assumed that bubble coalescence should not affect accumulation of pores at the top which remain stable in size during further annealing. With prolonged annealing, a pronounced viscosity increase by more than three orders of magnitude was observed. As a result, the ratio of bubble ascent velocity (Stokes’ law) to bubble growth rate (Eq. (11)) changes from >1 at low viscosity to <1 at high viscosity, Fig. 7. Estimation of bubble size after
curing at 200 °C for the growth period indicates the bubble size at the bottom being three times larger as compared to the bubble size at the top due to the non-linear viscosity change as shown in Fig. 2.

3.2. Structure gradient

The fractional density \( q_f(y) \) as a function of porosity gradient \( g(y) \) can be expressed by

\[
q_f(g) = q_f(0) + (q_f(h) - q_f(0)) \cdot g(y)
\]

with

\[
g(y) = \left(\frac{y}{h}\right)^m.
\]

Here, \( y \) denotes the direction of the gradient and \( h \) is the sample height [60]. Fig. 8 shows a 3D reconstruction of a micro computer tomography of ceramic foam blown at 245 °C. \( g(y) \) is defined to range from 0 at the top \( (y = 0) \) of the foam to 1 \( (y = 35 \text{ mm}) \) at the bottom. \( \rho_f(g(y)) \) for foaming temperatures 245 and 260 °C is given in Fig. 6. \( g(y) \) is linear for both temperatures and thus \( m = 1 \). However, \( \rho_f(0) \) and \( \rho_f(1) \) show a dependence on the temperature. Foaming at 245 °C resulted in \( \rho_f(0) = 0.52 \) and \( \rho_f(1) = 0.07 \) whereas at 260 °C corresponding fractional densities of 0.30 and 0.24 as the foam borders were reached. From Eq. (13), the overall porosity \( V_p \) in the foam can be calculated by

\[
V_p = 1 - \frac{1}{h} \int_0^h \rho_f(y) dy.
\]

Here, \( V_p \) equals 71.5% when foaming was carried out at 260 °C and 70.5% for 245 °C, respectively. The porosity gradient is controlled by adjusting the foaming temperature while keeping a constant mean fractional density.

The connectivity density \( CD \), the surface/volume ratio, the \( SMI \) and the mean strut thickness and cell diameter were correlated to \( g(y) \) and \( \rho_f \). Fig. 9 shows the dependence of the mean strut thickness and of the mean cell diameter on the fractional density. The mean strut thickness shows an exponential rise with increasing fractional density. At \( g(y) = 0 \), the struts were 0.2 mm in diameter and increased to 1.0 mm at a fractional density...
of 0.5. The cell diameter increased linearly from 1.0 mm at \( \rho_f = 0.1 \) to 1.6 mm at \( \rho_f = 0.35 \). In addition, pore coalescence took place resulting in larger pores. This is confirmed by the SMI, Fig. 10. At \( g(y) = 0 \) a SMI of 3 was obtained which describes nearly ideal spherically shaped cells. The SMI decreased linearly to -1 at \( \rho_f = 0.45 \) which denotes a significant deviation of the spherical shape of foam cells. The irregularly shaped foam cells were confirmed by microscopic and tomographic analysis, Fig. 6. The deviation of the cell shape from the theoretically predicted sphere morphology is caused by a combination of processes including pore coalescence and cell collapse [1].

Fig. 11 shows the surface/volume ratio as a function of the fractional density and of the location \( g(y) \) ranging from 16 mm\(^{-1}\) at \( g(y) = 0 \) to 2 mm\(^{-1}\) at \( g(y) = 1 \). Using a least squares algorithm (gnufit 1.2, part of gnuplot 3.7 software package), the curve was fitted numerically by an exponential decay function. The dependence of the surface/volume ratio is expressed by

\[
\frac{S}{V} = 1.53 + 22.5 \cdot \exp\left(-\frac{\rho_f}{0.16}\right) \text{ (mm\(^{-1}\))}.
\]  

(16)

Fig. 11 shows the dependence of the connectivity density \( CD \) on the fractional density \( \rho_f \) that can be expressed by

\[
CD = 0.09 + 6.81 \cdot \exp\left(-\frac{\rho_f}{0.10}\right) \text{ (mm\(^{-1}\))}.
\]  

(17)

\( CD \) showed a similar dependence on the fractional density as the surface/volume ratio. As the theoretical maximum fractional density of fully interconnected open cell foams is \( \rho_c = 0.26 \) [61], it is obvious that the lower part of the samples, which was characterized by \( 0.3 < \rho_f < 0.5 \), contained isolated closed cells whereas the upper part of the foam showed increasing amounts of cell windows in the structure. According to Peng’s relation (Eq. (18)), the diameter \( d \) of the cell window which connects two foam cells of the same diameter \( D \) correlates to the fractional density \( \rho_f \) [61]:

\[
\rho_f = \frac{\pi}{\sqrt{2}} \left[ \frac{3}{1 - (d/D)^2} - \frac{3}{5} \left( \frac{1}{\sqrt{1 - (d/D)^2}} \right)^3 \right].
\]  

(18)

At the top, \( dD \) equalled 0.4 and the cell window diameter \( d \approx 400–500 \) \( \mu \)m. At \( \rho_f = 0.2 \), the window diameter decreased to \( d \approx 300 \) \( \mu \)m, Fig. 12. At \( \rho_f > 0.26 \), \( dD < 0 \) and the formation of closed cells was inevitable.

3.3. Properties

3.3.1. Gas permeability

The permeability of porous ceramics is determined by the manufacturing process and pore structure. Ceramic
foams produced by reticulation processes are characterized by a permeability which is three to four times higher than the permeability of foams of the same fractional density fabricated by bubble generating techniques. The relation of porosity and permeability of porous materials ranging from low porous lime stone to high porous ceramic foams has been studied experimentally [62,63]. A linear dependence of the permeability on the porosity was noted for low porous salt compacts having a fully interconnected pore cell network [64]. However, highly porous materials may show a significant deviation of the linear dependence. Percolation Theory suggests a power law relation between the permeability \( k \) and the fractional density \( \rho_t \) [65]:

\[
\kappa = c \cdot (\rho_{t,cr} - \rho_t)^\mu,
\]

where \( c \) and \( \mu \) are empirical constants and \( \rho_{t,cr} \) is the percolation threshold which is the maximum fractional density that still shows percolation of the pores. Assuming monomodal spherical pores, the percolation threshold lies at \( \rho_{t,cr} = 0.26 \) [61]. The permeability as a function of \( g(y) \) was determined by measuring the slices that were cut out of the cylindrical sample. The permeability of each slice represented the corresponding value of the foam part where it was cut out. The permeability of the open cell foam fitted well to Eq. (19) for \( \rho_t < 0.26 \) by

\[
k(g(y)) = 206 \cdot (0.26 - \rho_t(g(y)))^{0.42},
\]

confirming the dependence of the gas permeability on the cell percolation. The Darcian air flow through the polymer derived ceramic foam depended on the cell window size: similar to the cell window diameter \( d \) the permeability \( \kappa \) of the open cell foam part decreased exponentially with increasing fractional density, Fig. 12. At \( \rho_t > 0.26 \), the permeability approached \( \kappa = 0 \) as no percolation of open cell structure existed any more.

### 3.3.2. Strength

The bending strength of the porosity graded material depended on the fractional density. Typical stress–strain diagrams are given in Fig. 13. When the low fractional density part of the specimen was loaded in tension and the high fractional density part in compression, a bending strength of 7.2 ± 1.6 MPa and a failure strain of 0.21 ± 0.06% was obtained. When loaded bottom up, a slightly higher failure stress of 8.5 ± 3.5 MPa and failure strain of 0.34 ± 0.12% were measured.

In the case of compression loading, the specimens always failed in the foam top region (\( g(y) = 0 - 0.2 \)). The compression strength did not depend on the pore gradient direction, i.e. if the sample was mounted in foaming direction or bottom up. The specimens always failed in the region with the lowest fractional density but did not show catastrophic fracture behaviour, Fig. 14(a). During loading the foam sample collapsed in a periodic manner with an approximate period of 5%. With increasing strain the...
Young's modulus raised as indicated by the systematic variation of the slope of the regression line. This is in accordance to the theoretical prediction that the Young's modulus of the foam $E^*$ is expected to increase with increasing fractional density $\rho_f$ [66]:

$$\frac{E^*}{E_s} = C \cdot \rho_f^{3/2}, \tag{21}$$

where $C$ is a geometrical constant set to 1 and $n = 1.4$ as in agreement to literature data [67]. $E_s$, the Young's modulus of the dense strut material is a material-dependent constant. Fig. 14(b) shows the crushing strength $\sigma_{cr}$ of samples that were ground from the top to different heights ($g(y) = 0.23, 0.34, 0.46, 0.57, 0.68, 0.80$ and 0.91) and therefore obtained different minimum fractional densities whereas the maximum fractional density remained constant at 0.52 for all specimens. Foams with a minimum fractional density of $\rho_f = 0.1$ obtained $\sigma_{cr} = 0.9 \pm 0.3$ MPa. The compression strength increased with increasing minimum fractional density. At half-height samples $g(y) = 0.5, \sigma_{cr} = 4.3 \pm 1.5$ MPa at a fractional density of 0.27. This is in agreement with data from homogeneous ceramic foams of the same composition and pyrolysis temperature [68]. At 8 mm high samples with a $\rho_f = 0.4$, a crushing strength of 8.6 $\pm$ 1.3 MPa was achieved.

The fractional strength of a brittle porous material $\sigma^*/\sigma_s$, where $\sigma^*$ is the failure strength of the ceramic foam and of a porous ceramic and $\sigma_s$ of the dense strut material can be expressed as a function of the fractional density [66]:

$$\frac{\sigma^*}{\sigma_s} = C \cdot \Phi^3 \cdot \rho_f^{3/2} + C'(1 - \Phi) \cdot \rho_f, \tag{22}$$

$\Phi$ is the fraction of the material located in the struts whereas $1 - \Phi$ is the material located in the cell faces of closed cells. $\Phi$ depends on $g(y)$. At $g(y) = 0$, the foam is fully open celled and $\Phi = 1$. $C$ and $C'$ are empirical constants and were set to 0.2 and 0.18, respectively, according to former results [69]. Eq. (22) can be expressed as a function of $g(y)$ and $\rho_f(y)$:

$$\sigma^*(g(y)) = \sigma_s \cdot \left(0.2 \cdot \Phi(g(y))^3 \cdot \rho_f(y)^{3/2} + 0.18 \cdot (1 - \Phi(g(y))) \cdot \rho_f(y)\right) \tag{23}$$

As $g(y)$ and $\rho_f(y)$ depend on $T$ and the foam height, $\sigma^*(y)$ can be controlled by setting the temperature $T$ and adjusting the height $h$. The modulus of rupture $\sigma_s$ of the strut material was calculated to be 146 $\pm$ 32 MPa at $g(y) = 0$. At $g(y) = 1, \sigma_s$ equals $103 \pm 33$ MPa. This is in good agreement to the fracture strength of dense silicon oxycarbide glass (153 MPa) [70] and of the modulus of rupture of the strut material of polymer derived ceramic foam filled with $\text{Al}_2\text{O}_3$ (90 $\pm$ 45 MPa) [71]. The theoretical prediction of Eq. (23) as a function of the fractional density $\rho_f$ is plotted in Fig. 14(b) and was confirmed by the experimental data. The structure independent modulus of rupture $\sigma_s$ of the strut material remains constant at 125 $\pm$ 20 MPa.

4. Conclusions

Si–O–C gradient foams were fabricated in a single step manufacturing process using in situ foaming of porous Si/ SiC loaded poly silsesquioxane. A porosity gradient was generated by variation of the foaming temperature. While the cell shape and the fractional density vary linearly with the foam height, the surface/volume ratio, the connectivity density and the mean strut thickness scale exponentially. The crushing and the bending strength are determined by the lowest fractional density of the material.

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