Small molecular polysilazanes were developed in our laboratory as a low friction coating for industrial sliding applications. These coatings are particularly advantageous for near-net shaping in the tribological field and were introduced into the market. The potential of pyrolytic silicon nitride (Si3N4) ceramic coatings on surfaces sliding against similar polymer-derived ceramics testifies to their potential in micro electro mechanical system (MEMS) applications. However, the potential of polymer-derived ceramics and ther-mosetting polymers with low friction properties is largely due to their good cross-linking. This cross-linking results in a stable Si/C/N polymer matrix with low friction properties. The Si/C/N polymer matrix is a good candidate for self-lubricating coatings on sliding surfaces. However, the potential of polymer-derived ceramics and ther-mosetting polymers with low friction properties is largely due to their good cross-linking. This cross-linking results in a stable Si/C/N polymer matrix with low friction properties. The Si/C/N polymer matrix is a good candidate for self-lubricating coatings on sliding surfaces.

**Abstract:**
The utilization of silicon-based polymers as a source of amorphous non-oxide ceramics obtained upon pyrolytic treatment of them is increasingly gaining attention in research and is currently expanding into the field of commercial products. This work is focused on the near-net shaped fabrication, mechanical and tribological properties of a polymer-derived Si/C/N system. Small sub-millimetre thick ceramic test discs and bars were fabricated by casting of polysilazane and/or polyacarbadion precursor mixtures into elastomeric polydimethylsiloxane forms, thermal cross-linking and subsequent pyrolysis. Additional carbon was introduced on the molecular level using triphenylvinylsilane as the precursor, its cross-linking with the polymers via hydrosilylation prohibits phase separation of graphite. The characteristic strength of nearly 700 MPa along with stable low friction coefficients in sliding against similar polymer-derived ceramics testifies to their potential in micro electro mechanical system applications.
Mechanical and tribological properties of polymer-derived Si/C/N sub-
millimeter thick miniaturized components fabricated by direct casting

Field of the invention

The invention relates to Polymer-derived ceramics (PDCs). PDCs are a relatively new class of non-oxide structural and functional materials gaining increasing interest from research and industry. The soft nature of the starting polymeric materials provides a unique opportunity for fabrication of various shapes (e.g. by liquid moulding), which are converted into rigid ceramic structures upon curing and subsequent pyrolytic treatment at 600 - 1000°C. The tailoring of the chemical structure of the starting polymeric precursor at the molecular level and varying pyrolysis conditions enables adjustment of the resulting composition, microstructure and properties. This approach was successfully commercialized for fibers (e.g. Tyranno Fiber®, Nicalon™) and ceramic matrix composites. It is currently extending into the fields of protective and functional coatings, porous bodies, filaments and is anticipated to gain a niche in fabrication of miniaturized components.

Background of the invention

Current micro electro mechanical system (MEMS) technology is mostly based on silicon, whose modest mechanical and tribological properties necessitate the identification and development of new alternative materials. Fabrication of various PDC fine structures based on variations in lithographic and soft lithographic techniques was reported over the last decade. However, in order to pave the way for a broad use of PDC MEMS, the state of their mechanical and application-specific properties, e.g. tribological should be validated. Similar to diamond and DLC, PDCs show
low wear friction coefficient in mild operating conditions and seem to be promising candidates for MEMS. However, the contact pressures in small moving and sliding parts can exceed maximal acceptable Hertzian stresses and lead to severe friction and wear conditions, causing failure.

Among the broad spectrum of preceramic polymers, the family of liquid CERASET® polysilazane precursors which lead to silicon carbonitrides has so far attracted highest attention in the PDC research community, being as well the material of choice for most of the works devoted to PDC MEMS. Additionally silicon oxycarbide and glassy carbon MEMS were presented. Remarkably, polycarbosilane which is industrially used for fabrication of the SiC matrix, i.e. is a polymer-derived Si/C system, in disc brakes and is thus promising for other frictional applications has not yet come into the focus of MEMS research.

In the few systematic studies on tribology of PDCs it was shown in the CERASET®-derived Si/C/N system that a transition from mild to severe wear regime occurs after reaching a threshold contact pressure. The attractive frictional properties in a mild wear regime were attributed to the free carbon. However, the question of optimal composition in the Si/C/N with respect to strength, friction and wear as well as the requirements and limitations imposed by these materials on engineering applications remain open.

Perhaps the main obstacle, which precludes comprehensive and exhaustive characterization of intrinsic properties of PDCs is the difficulty in fabrication of monolithic macro-sized test specimens, the latter is due to cracking caused by substantial gas evolution and shrinkage during pyrolysis. The majority of test specimens containing a PDC matrix were produced using fillers and/or pressing techniques which are not suitable for MEMS fabrication and the results of these studies are affected by processing steps. The method of pressure casting reported by Shah and Raj and modified by Janakiraman seems to present a breakthrough in the problem. Its applicability for MEMS is however yet to be proven.
While it appears possible to produce components, these are not satisfactory in terms of their mechanical resistance and their tribological properties.

Here we report on fabrication of polymer-derived ceramic sub-millimetre-thick components by a direct casting method suitable for production of MEMS and their characterization with respect to strength and friction behaviour.

Summary of the invention

The aim of the present invention is to fully or partially remedy the disadvantages indicated above by proposing a novel type of precursors suitable for use in forming reinforced ceramic micromechanical components.

The invention relates to the utilization of silicon-based polymers as a source of amorphous non-oxide ceramics obtained upon pyrolytic treatment of them. This invention is focused on the near-net shaped fabrication, mechanical and tribological properties of a polymer-derived Si/C/N system.

Small sub-millimetre thick ceramic test discs and bars were fabricated by casting of polysilazane and/or polycarbosilane precursor mixtures into elastomeric polydimethylsiloxane forms, thermal cross-linking and subsequent pyrolysis. Additional carbon was introduced on the molecular level using triphenylvinylsilane as the precursor, its cross-linking with the polymers via hydrosilylation prohibits phase separation of graphite. The characteristic strength of nearly 700 MPa along with stable low friction coefficients in sliding against similar polymer-derived ceramics testifies to their potential in micro electro mechanical system applications.

On this basis, the invention relates to a ceramic polymer precursor including a polymer-derived Si/C/N system characterised in that it further includes a polymer-derived Si/C system and at least one carbon-rich
chemical substance in order that precursor fabrication inherits strength from polymer-derived Si/C/N system, stiffness from polymer-derived Si/C system and decreased coefficient of friction from said at least one carbon-rich chemical substance.

The peculiarity and advantage of the present invention is the fact that all components are present in low-viscous liquid or soluble state, which allows the fabrication of various complex structures by numerous and versatile techniques including microfabrication. The homogeneous distribution of carbon and silicon carbide components enables smooth defect-free surface and high strength.

According to other features of the invention:
- the precursor includes 49-79 wt.% of said polymer-derived Si/C/N system, 10-40 wt.% of said polymer-derived Si/C system and it includes 2-20 wt.% of said at least one carbon-rich chemical substance;
- said polymer-derived Si/C/N system includes at least one polysilazane sequence;
- said polymer-derived Si/C system includes at least one polycarbosilane sequence;
- said at least one carbon-rich chemical substance includes triphenylvinylsilane.

The invention further deals with a process for the production of a micromechanical component made of reinforced ceramic material, characterised in that it includes the following steps:

a-b) producing an improved ceramic polymer precursor;
c) filling a mould with the shape corresponding to the future micromechanical component using said improved ceramic polymer precursor;
d) conducting, at least partially, a reticulation of said precursor in order to form a green compact without graphitization;
e) de-moulding the green compact;
f) conducting a pyrolysis operation to obtain the reinforced ceramic micromechanical component inheriting strength and stiffness from ceramic matrix and decreased coefficient of friction from embedded amorphous carbon and/or graphene.

According to other features of the invention:
- the process includes a step a): providing a polymer-derived Si/C/N system, a polymer-derived Si/C system and at least one carbon-rich chemical substance and a step b): stirring all elements to manufacture improved ceramic polymer precursor;
- the process further includes, between step b) and step c), the step g): mixing a cross-linking initiator to promote reticulation of step d);
- said precursor includes 0.1 -5 wt.% of said a cross-linking initiator;
- said a cross-linking initiator includes I,1'-azobis-cyclohexanecarbonitrile;
- the pyrolysis is conducted between 1100°C and 1450°C in a low pressure inert gas atmosphere in order to avoid cracking;
- the mould cavity is less than 1 mm deep in order to avoid bloating.

**Brief description of the drawings**

- Figure 1 represents load-deflection curves of 3-point-bending tests of green preceramic bars (20 x 2.2x 0.25 mm) (1) based on 100 % of Ceraset® PSZ 20 (mixture C), 2) with addition of 60 wt. % of SMP-10;
- Figure 2a represents casted and cross-linked transparent polysilazane disc and resulting ceramics: intact bar and disc (left), cracked disc (right);
- Figure 2b represents surface of disc from figure 2a pyrolized under high flow rate of nitrogen reveals severe chipping;
- Figure 2c represents convex (left) and concave (right) discs pyrolized under moderate flow rate (~5 cm³/min) of nitrogen;
- Figure 3 represents thermogravimetric curves of cross-linked specimens with compositions given in Table 1;
- Figure 4 represents absorption spectra of powdered specimens A and B reveal higher amount of Si-N bonds in material B as a shoulder in short-wavelength region of Si-C band;
- Figure 5 represents X-Ray diffraction pattern of ceramic A pyrolyzed at 1370°C;
- Figure 6 represents Weibull plot for 3-point bending tests of rectangular bars (20 mm x 1.5 mm x 0.18 mm) of material A;
- Figure 7a represents the evolution of coefficient of friction during continuous sliding against alumina counter body as compared to SiC derived from SMP-10 both at 1N load and 5 mm/s sliding velocity;
- Figure 7b represents the evolution of coefficient of friction during continuous sliding against alumina and against SiC with 5% of additional carbon (F) at both at 5N load and 5 mm/s sliding velocity;
- Figure 7c represents the evolution of coefficient of friction during continuous sliding counter body derived from SMP-10 with ca. 10% of additional carbon (mixture E) in sliding against A and B both at 1N load and 10 mm/s sliding velocity.
- Figure 8a represents a wear track of Sample A after sliding against alumina (1N, 14mm/s, 100m) directly after testing;
- Figure 8b represents a wear track of Sample A after sliding against alumina (1N, 14mm/s, 100m) after removing of debris in ultrasonic bath;
- Figure 9a represents a comparison of wear tracks on sample B after sliding against alumina (1N, 14mm/s, 100m);
- Figure 9b represents a comparison of wear tracks on sample B against SiC derived from SMP-10 (1N, 5mms);
- Figure 10a represents EDX spectra taken on wear track of sample B from center ("C" on Figs. 9a);
- Figure 10b represents EDX spectra taken on wear track of sample B from lateral sediment spurs ("L" on Fig. 9a).
Detailed description of the preferred embodiments

The objective of the invention is to provide a new type of ceramic polymer precursors intended for the production of a micromechanical component that can withstand elevated mechanical stresses. In particular, studies are directed towards application to a moving part for a timepiece, for which is sought a mechanical resistance of more than 500 MPa, a coefficient of internal friction of less than 0.2 and a surface roughness, wherein the peak-to-valley distance (Ra) is less than 25 nm.

Moreover, with respect to the process for producing the micromechanical component that preferably uses a mould, it is also necessary that the viscosity of the precursor must be comprised between 2 and 200 mPa.s and, preferably, around 50 mPa.s, in order to facilitate filling the mould, i.e. to prevent the precursor from trapping air in the corners of the mould.

During the study it was found that it is possible to meet all the above conditions by chemically modifying a precursor by incorporating carbon-rich substances. The base precursor preferably contains at least one polysilazane sequence such as e.g. the product Ceraset® polysilazane 20 from Kion®. However, polyureasilazane products can be used as an alternative such as the Ceraset® polyureasilazane from Kion®.

In fact the ceramic obtained by pyrolysis of this improved precursor contains amorphous carbon and/or graphenes that decrease quite considerably its coefficient of friction in particular.

It has been found that there is a large variety of carbon-rich substances that can be incorporated into the base precursor, as soon as they incorporate linker groups, reacting chemically with hydrosilyl, vinyl or allyl groups of the base polysilyzane precursor. The most suitable linker moieties of carbon-rich substances are hydrosilyl and vinyl groups attached to the silicon atom. The carbon-bearing moieties of the said carbon-rich substances are preferably aryl, phenyl or naphthyl groups. Hence,
inclusions are possible with the following commercially available substances, among others:

- Triphenyl vinyl silane:

- Diphenyl silane:

- Triphenyl silane:

- Allyl-triphenyl silane:

- Phenyl silane:

- Diallyl-diphenyl silane:

- 1,3,5,7-Tetravinyl-1,3,5,7-tetramethyl-cyclotetrasilazane:
1,3,5-trivinyl-1,3,5-trimethyl-cyclotrisilazane:

\[
\begin{array}{c}
\text{H} \\
\text{Si} \\
\text{N} \\
\text{Si} \\
\text{N} \\
\text{Si} \\
\text{H} \\
\text{Si} \\
\text{N} \\
\text{Si} \\
\text{N} \\
\text{Si} \\
\text{H}
\end{array}
\]

1,3-divinyl-1,3-diphenyl-1,3-dimethyl-disilazane:

\[
\begin{array}{c}
\text{phenyl} \\
\text{Si} \\
\text{N} \\
\text{Si} \\
\text{N} \\
\text{Si} \\
\text{phenyl}
\end{array}
\]

tetravinyl silane:

\[
\begin{array}{c}
\text{Si} \\
\text{Si} \\
\text{Si} \\
\text{Si}
\end{array}
\]

It has also been found that the inclusions can be facilitated by increasing the concentration of Si-H reactive groups in the mixture of the base precursor and carbon-rich substance. This is achieved by adding at least one polycarbosilane sequence, for example. In the case where the carbon-rich substance contains triphenylvinylsilane (TVPS) said polycarbosilane is preferably of the type SMP-10 from Starfire® Systems.

Following said inclusions of 2 to 20% of at least one carbon-rich substance, i.e. after chemical improvement of the base precursor, the improved precursor can be used for the production of a micromechanical component.
The invention uses commercially available liquid preceramic polymers selected for this study were Ceraset® polysilazane 20 (Clariant Charlotte, NC, USA) and allylhydridopolycarosiliane SMP-10 (Starfire® Systems, Malta, NY, USA). Triphenylvinylsilane (TVPS). The source of additional free carbon was purchased at ABCR GmbH (Karlsruhe, Germany). In order to promote reticulation a cross-linking initiator in amount of 0.1 to 5 wt.%, preferably 0.3 to 1 wt.% is dispersed in the precursors. 1,1’-azobis(cyclohexanecarbonitrile) was used as radical initiator for thermal cross-linking of polymeric precursors (Sigma-Aldrich, Buchs, Switzerland).

Two-component elastomeric polydimethylsiloxane (PDMS) Sylgard® -184 (Dow Corning, Midland, USA) was used for replication of soft molds from a SU-8 (MicroChem Corp., Newton, USA) photoresist master. All chemicals were used as received without any purification or modification.

The manufacturing method according to the invention uses a master SU-8 structures with dimensions of 20 mm x 2.1 mm x 0.3 mm (bars) and 20 mm (diameter) x 0.3 mm (discs) on silicon wafers were created by means of lithography. For the fabrication of PDMS moulds two components of Sylgard® -184 with mass ratio 1:10 as prescribed by the vendor were mixed, degassed under 2 - 4 mbar vacuum for 15 minutes and poured onto a silicon wafer bearing the complementary SU-8 master pattern. After manual tilting of the wafer for a uniform distribution of PDMS, the wafer was placed into a drying box and the temperature was increased to 140°C with a heating rate of 20 - 40°C/h and held for 2 hours. After cooling the PDMS replica was gently peeled off, cut into circles of 50 mm diameter and glued with the unstructured side onto 7 mm thick PTFE discs, which act as a rigid support for flexible PDMS. For the fabrication of thicker (0.6 mm) PDC specimens the corresponding cavities were grinded directly in PTFE discs (depth -0.8 mm).
Table 1. Composition of precursor mixtures

<table>
<thead>
<tr>
<th>Sample</th>
<th>PSZ 20 [wt.%]</th>
<th>SMP-10 [wt.%]</th>
<th>VTPS [wt.%]</th>
<th>R.I. [wt.%]</th>
<th>Pyrolysis</th>
<th>Hv 0.5 [GPa]</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>49</td>
<td>40</td>
<td>10</td>
<td>1</td>
<td>1370°C, Ar, closed boat</td>
<td>11.2 ± 0.3</td>
<td>2.29</td>
</tr>
<tr>
<td>B</td>
<td>79</td>
<td>10</td>
<td>10</td>
<td>1</td>
<td>1370°C, N₂, open boat</td>
<td>13.5 ± 0.7</td>
<td>2.27</td>
</tr>
<tr>
<td>C</td>
<td>99</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1370°C, Ar, closed boat</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>D</td>
<td>0</td>
<td>99</td>
<td>0</td>
<td>1</td>
<td>1370°C, Ar, closed boat</td>
<td>12.6 ± 0.3</td>
<td>–</td>
</tr>
<tr>
<td>E</td>
<td>0</td>
<td>89</td>
<td>10</td>
<td>1</td>
<td>1370°C, Ar, closed boat</td>
<td>13.7 ± 0.5</td>
<td>–</td>
</tr>
<tr>
<td>F</td>
<td>0</td>
<td>94</td>
<td>5</td>
<td>1</td>
<td>1370°C, Ar, closed boat</td>
<td>14.0 ± 0.3</td>
<td>–</td>
</tr>
<tr>
<td>H*</td>
<td>59</td>
<td>40</td>
<td>0</td>
<td>1</td>
<td>1370°C, Ar, closed boat</td>
<td>9.5 ± 1</td>
<td>–</td>
</tr>
</tbody>
</table>

* 0.6 mm thick samples, casted in PTFE

The precursors were mixed in the proportions given in Table 1, using for the sake of homogeneity and process acceleration a small ultrasonic horn (5W) for 30-60 second (liquid is heated up to 60°C). The mixtures were degassed at 0.3-0.5 mbar for 20-30 minutes whilst intensively stirring (800-1 100 rpm) and thereafter cast using a micropipette into previously lubricated (with silicon grease) PDMS moulds. The usefulness of the degassing procedure is dictated by the fact that both preceramic polymers contain volatile oligomers and slowly expel hydrogen and/or ammonia even during normal storage, causing macroporosity and even bloating of the samples upon heating and evaporation of dissolved volatile species. Caution was paid to the volume injected into the mould cavities in order to minimize the meniscus built on the top. For the fabrication of PDC counter
bodies for tribological tests, drops of precursor were placed directly onto PTFE support without PDMS.

It is also thus possible, amongst other things, to form a resin mould by photolithography, a silicon, quartz or corundum mould by dry or wet engraving. Moreover, filling is conducted by any process such as e.g. injection, casting, sputtering or even pressing. The mould is preferably agitated and/or compressed in order to restrict the trapping of gas in the improved precursor.

Due to the high contact angle between polymers and PTFE the drops do not spread and solidify during cross-linking in the form of hemispheres. The latter being pyrolytically converted into ceramics were glued onto an aluminium pin and fixed to a strain gauge in a tribometer (see next paragraph). The filled supported moulds are stacked onto each other and transferred into a hermetically tight Buchi miniclave chamber (Buchi AG, Uster, Switzerland) which is evacuated and flushed with argon twice. Thereafter, Ar pressure of 3 bar is applied and the chamber is heated to the target temperature of 165-175°C over 4h period using a silicon oil bath and kept at 175°C overnight for cross-linking in order to form a green compact. More generally, the reticulation is achieve by prolonged (2-96h), preferably 8-36h action of heat, at temperature 70-220°C, preferably 140-190°C. Additionally, action of UV-light might be applied before thermal reticulation.

After cooling the solidified samples are released mechanically from the moulds, placed into open or closed SiC boats and pyrolyzed in an alumina tube furnace (Carbolite STF 16/610, Carbolite Ltd., Hope Valley, UK) under flowing nitrogen (Alphagasl, purity 99,999%) up to the target temperature. The heating and cooling rates were 0.45 and 3.3 K/min respectively, the annealing time was 2h.

More generally, the pyrolysis is preferably conducted in a controlled atmosphere such as e.g. an inert (nitrogen, argon, etc.) or vacuum atmosphere, in the temperature range of 1000° to 1450°C. The heating rate
is in the range of 0.5 to 10 K.h⁻¹, preferably from 10 to 60 K.h⁻¹. The dwell time at the maximal temperature is 0 to 96h and, preferably, from 2 to 12h.

The strength of rectangular specimens was measured on a Zwick-testing machine Z005 (Zwick GmbH, Ulm, Germany) in 3-Point-bending mode using a 8 mm span, 0.2 N preloading force and 0.5 mm/min cross-head speed. The data were processed according to two-parameter Weibull statistics using maximum likelihood regression. Fracture toughness was measured according to single edge V-notched beam method on four 0.6-mm bars of material H (Table 1). For this purpose a -0.1 mm deep notch was polished in the middle of the bars using a steel razor blade and diamond grinding paste. The bars were loaded in 3-Point bending mode (I-mode) similarly to the strength tests described above.

Hardness was measured on a Leitz Durimet microhardness tester equipped with a Vickers indenter using a 500 g load. A home-made tribometer comprising of a linear actuator and strain gauge detecting the tangential force was used for friction measurements. The disc specimens were glued onto the stage driven by the actuator, the counter body was loaded with a prescribed weight, fixed to a strain gauge and was brought in contact with the specimen to achieve sliding friction. FT-IR spectra were measured on a Golden Gate ATR. Scanning electron micrographs were acquired on VEGA Tescan (Brno, Czech Republic) using acceleration of 10 kV and secondary electron detector.

Fabrication PDC specimens by direct casting and pyrolysis

The compositions of samples used for this study (Table 1) are dictated by the aim to reveal the effect of the precursor on the process of fabrication, the microstructure, mechanical and tribological properties of macroscopic PDCs. The fabrication of freestanding test specimens faces several challenges which arise from expelling of volatile species and shrinkage during both stages of cross-linking and pyrolysis. Among the series of Ceraset ® products, the Polysilazane 20 has a lower difference
between densities of liquid and cured solid compared to polyureasilazane. In order to minimize shrinkage during cross-linking and tensions associated with it, we chose the former one. The SMP-1.0 polycarbosilane has a density of ~1.0 g/cm³ both in the raw and cured states.

The challenge of gas expulsion and bloating can be addressed by keeping the thickness of the polymer layer below 0.7 mm while using degassing and a slow uniform heating as described in the experimental section. The peculiarity of the presented approach is the absence of hermetically tight pressurized moulds used in and thus its suitability for MEMS. Further challenges of cracking and/or deformation arise during the stage of pyrolysis and were described in literature. Variation of experimental parameters (composition, heating- and gas flow rates, sample geometry and dimensions, holder etc.) allowed us to ascertain the origin of forces acting on a specimen during pyrolysis leading to a non-uniform shrinkage within the specimen and discern external and internal factors affecting form fidelity.

The external factors are those conditions of pyrolysis, which determine the uniformity of heat distribution and its transfer to the sample, i.e. thermal conductivity of the specimen holders, length of the heating zone and gas flow rate. The flow of inert gas which protects specimens from oxidation was in our experiments the main source of temperature perturbations and must be reduced to the minimum level, yet remain high enough to maintain low overpressure inside the tube and prohibit air entrapment into the heating zone.

Internal parameters inherent to the specimen are the stiffness of the green body, presence of curvature and the aspect ratio. Thicker discs were less prone to warpage than the thinner ones. Additionally, we found that the degree of deformation correlated with the content of SMP-1.0 precursor and thus with flexibility of the green bodies (Fig. 1.). Furthermore, discs and bars with larger diameters and length respectively were more deformed, than those with smaller linear dimensions.
The direction of warpage during pyrolysis was predetermined by the curvature of the surface, which stems from the meniscus built on the top of the liquid prior to solidification. Positive curvature (derived from convex meniscus) as well as the negative one (concave meniscus) increased in magnitude during pyrolysis affecting also the initially flat counter side. Flat samples (negligible curvature) being exposed to considerable temperature gradient, e.g. created due to a high flow rate of inert gas experienced extensive cracking (Fig. 2).

Small cracks on the edge of flat specimens grew, if the latter were exposed to non-optimized pyrolysis conditions. These deformations occurred at temperatures below 500 °C, cracks appeared in the range 540 - 570 °C. These observations could be explained as follows. The temperature gradient which is created along the sample due to external factors of limited thermal conductivity and/or due to cooling by a stream of inert gas causes different shrinkage and stresses within it. Larger samples were exposed to larger differences in temperature on the opposite ends and offered leverage for warpage-causing tensions, whereas high stiffness (E-Modulus) and thickness of the samples (internal factors) resist deformation. The presence of positive or negative curvature of the surface (with Laplace pressure directed outwards or inwards respectively) triggers the direction of forces determining thus the convex or concave form of the sample and relieves the tensions.

**Phase composition**

Carbon species, homogeneously distributed within an amorphous Si/C/N matrix are regarded as the lubrication component in PDCs. On the other hand, poor mechanical and wear properties of graphite should restrict its content for structural applications and necessitate the possibility of controlled introduction of carbon into the starting materials. This can be achieved using triphenylvinylsilane (TVPS) as the carbon source which is soluble in preceramic polymers and bonds to them during cross-linking via
hydrosilylation. As a result of the bonding, the conservation of carbon from TVPS is achieved, as indicated by thermal gravimetry (Fig. 3), which shows increased ceramic yield compared to pristine polysilazane or polycarbosilane.

Increased polycarbosilane content leads to a SiC-enriched sample A, the sample B shows detectable amount of Si-N bonds (Fig. 4). X-Ray diffraction pattern (Fig. 5) reveals β-silicon carbide nanocrystals and amorphous carbon. The absence of graphite crystalline phases in carbon-enriched material A, treated at temperatures as high as 1370°C is remarkable since the formation of graphite is usually observed at 1200°C. Mutin has shown, that the chemical structure of amorphous Si/C/O system depends only on brutto-composition and is developed via redistribution reactions between SiCₓO₄ₓ tetrahedral. Analogously, one could expect redistribution reactions between SiCₓN₄₋ₓ tetrahedra and formation of mixed silicon carbonitrides from polysilazane and polycarbosilane moieties.

However, the precipitation of silicon carbide (even for materials with low content of polycarbosilane) suggests, that the possibility of chemical interaction between silazane and carbosilane fragments is limited during pyrolysis and SiC and Si/C/N derived from corresponding precursors exist in separated domains. This can be explained by the macromolecular nature of the starting materials, which are presented mostly as entangled chains even under/after intensive shear during mixing. The cross-linking further restricts the chain mobility and low diffusion coefficients of amorphous Si/C/N/H hybrid materials (duromers) and make either redistribution reactions or graphitization of carbon not possible.

The pyrolysis conditions influence the composition as well and whereas pyrolysis under a stream of nitrogen (specimen B) results in silicon carbonitride ceramics, the treatment under standing atmosphere consisting predominantly of expelled hydrocarbons, leads to carbon enriched SiC (specimen A). These variations along with the polycarbosilane content
determine the composition of the Si/C/N and have a strong effect on the tribology.

**Mechanical properties**

The difficulties in direct fabrication of monolithic carbon- and silicon-based test samples have restricted characterization of their intrinsic mechanical properties so far. A characteristic strength of 1100 MPa for polished pressure-casted Ceraset®-derived ceramics was reported. However, the microstructure, particularly the porosity of PDCs is highly process-related and any variations in the preparation steps make the mechanical properties difficult to predict. For the samples prepared in the present study the 3-Point bending tests (Fig. 6) revealed a characteristic strength of approximately 700 MPa, which slightly exceeds that obtained for unpolished pressure-casted samples prepared by Shah.

In our experiments the variations in content of SMP-10 in the range of 0 - 50 wt. % and pyrolysis temperature (1130 - 1370°C) did not affect the strength significantly and slight variation in the value could be mostly attributed to the statistical nature of the parameter. Indeed, the relatively low Weibull modulus of 6.1 in the present work resembles highly probabilistic behaviour of glass fibers, whereas pressure-casted samples by ref. 23 revealed higher (polished) or lower (unpolished) flexural strength. For such low toughness materials the surface finish of the specimens is the key factor with respect to strength and the small size of MEMS should make them an appropriate niche for PDCs' application.

It was also possible to fabricate 0.6 mm thick bars of composition H for SEVNB, whilst thick samples with other compositions usually suffered from cracking during pyrolysis. The material H reveals toughness of $1.3 \pm 0.2$ MPa-m$^{1/2}$. This value roughly corresponds to that evaluated by Janakiraman et al. for a Ceraset®-derived Si/C/N annealed at the same temperature range. To the best of our knowledge it is the first report on
fracture toughness of monolithic filler-free Si/C/N PDCs measured by
SEVNB mode-I loading technique.

Tribological properties

The potential of PDCs for tribological applications was recognized
nearly a decade ago. In systematic studies on polysilazane-based systems
the increase of performance with increasing annealing temperature was
reported and the material of the counter body, either alumina or steel, was
found to be irrelevant to the characteristics of friction. In the present study
PDC counter bodies revealed a lower CoF compared to alumina and the
difference was more pronounced with increasing load (Fig. 7a, 7b).

This observation can be attributed to the higher carbon content in the
contact zone and/or reduced Hertzian contact stress due to a lower
Young's Modulus of amorphous PDCs compared to alumina. Indeed, the
content of TVPS-derived carbon in the pin lowers the CoF against material
A (Fig 7a and 7c). The SiC-enriched sample A performs better than B (Fig 7c),
one of the possible explanations is the thermal conductivity of nanocrystalline SiC which results in faster heat dissipation. Remarkable
here is the absence of a soft graphite phase (Fig. 5) despite the presence of
additional carbon source (TVPS) indicating efficiency of cross-linking
reactions in impeding graphitization.

The amorphous carbon is an excellent lubricating constituent, which
does not suffer from poor mechanical properties as its graphitic counterpart.
The measured hardness (Table 1) supports this conclusion. All the
materials tested reveal comparable hardness, which is far below that of 15-
26 GPa obtained by Shah et. al., but slightly exceeds that measured in ref.
24. The strong impact of pre-pyrolytic processing and other parameters on
mechanical properties has been stressed by Janakiraman and we believe
that the remarkably lower hardness of material H (Table 1) has to be
attributed to the increased thickness of the test specimens (0.6 mm vs. 0.2
mm for the rest of the samples).
The comparison of the materials pyrolized in argon demonstrates that the secondary additives for Ceraset®, i.e. polycarbosilane and/or TVPS, have a slightly positive effect on hardness. We attribute increased hardness of B compared to A to the partial nitridation of the surface of the former material. It also contributes to the large scattering of the measured hardness and reduced frictional properties.

SEM observation of the wear tracks reveals a peculiar behaviour of the debris: in contrast to the wear track of material A (Fig. 8), which is covered and probably thus protected by debris, the aluminium-containing debris are shifted to the periphery in the sample B (Fig. 9, Fig. 10). This continuously exposes fresh surface to the friction stresses leading to a greater degree of wear.

Thus, according to the invention, small PDC objects with one of the dimensions below 1 mm can be fabricated by direct casting, cross-linking and pyrolysis of polysilazanes and polycarbosilanes. Adjustment of the matrix composition and content of additional carbon can be achieved by proper choice of matrix precursors and pyrolysis conditions. The resulting ceramics reveal considerable strength (~700MPa) and low coefficient of friction (<0.1) in sliding against PDCs. Decrease of CoF is achieved by increase of carbon and/or SiC content. This combination of properties is highly promising for MEMS applications.

Example

6 g of Ceraset® Polysilazane 20 (Clariant Charlotte, NC, USA), 3g of allylhydridopolycarbosilane SMP-10 (Starfire® Systems, Malta, NY, USA), 1g of Triphenylvinylsilane (ABCR GmbH, Karlsruhe, Germany) and 0.1 g of 1,1′-azobis(cyclohexanecarbonitrile) (Sigma-Aldrich) were mixed in the 25-ml vial using for the sake of homogeneity ultrasonic horn during 30-60 second (liquid is heated up to 60°C). Hence, solution includes ca. 59 wt.% of Ceraset® Polysilazane 20, ca. 30 wt.% of SMP-10, ca. 10 wt.% of TVPS and ca. 1 wt.% of cross-linking initiator.
The resulting mixture is evacuated at 0.3-0.6 mbar for 20-30 minutes whilst intensively stirred (800-1100 rpm), and thereafter casted PTFE moulds. The filled moulds are transferred to a hermetically tight chamber. The chamber is heated to the target temperature of 165-175°C and kept overnight.

After cooling the cured solidified samples are released mechanically from the moulds, placed into SiC boots and pyrolyzed under flowing Nitrogen up to the 1350°C with heating rate of 10 K.h⁻¹ and dwell time of 6h. After cooling (with rate of 300 K.h⁻¹) the pieces revealed average flexural strength of 0.6 GPa, maximal surface roughness Ra of 20 nm and coefficient of friction 0.03-0.08 against itself and 0.15-0.2 against alumina.

It is understood that the present invention is not restricted to the illustrated example, but is capable of various variants and modifications that will be evident to a person skilled in the art. In particular, other base precursors and/or other carbon-rich substances and/or other additions are conceivable.

Moreover, other applications than a moving part in or outside the field of watchmaking are also conceivable because of the improved mechanical qualities of the ceramic obtained as a result of the invention.

Finally, other processes for the production of the reinforced ceramic that do not necessarily use a mould are also conceivable.
CLAIMS

1. Ceramic polymer precursor including a polymer-derived Si/C/N system characterised in that it further includes a polymer-derived Si/C system and at least one carbon-rich chemical substance in order that precursor fabrication inherits strength from polymer-derived Si/C/N system, stiffness from polymer-derived Si/C system and decreased coefficient of friction from said at least one carbon-rich chemical substance.

2. Precursor according to the preceding claim, characterised in that it includes 49-79 wt.% of said polymer-derived Si/C/N system.

3. Precursor according to the preceding claim, characterised in that said polymer-derived Si/C/N system includes at least one polysilazane sequence.

4. Precursor according to any of the preceding claims, characterised in that it includes 10-40 wt.% of said polymer-derived Si/C system.

5. Precursor according to the preceding claim, characterised in that said polymer-derived Si/C system includes at least one polycarbosilane sequence.

6. Precursor according to any of the preceding claims, characterised in that it includes 2-20 wt.% of said at least one carbon-rich chemical substance.

7. Precursor according to the preceding claim, characterised in that said at least one carbon-rich chemical substance includes triphenylvinylsilane.

8. Process for the production of a ceramic polymer precursor, characterised in that it includes the following steps:

   a) providing a polymer-derived Si/C/N system, a polymer-derived Si/C system and at least one carbon-rich chemical substance;
b) stirring all elements to manufacture improved ceramic polymer precursor.

9. Process according to the preceding claim, characterised in that it includes 49-79 wt.% of said polymer-derived Si/C/N system.

10. Process according to the preceding claim, characterised in that said polymer-derived Si/C/N system includes at least one polysilazane sequence.

11. Process according to any of the preceding claims 8 to 10, characterised in that it includes 10-40 wt.% of said polymer-derived Si/C system.

12. Process according to the preceding claim, characterised in that said polymer-derived Si/C system includes at least one polycarbosilane sequence.

13. Process according to any of the preceding claims 8 to 12, characterised in that it includes 2-20 wt.% of said at least one carbon-rich chemical substance.

14. Process according to the preceding claim, characterised in that said at least one carbon-rich chemical substance includes triphenylvinylsilane.

15. Process for the production of a micromechanical component made of reinforced ceramic material, characterised in that it includes the following steps:

a-b) producing an improved ceramic polymer precursor according to any of claims 8 to 14;

c) filling a mould with the shape corresponding to the future micromechanical component using said improved ceramic polymer precursor;

d) conducting, at least partially, a reticulation of said precursor in order to form a green compact without graphitization;

e) de-moulding the green compact;
f) conducting a pyrolysis operation to obtain the reinforced ceramic micromechanical component inheriting strength and stiffness from ceramic matrix and decreased coefficient of friction from embedded amorphous carbon and/or graphene.

16. Process according to the preceding claim, characterised in that it further includes between step b) and step c), the step:
   g) mixing a cross-linking initiator to promote reticulation of step d).

17. Process according to the preceding claim, characterised in that said precursor includes 0.1 - 5 wt.% of said a cross-linking initiator.

18. Process according to the preceding claim, characterised in that said a cross-linking initiator includes 1,1'-azobis-cyclohexanecarbonitrile.

19. Process according to any of the claims 15 to 18, characterised in that the pyrolysis is conducted between 1100°C and 1450°C in a low pressure inert gas atmosphere in order to avoid cracking.

20. Process according to any of the claims 15 to 19, characterised in that the mould cavity is less than 1 mm deep in order to avoid bloating.
Fig. 7a

- disc: A; pin: alumina
- disc: A; pin: D

Fig. 7b

- disc: A; pin: alumina
- disc: A; pin: F