Advancements in Polymer-Filler Derived Ceramics

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ABSTRACT

Microstructure tailoring of filler loaded preceramic polymer systems offers a high potential for property improvement of Si-based ceramics and composites. Advancements in manufacturing of bulk materials by controlling microstructure evolution during thermal induced polymer-ceramic transforma-tion and polymer-filler reactions will be presented. Rate controlled pyrolysis, multilayer gradient laminate design and surface modification by gas solid reaction are demonstrated to yield ceramic compo-

Key words : Polymer-filler derived ceramics, Rate controlled pyrolysis, Surface modification

1. Introduction

Tailoring of composition and molecular structure combined with excellent plastic shaping technologies offers a great potential for development of advanced materials from organo-silicon based polymer precursor systems.\(^1\) Polymer derived ceramics with compositions in the system Si-C-N-O (-M) with M = B, Al, Ti, Zr, etc. offer excellent thermal stability\(^2\) as well as interesting electrical, piezoelectrical, magnetical, optical and chemical properties.\(^1\) While up to temperatures of approximately 1200°C an amorphous structure of Si atoms bonded tetrahedrally to C, N, or O and containing nanoscale domains of carbon (graphene like turbostratic carbon) dominates, major crystal-line phases at higher temperatures are SiC, Si\(_3\)N\(_4\), Si\(_2\)N\(_2\)O, SiO\(_2\) and graphitic carbon or Si, Fig. 1.

Maximum values for Young’s modulus of 155 GPa, Vickers hardness of 26 GPa, fracture toughness of 3 MPa\(_m\)\(^{1,2}\), and fracture strength of 1100 MPa can be found in literature.\(^3\) A superior creep resistance at temperatures even exceeding 1500°C\(^4\) was attributed to the evolution of a nanodomain network of graphene which was hypothesized to support stress even at very high temperatures.\(^5\) These property values, however, often were measured on specimens of very small volume (a few mm\(^3\)) or low dimensionality (fibers, coatings) applying nano-techniques. Current applications are therefore mainly limited on low dimensional product shape such as high temperature resistant fibers,\(^6,7\) coatings,\(^8\) joints and seals,\(^9\) micro- and macro-cellular foams,\(^10\) sensor sheets\(^11\) and micro electro-mechanical systems (MEMS).\(^12\)

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Reduction of porosity and dimensional changes associated with the polymer to ceramic conversion is achieved by loading reactive fillers (metals, intermetallics, ceramics), Fig. 2. Upon thermal degradation the fillers may react with the solid polymer residue and the gaseous decomposition products to form carbides, nitrides, oxides, or mixtures thereof.\(^1\) Volume dilatation of the polymer phase may be compensated by an appropriate expansion of a filler reaction phase.\(^1\) Grain boundaries between the filler reaction phases are formed which generate a rigid skeleton stabilizing the shape and size of a component during thermally induced transformation from polymer to ceramic. Furthermore, release of volatile decompositions products which cause pore formation is reduced and yield of ceramic residue increases significantly.

### 3. Rate Controlled Pyrolysis

Evaporation of volatile decomposition products during pyrolysis of the polymer precursor phase is a critical step in microstructure evolution during thermal induced polymer-to-ceramic conversion. Above approximately 300-400°C an interconnected pore network is formed (transient pore network) which provides transport path for evolution of gaseous decomposition products (H, CH\(_x\), C\(_3\)H\(_y\), ...). At temperatures above 600-800°C this transient pore network tends to shrink by viscous flow and sintering.\(^1\) Depending on the polymer precursor composition and the pyrolysis conditions a minimum of porosity may be attained in the amorphous ceramic residue at 1000-1200°C.\(^1\) SiO and CO are the major gaseous species that form on polysiloxane based precursor polymers at temperatures higher than 1000°C. With increasing component size, however, porosity reduction suffers from volume dependent constraints of mass-transport which often may result in large pores and cracks. Impediment of mass trans-

\[
\nabla \sigma_{ij} = \varepsilon \nabla p
\]

(1)

Once the mechanical stress reaches a critical threshold corresponding to the strength of the filler-loaded polymer body flaw formation and cracking is likely to occur. Rate controlled pyrolysis envisages a constant polymer degradation rate (e.g. weight loss rate \(\alpha = -\frac{dw}{dt} = A \exp (-E/RT)\) for first order reaction) in order to control the evaporation pressure during polymer-to-ceramic conversion. Keeping the internal gas pressure \(p_i\) of a pore in the centre of a body with distance \(L_x\) from surface \((p_s)\), Fig. 3, below a critical threshold value \(p_{crit}\) an upper limit of evaporation rate \(a_{ev}\) may be derived:\(^2\)

\[
\alpha_{ev} \leq A \frac{k_s}{L_x^2 T} \left[ \frac{p_{crit}}{p_0} \right]^2 - 1
\]

(2)

\(T\) is the temperature and \(k_s\) the permeability of the polymer residue (given by Kozeny-Carman-equation \(k = \frac{\varepsilon^3}{k(1-\varepsilon^3)S^2}\)) where \(\varepsilon\) denotes the porosity, \(S\) is the specific surface and \(k\) is a constant). \(A\) is a constant taking into account density and viscosity of evaporating gaseous species. Since evolution of strength with temperature and degree of polymer degradation is not known a multi-step heating program was derived based on thermogravimetric analyses data.\(^2\) Thus for example, for a polymethylsiloxane body loaded with 40 vol % filler a linear decomposition rate \(\alpha \approx 0.003 \% / \text{min}\) was found to yield crack free and homogeneous residue products for \(L_x = 10\) mm. Fig. 3 shows that in the temperature regime (300-600°C) where maximum decomposition rate creates a maximum in gas pressure the heating rate has be limited to values lower compared to temperatures below and above this period.

Equ. (2) shows that \(a_{ev}\) scales inversely with the square of the transportation length \(a_{ev} \propto 1/L_x^2\), and hence bulk compo-
nents of large volume require extremely low evaporation rates $\alpha_{\text{crit}}$ and extended pyrolysis cycle periods $t_{\text{pyr}}$.

$$t_{\text{pyr}} = \int_{w_0}^{w_1} \frac{dw}{\alpha_{\text{crit}}}$$ (3)

Fig. 4 displays the correlation of total pyrolysis period with component dimension (e.g. $t = A^* L^x$). Rate controlled pyrolysis, however, may achieve significant improvement in reducing pyrolysis cycle period and producing low porosity and crack free microstructure.

4. Multilayer Laminate Design

Three layer sandwich type multilayer structures were manufactured from filler (40 vol%) loaded polymethylsiloxane tapes pyrolysed in reactive $N_2$-atmosphere at a peak temperature of 1400°C. The sandwich specimens were composed of 8-10 layers with a mean individual tape thickness of 0.5 mm. The core was covered symmetrically by one or two tape layers. $Si_2N_2O$ was detected by XRD in the outer surface layer as a reaction product. Both modulus of rupture measured by 3 ball on 1 ball method (two dimensional loading) as well as fracture toughness measured by indentation technique revealed a pronounced variation with multilayer design, Fig. 5. Compared to multi-layer specimens composed of the same precursor composition only the sandwich type specimens attained higher fracture stress and toughness values with maximum values exceeding twice the values of the non-graded reference materials.

Residual stress profiles perpendicular to the surface were derived from measurement of strain relaxation upon removing surface layer by strain gauge technique. Making use of thermal expansion mismatch between the outer surface layer (Si 30 - SiC 10, CTE $\approx$ 3.8 ppm/K) and the core region (Si 10 - SiC 30, CTE $\approx$ 4.7 ppm/K) cooling from pyrolysis temperature (1400°C) generated two dimensional compression surface stresses balanced by moderate tensile stress in the core, Fig. 6. Maximum compression stresses of $\sigma_z = -30$ MPa and moderate tensile stresses $\sigma_{z=0} \leq +5$ MPa were detected with the point of stress inversion located at a surface distance $z_0 = 0.8$ mm which corresponds to the thickness of the two surface layer. Even though the residual compression stresses measured are relatively low, reduction of surface porosity and defects will be favoured and are supposed to promote improvement of mechanical properties. Furthermore, the higher Si filler content on the surface results in a higher fraction of nitridation product phases ($Si_2N_2O$, $Si_3N_4$) when annealed in $N_2$-atmosphere at temperatures exceeding 1200°C which give rise for enhanced density, strength and toughness.
5. Surface Crack Healing and Densification

Substantial changes in microstructure are attributed to the specific volume expansion associated with a nitridation reaction on the surface of filler loaded preceramic polymers. While nitridation of Si-O-C based ceramic residue was reported to require temperatures exceeding 1200°C significantly lower reaction temperatures below 1000°C were observed in the presence of catalytically active metal silicide fillers (MeSi₂ with Me = Fe, Cr, V, ...). Thermochemical calculations of equilibrium phase compositions for a polysiloxane filled with carbide and metal silicide fillers indicate, that Si₃N₄ and Si₂N₂O are the major nitridation reaction products with their stability regions extending to higher pyrolysis temperatures with increasing N₂-pressure applied, Fig. 7. Since N₂-activity is high on the surface but low in the core of the body the nitridation reaction zone is limited to the surface with a penetration depth of 20 µm upon annealing at 1300°C for 2 h.

Thus, in the region of nitridation reaction volume expansion may give rise for reduction of porosity and healing of cracks. In order to demonstrate the healing capacity a micro-indent crack pattern was prepared by Vickers indentation on a pyrolysed and ground filament surface. After annealing in flowing nitrogen at 1300°C for 2 h the radial indent cracks were completely filled with nitride reaction product, Fig. 8.

The pronounced volume increase associated with these reactions is likely to promote closure of open cracks and pores. Depending on the ceramic residue composition

\[ \text{SiO}_x\text{C}_y \rightarrow 0.5 \text{SiC} + \frac{x}{2}\text{SiO}_2 + (\frac{x}{2} + y - 1) \text{C} \]  

a volume expansion factor \( \Phi \) may be derived

\[ \Phi = \frac{\sum n_i V_i (\Delta V_{i} + 1)}{V_F^* (1 - V_F^*)} \]  

where \( n_i \) are the mole fractions of species \( i \) (e.g. SiO\(_2\), SiC, C) in the residue composition and \( V_F^* \) denotes the filler volume fraction. Inserting values for PMS derived SiO\(_x\)C\(_y\) of \( x = 3/2 \) and \( y = 1/3 \) and \( V_F^* = 0.4 \) volume expansion factors of \( \Phi \approx 0.024 \) and 0.071 are calculated. For the case volume increase is compensated by linear expansion perpendicular to the surface only e.g. lateral expansion is restricted, the maximum crack opening \( d_{op} \) to be filled by the nitridation reaction product is given by

\[ d_{op} = 2d_N\Phi^{1/3} - 1 \]  

Thus for nitrogen penetration depth \( d_N = 20 \mu m \) as

![Fig. 7. Thermochemical calculation of nitridation reactions (HSC 4.0) for a polymethylsiloxane (50 vol %) loaded with filler (metal silicides + carbides)). For simplicity the diagram only shows the amounts of Si₃N₄ and Si₂N₂O reaction products formed on the surface at different nitrogen pressures (p\(_{N_2}\)), even though major gaseous and condensed phases were considered in the calculations.](image)

![Fig. 8. Scheme of crack healing by nitridation reaction (left); crack healing observed on an indent crack prepared on a metal silicide loaded polysiloxane based system (L. Schlier, 2012).](image)
observed experimentally cracks and large pores with a maximum opening of approximately $d_{op} \approx 1 \mu m$ and $d_{op} \approx 0.3 \mu m$ are expected to be filled with the nitride reaction product resulting from the volume expansive nitridation reactions (4) and (5). For the case that nitridation reaction involves filler nitridation modified equ (7) predicts even larger crack openings that can be filled by the reaction product.

Analysis of cross sections prepared perpendicular to the surface revealed that an indent crack was completely filled with nitride reaction product even at a surface distance of $c_z = 50 \mu m$, Fig. 8. Experimental measurements of porosity distribution confirm the trend of porosity gradient formation upon nitridation treatment. Near the surface a minimum porosity of less than 0.5% compared to significantly higher values in the core region were determined. Removing the surface nitridation reaction layer by grinding and reannealing in nitrogen atmosphere resulted in a complete recovery of the initial modulus of rupture, Fig. 9. Hence, filling of pores and healing of cracks accessible to the nitrogen atmosphere resulted in a complete recovery of the initial modulus of rupture. Fig. 9. Hence, filling of pores and healing of cracks accessible to the nitrogen atmosphere resulted in a complete recovery of the initial modulus of rupture. Fig. 9. 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5. Emerging Fields of Application

Based on pronounced progress achieved in polymer precursor synthesis and manufacturing technologies polymer/filler derived ceramics and composites of variable filler distribution including dispersion, percolation, (surface) layer and porous cellular microstructures were developed, Fig. 10.

Combining functional fillers which provide specific electric, magnetic, and even biological properties with optimized mechanical properties polymer/filler derived material systems have now become of increasing interest for transfer into industrial processes and product developments.

Table 1 summarizes a selection of emerging fields of applications based on wide variation of polymer and filler compositions, microstructures and surface treatments.

Tailoring functional properties of polymer-filler derived ceramics and composites is achieved by adding fillers of specific electrical, dielectrical and magnetical properties. Ceramics with the electrical resistivity varying from insulator ($> 10^8 \Omega \text{cm}$) to semiconductor and to conductor ($< 10^{-2} \Omega \text{m}$) were fabricated by loading silicon or metal silicide fillers into polymer precursor systems of variable composition. Extreme variation of resistivity values were demonstrated by control of the filler inter-particle distance and by inducing formation of a filler (and a turbostratic carbon) percolation network. Stress dependent piezoresistivity of tunneling percolation systems might be of particular interest for development of stress and vibration sensing devices. Based on early development of diesel glow plug recent work focused on pressure and vibration sensor devices as well as heat flux sensors operating at
high temperatures and harsh environment.\textsuperscript{35} Ferromagnetic behaviour was achieved by embedding metal particles (Fe, Mn, Co, Ni) into polysilazanes\textsuperscript{36} or Fe-silicides into polysiloxanes.\textsuperscript{37} Magnetic anisotropy and higher remanent magnetization and coercivity were observed for polysiloxane derived ceramic composite materials. These multifunctional materials could have a wide range of applications, from active structural components to sensing elements in macro- and particularly micro-system applications.\textsuperscript{38}

Composite materials with the mechanical and tribological properties varying in a wide range were investigated for bearing and friction applications. Linear sliding and roller bearings are used in various industries like the food/pharma or semiconductor sector. Ceramic bearings, however, are still a niche product only, due to their high production costs. Polymer-derived ceramics, made out of polysiloxane loaded with inorganic fillers like MoSi\textsubscript{2}, FeSiCr, SiC and Al\textsubscript{2}O\textsubscript{3} offer the opportunity for a cost efficient production of low friction ceramic bearing components, using injection moulding shaping.\textsuperscript{39} Friction elements including brake pads and clutches based on polymer/filler derived multilayer fibre reinforced laminate structures are of interest for lights, rail and heavy weight vehicles as well as high speed train systems and elevators. Distinguished by a significantly lower weight compared to conventional metallic components polymer/filler derived multifunctional gradient structure combining a high wear resistance with superior heat conductivity, toughness, and vibration damping might offer a high potential to be applied in electric powered light weight vehicles.

Since the filler loading allows matching the thermal expansion behaviour and promotes coating-to-substrate bonding a variety of polymer/filler based environmental barrier coating systems were investigated for ceramic as well as metallic substrate materials. Passive filler (ZrO\textsubscript{2}) loaded polysilazane based multilayer coating systems and active filler loaded polysiloxane based multilayer systems were explored for long term protection of steel at temperatures up to 700°C and of super alloys at temperatures exceeding 800°C, respectively.\textsuperscript{40,41} Filler loaded polysiloxanes were demonstrated to show promising properties for joining of silicon nitride based engineering ceramics due to inter-diffusion which causes a homogeneous joint microstructure to develop matching the microstructure and properties of the parent materials.\textsuperscript{42} Low density foams with open cellular microstructure and cell sizes ranging from mm down to a few µm were fabricated from polymer/filler systems. Filling the pore space by squeeze casting of light metals (Al, Mg) was shown to yield interpenetrating phase composites of improved mechanical properties at elevated temperatures compared to the unreinforced metal alloy.\textsuperscript{43} Interface bonding between the metal phase and the ceramic skeleton was triggered by controlled pre-oxidation of Si-filler on the ceramic foam surface and gave rise for significant improve-ment of the crushing strength.\textsuperscript{44}

6. Conclusions

Despite of tremendous progress achieved in processing and shaping of low dimensional and small size polymer derived materials, production of large volume components is still challenging for industrial translation. Microstructure evolution during polymer-to-ceramic conversion by means of inert and reactive fillers is a key aspect in developing polymer derived ceramics with tailored functional and mechanical properties. We have shown that rate controlled pyrolysis may both improve the microstructure and reduce annealing cycle period significantly. Multilayer lamination of precursor tapes differing in degradation and reaction behaviour may offer a high potential for creating materials with tailored surface properties. Furthermore, lamination facilitates formation of materials with multi-functional property combinations. Modification of surface microstructure and composition by annealing in a reactive atmosphere (N\textsubscript{2}) was demonstrated to yield a reduction of porosity and healing of defects resulting in a pronounced improvement of mechanical properties. Since post-fabrication treatment in a reactive atmosphere is independent on the component shape and size, formation of a surface reaction zone with optimized microstructure (reduced porosity and flaws) may offer a versatile route for improving properties of bulk polymer derived components and devices.

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