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Modelling of dimensional changes during polymer–ceramic conversion for bulk component fabrication

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Shrinkage and porosity generation during conversion of polymer–filler systems into ceramic bodies during pyrolysis is examined. In the presence of an inert filler phase such as Si_3N_4 or SiC powder dispersed in an organosilicon polymeric matrix only porous microstructures may be obtained without any shrinkage. By using an active filler phase such as carbide- or nitride-forming transition metals, however, shrinkage of the polymer matrix may be compensated by appropriate expansion of the filler phase. A model is derived to predict the critical volume fractions of various potential active filler systems in inert and reactive gas atmospheres, which can be effective in controlling shrinkage and porosity during the fabrication of ceramic components from polymer-derived precursor materials.

Nomenclature

P	Polymer phase
C	Condensed polymer pyrolysis product (ceramic)
G	Gaseous polymer decomposition product
F	Inert filler phase
T	Active filler phase (e.g. transition metal)
M	Reaction product of active filler phase (e.g. carbide, nitride)
m	Mass
V	Volume fraction
$V_{F,T}^{max}$	Maximum packing density of an inert (F) or active (T) filler powder
$V_{F,T}^{*}$	Critical volume fraction of an inert (F) or active (T) filler powder in the starting polymer–filler mixture
V_v	Residual porosity in the polymer pyrolysis product
V_v^{pf}	Residual porosity in the polymer–inert filler system after pyrolysis
α	Ceramic yield of polymer after pyrolysis
α^{TM}	Weight change of active filler phase during reaction pyrolysis
β	Density ratio of polymer to polymer pyrolysis (ceramic) product
β^{TM}	Density ratio of active filler to filler reaction product
ε^{p}	Linear shrinkage of the polymer phase during pyrolysis
ε^{pf}	Linear shrinkage of a polymer–inert filler system during pyrolysis
ε^{paf}	Linear shrinkage of a polymer–active filler system during reaction pyrolysis
ε^{TM}	Linear shrinkage/expansion of the filler phase during reaction
ρ	Density

1. Introduction

The fabrication of bulk ceramic components from easily shapable polymer precursors has become a subject of increasing interest since organosilicon polymers of high ceramic yield could be synthesized. A variety of polymeric precursors based on polymerized silanes, silazanes, carbosilanes, borocarbosilanes, siloxanes, alanes etc. are now available, suggesting the possibility of making a number of amorphous or crystalline ceramic compounds such as SiC, Si_3N_4, SiO_2, B_4C, AlN and mixtures [1–10]. Different ceramic products could be formed via the polymer pyrolysis route such as powders, whiskers, fibres, foams and coatings [9, 11–15]. These polymers are also considered as a new class of "low loss" binder and plastifier systems in powder processing and shaping of non-oxide powders, as well as for sealing and joining of ceramic bodies [16–18]. Recently, polymer precursors were used to tailor the Si–C–O matrix in continuous fibre-reinforced composite ceramics [19].

While the possibilities of various forms or types of product and potential applications have been discussed, only high-strength ceramic fibres have yet attained greater significance. Due to the large density differences and hence resulting shrinkages between the polymer precursor ($\rho_p \sim 1$–$1.5\ g\,cm^{-3}$) and the ceramic product (C, BN $\rho_c \sim 2.2\ g\,cm^{-3}$; Si_3N_4/SiC $\rho_c \sim 3\ g\,cm^{-3}$), significant limitations for the use of polymer pyrolysis technology for the fabrication of bulk materials and dense matrices in ceramic composites still exist. For example a 60 wt % ceramic yield after pyrolysis of a material having a density of about

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3 g cm^{-3} results in an actual linear shrinkage to a fully dense body of 35%. Since bulk pyrolysis products typically retain a substantial porosity of 30 to 40% [19], about half of the potential shrinkage will be accommodated by porosity and cracks and approximately 10–20% will occur as actual shrinkage.

The use of polymer–filler systems seems to offer a possibility of reducing the inherent problems of shrinkage and porosity formation during polymer–ceramic conversion, as demonstrated with a carborane-derived polymer containing SiC, B_4C or BN particles [20]. Even better shape retention could be achieved with B additives due to converting the excess carbon from the polymeric binder to B_4C. Recently, near net-shape pyrolysis of polymer bodies was successfully performed using carbide-forming transition metals as active filler media in a polysiloxane matrix [21, 22]. The active filler is used to control and tailor the microstructure formation and dimensional changes during polymer–ceramic conversion. Full density and low shrinkage (down to zero) may be achieved by this active filler-controlled polymer pyrolysis (AFCOP) process, even in bulk component fabrication.

It is the object of the present paper to examine the influence of the volume changes of the various fractions in a starting polymer–filler mixture which may exhibit dilatation (polymer), dilatation or expansion (active filler) or remain constant (inert filler) during the pyrolysis process. The ceramic yield of the polymer, the density change from the polymer to the ceramic product, and the volume change of the filler due to carbide or nitride formation are important variables which will be considered in inert (argon) as well as in reactive (nitrogen) atmospheres. Thus, critical conditions for polymer and filler properties and their volume fractions are derived to control the dimensional change of polymer-based precursor systems during pyrolysis.

2. Model derivation

2.1. Single-phase polymer

The pyrolytic degradation of a pre-ceramic polymer precursor (P), like a polysilane, polysiloxane, polysilazane or polycarbosilane results in a series of complex thermally induced processes such as rearrangement, crosslinking and cleavage of carbon–hydrogen bonds which yield condensed (C) and gaseous (G) reaction products:

$$P(s, l) \xrightarrow{\Delta} C(s) + G(g) \qquad (1)$$

During pyrolysis of the polymer body, the mass of the residue is reduced by the loss of volatile species

$$\Delta m = m_P - m_G \qquad (2)$$

and this change in mass defines the ceramic yield

$$\alpha = \frac{\Delta m}{m_P} \qquad (3)$$

Due to the higher densities of the pyrolysed ceramic product(s), ρ_C, compared to the starting polymer, ρ_P, a density ratio may be defined as

$$\beta = \frac{\rho_P}{\rho_C} \qquad (4)$$

Assuming isotropic dimensional change, the total linear shrinkage of a polymer body ε^P may be expressed by the polymer–ceramic transformation variables α and β

$$\varepsilon^P = 1 - \left(\frac{\alpha\beta}{1 - V_v}\right)^{1/3} \qquad (5)$$

where V_v is the residual fraction of pores or voids in the ceramic residue. Fig. 1 shows the calculated linear shrinkage of a polymer body as a function of α and β. For a completely dense product a tremendous shrinkage would be necessary which may prevent the fabrication of larger bulk components. Only for polymer precursors with very high ceramic yield values $\alpha > 0.7$ but small density changes $\beta > 0.7$ would a linear shrinkage smaller than that for conventional sintering ($\varepsilon^s \sim$ 15–20%) be obtainable. For most of the organosilicon polymer precursors the maximum values of α and β do not exceed 0.9 and 0.5, respectively (Table I), suggesting that it is impossible to fabricate a fully dense ceramic product from a polymer precursor without any shrinkage.

2.2. Polymer containing an inert filler phase

Dispersing a non-reactive (inert) filler phase (F) such as Si_3N_4 or SiC powder in the starting precursor reduces the shrinkage according to the reduction of the polymer volume fraction, V_P, which is given as

$$V_P = 1 - m_F\rho_P[\rho_F(1 - m_F) + \rho_P m_F]^{-1} \qquad (6)$$

with

$$V_P + V_F = 1 \qquad (7)$$

V_F, m_F and ρ_F are the volume fraction, mass and

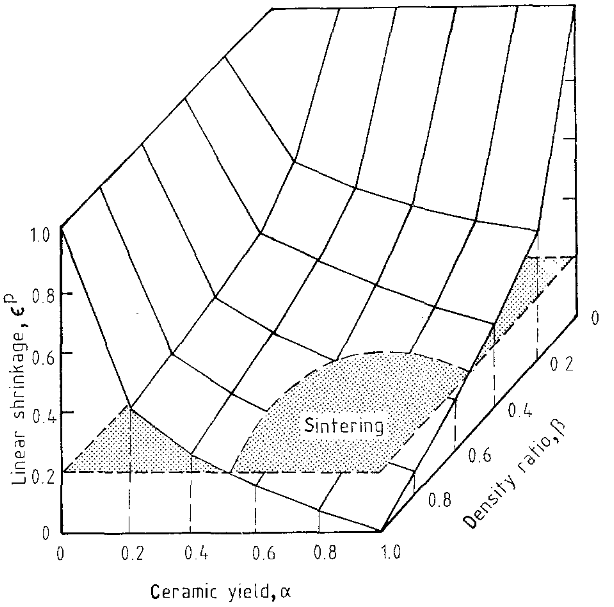

Figure 1 Maximum linear shrinkage of polymer precursor as a function of ceramic yield α and density ratio β (for $V_v = 0$).

TABLE I Pyrolysis properties of organometallic polymers used as pre-ceramic precursor materials

Polymer precursor	Products[a]	Temperature (°C)/atmosphere	α	β	Reference
Hydridopolysilazane	Si_3N_4	1200/N_2	0.74	0.44	[23]
Vinylphenylpolysilazane	Si_3N_4	1000/N_2	0.85		[24]
Polyborasilazane	BN/Si_3N_4	1000/Ar	0.90	0.55	[25]
Polycarbosilane + Al amide	Si_3N_4/AlN	1000/NH_3	0.54		[26]
Polycarbosilane + Al amide	SiC/AlN	1000/NH_3	0.4		[26]
Cyclomethylpolysilazane	Si_3N_4/SiC	1000/Ar	0.88		[15]
Methylvinylpolysilane	SiC	1000/	0.83		[27]
Polycarbosilane + Ti butoxide	SiC/TiC	1400/N_2	0.72		[28]
Methylpolysiloxane	SiO_2/SiC	1000/He	0.85	0.46	[29]
Diphenylpolyborosiloxane	SiC/B_4C	950/Ar	0.45	0.58	[26]
Aminoborazine	BN	1000/Ar	0.55		[30]
Polyiminoalane	AlN	600/N_2	0.42		[31]
Ti propoxide ethanolamine	TiN	1600/N_2	0.85		[32]

[a] In general the pyrolysis products are amorphous and contain various amounts of O and C.

density, respectively, of the filler phase in the starting precursor mixture. The total linear shrinkage of the polymer–filler system, ε^{pf}, may then be expressed by

$$\varepsilon^{pf} = \left(\frac{V_F^{max} - V_F}{V_F^{max}}\right)\varepsilon^{p} \qquad (8)$$

and the residual porosity V_v^{pf} of the pyrolysis product by

$$V_v^{pf} = (1 - V_F)V_v \qquad (9a)$$

for $V_F < V_F^*$ and

$$V_v^{pf} = (1 - V_F)V_v + (V_F - V_F^*) \qquad (9b)$$

for $V_F > V_F^*$. The critical filler loading V_F^* is given if the filler particles form a rigid network on shrinkage of the polymer matrix phase. Thus, V_F^* is always smaller than the maximum packing density V_F^{max} of the same filler powder without polymer. For closest packing of equally sized spheres (f.c.c. or h.c.p.) the value of V_F^{max} is 0.74, which however decreases for random packing with decreasing grain size to $V_F^{max} < 0.5$ [33]. The critical filler volume fraction in the starting precursor mixture, V_F^*, is related to the maximum filler volume fraction in the pyrolysed product by

$$V_F^* = V_F^{max} - (1 - \alpha\beta)(1 - V_F^{max}) \qquad (10)$$

Fig. 2 shows the influence of the filler fraction in the starting precursor mixture on the expected shrinkage and porosity of a pyrolysed polymer–filler system. Three major regions may be distinguished:

(A) at low filler fractions ($V_F < V_F^*$) a dense material may be obtained when the volume change is completely compensated by shrinkage ($V_v = 0$);

(B) above the maximum filler fraction V_F^{max} no shrinkage may occur and the volume change upon polymer pyrolysis is fully accomodated by porosity as shown by mathematical modelling [34];

(C) in an intermediate region ($V_F^* < V_F < V_F^{max}$) both shrinkage and residual porosity will always occur, even if the polymer described as single-phase would pyrolyse to a dense ceramic product ($V_v = 0$).

Fig. 3 schematically shows the microstructure in the three regions A–C which develop upon polymer pyrolysis. Decreasing the difference between V_F^* and V_F^{max} is necessary to evaluate an optimum compositional range where both shrinkage and residual porosity can be minimized.

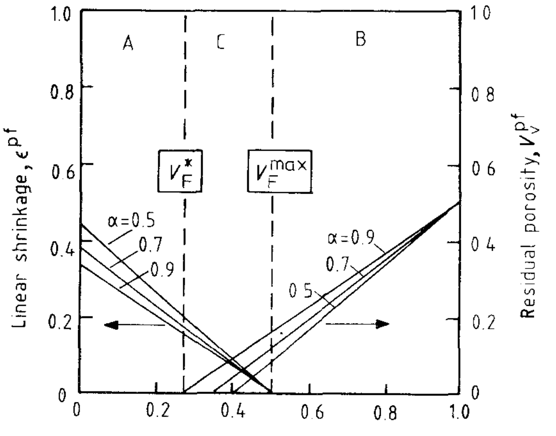

Figure 2 Linear shrinkage and residual porosity of a polymer–inert filler system as a function of the initial filler volume fraction for $V_v = 0$, $V_F^{max} = 0.5$ and $\beta = 0.5$.

2.3. Polymer containing a reactive filler phase

A substantial change of the situation is obtained by using an active filler phase (T) instead or in addition to an inert filler. The active filler phase may react with solid or gaseous decomposition products of the polymer, e.g. carbon (K) or hydrocarbon species (G), to form new carbide phases (M). The volume change can be attributed to the separate reactions of polymer decomposition and active filler reaction according to

$$P(s, l) \longrightarrow C(s) + K(s) + G(g) \qquad (11a)$$

$$T(s) + K(s) + G(g) \longrightarrow M(s) + G'(g) \qquad (11b)$$

$$P(s, l) + T(s) \xrightarrow{\Delta} C(s) + M(s) + G'(g) \qquad (11c)$$

For the case where the active filler also reacts with the gaseous decomposition products of the pyrolysis reaction a gaseous phase G′(g) results which is different to

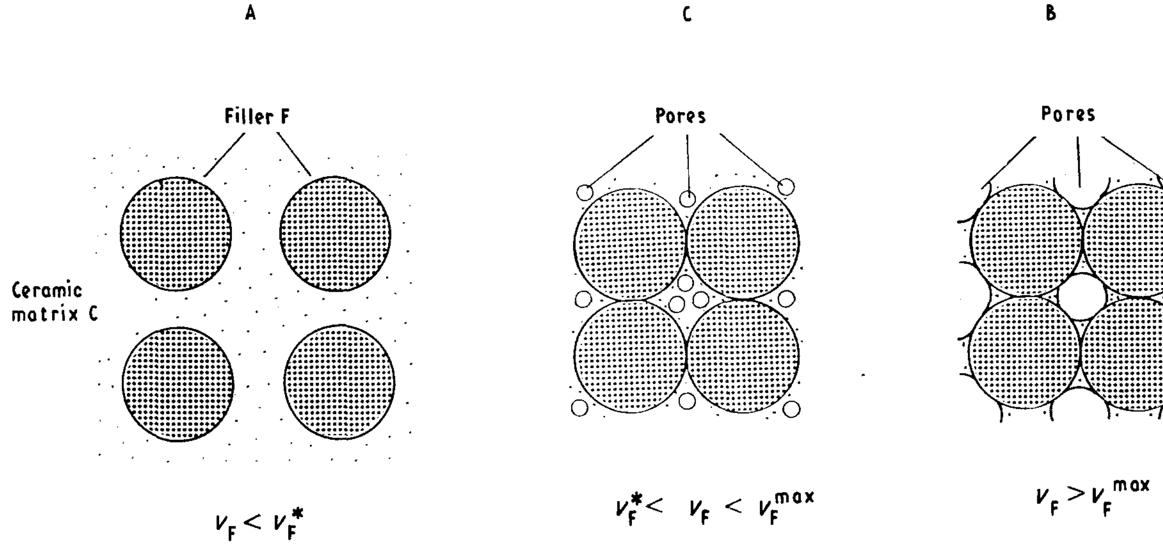

Figure 3 Schematic model of microstructures generated after polymer pyrolysis in systems containing various volume fractions of an inert filler powder.

that released during pyrolytic decomposition of the single-phase polymer. While polymer degradation (Equation 11a) always results in a volume reduction, e.g. shrinkage of a green body, the filler reaction (Equation 11b) may compensate for this shrinkage, if the specific volume of the product phase (M) is larger than the sum of the corresponding volumes of the starting filler phase (T) and the condensed reactant (K). The total linear shrinkage of a polymer–active filler system, ε^{paf}, may then be expressed by

$$\varepsilon^{paf} = \left(\frac{V_T^* - V_T}{V_T^*}\right)\varepsilon^p + V_T\,\varepsilon^{TM} \qquad (12)$$

V_T^* is a critical filler volume fraction in the starting mixture

$$V_T^* = V_T^{max}(3 - \alpha\beta - \alpha^{TM}\beta^{TM}) - (1 - \alpha\beta) \quad (13)$$

which determines the maximum particle packing of the reacted filler phase in the pyrolysed product. ε^{TM} is the shrinkage/expansion value resulting from the filler transformation reaction (Equation 11b) which may be defined by analogy with the single-phase polymer conversion variables by

$$\varepsilon^{TM} = 1 - (\alpha^{TM}\beta^{TM})^{1/3} \qquad (14)$$

The filler yield and the density ratio are given by

$$\alpha^{TM} = \frac{m_M}{m_T + m_K} = 1 + \frac{m_G - m_{G'}}{m_T + m_K} \qquad (15)$$

and

$$\beta^{TM} = \frac{\rho_{T+K}}{\rho_M} \qquad (16)$$

For a filler phase (T) reacting only with the solid carbon (K), for example, $m_G = m_{G'}$ and thus $\alpha^{TM} = 1$; if the filler also reacts with carbon from gaseous species (G) $m_G < m_{G'}$ and hence $\alpha^{TM} > 1$. β^{TM} only exceeds unity if the density of the carbide product (M) is smaller than the overall density of the filler (T) and solid carbon (K) mixture ($\rho_{T+K} = V_T\rho_T + V_K\rho_K$ with $V_T + V_K = 1$).

Equations 12–16 can be used to generate an expression for the filler volume fraction required to achieve a certain shrinkage ε^{paf} as a function of the polymer and filler transformation variables α, β, V_v, α^{TM}, β^{TM} and V_T^*

$$\frac{\varepsilon^{paf}}{\varepsilon^p} = 1 - \frac{V_T}{V_T^*}\left\{1 - \frac{V_T^*}{\varepsilon^p}[1 - (\alpha^{TM}\beta^{TM})^{1/3}]\right\} \quad (17)$$

In Fig. 4 the normalized linear shrinkage $\varepsilon^{paf}/\varepsilon^p$ is plotted versus the normalized filler volume fraction V_T/V_T^*. With increasing filler expansion characteristics ($\alpha^{TM}\beta^{TM} > 1$), the total shrinkage decreases for a given filler volume fraction in the starting mixture. The critical filler volume fraction necessary to attempt zero shrinkage, where polymer shrinkage is fully compensated by the filler expansion, decreases from $V_T/V_T^* = 1$ for $\alpha^{TM}\beta^{TM} = 1$ to approximately 0.6 for $\alpha^{TM}\beta^{TM} = 2$.

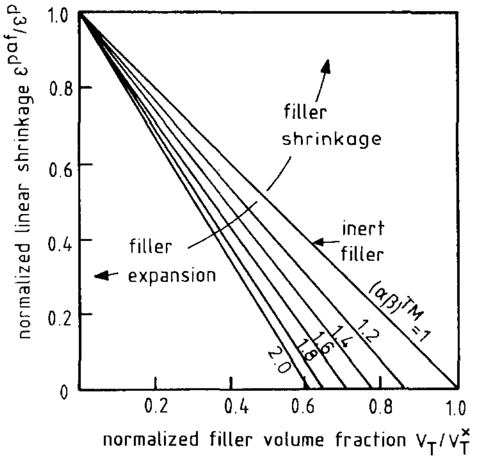

Figure 4 Linear shrinkage of a polymer–active filler system as a function of the filler volume fraction in the starting precursor mixture.

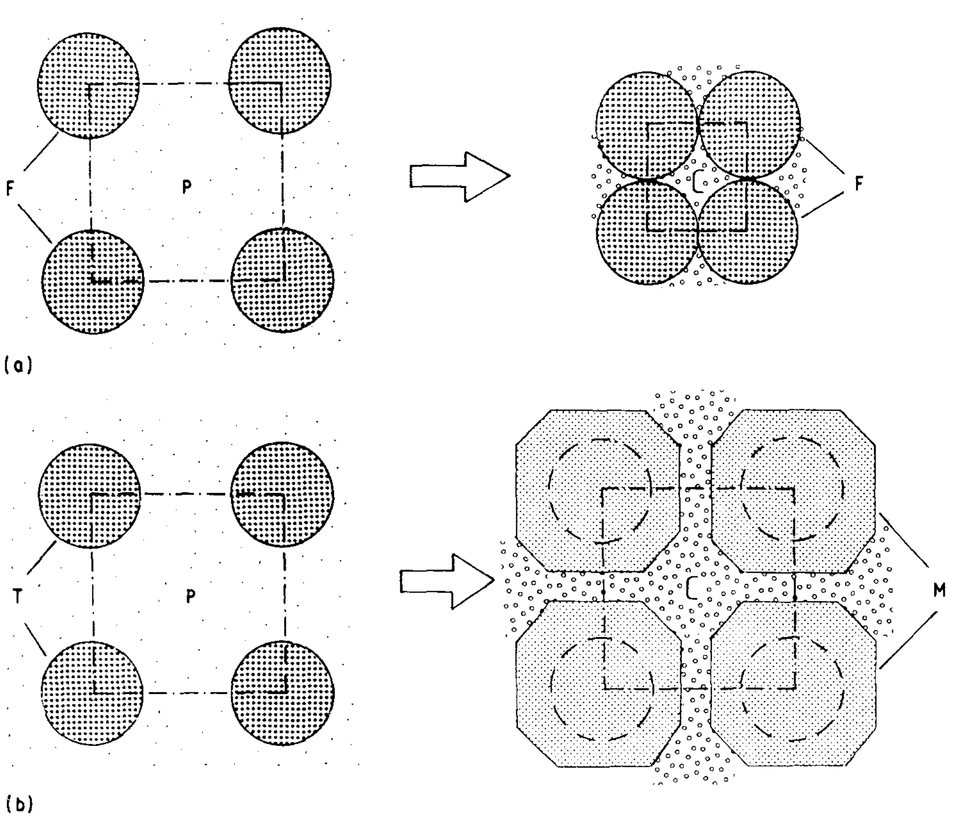

Figure 5 Schematic model of microstructures generated in (a) a polymer–inert filler and (b) a polymer–active filler system, where grain growth of the filler reaction product may avoid shrinkage.

3. Discussion

Fig. 4 shows that near-net shape polymer → ceramic transformation should be possible in the presence of an active filler phase which exhibits a volume expansion upon reaction ($\alpha^{TM}\beta^{TM} > 1$). The critical conditions with respect to the filler transformation behaviour may be derived from Equation 17. Thus, the necessary amount of active filler phase to obtain zero shrinkage is given by

$$\frac{V_T}{V_T^*} = \left\{1 - \frac{V_T^*}{\varepsilon^P}\left[1 - (\alpha^{TM}\beta^{TM})^{1/3}\right]\right\}^{-1} \qquad (18)$$

Equation 13 shows that V_T^* is a function of the polymer $(1 - \alpha\beta)$ and characteristics of the filler volume changes $(1 - \alpha^{TM}\beta^{TM})$, assuming that the spherical shape of the initial filler particles is not changed during carburization, nitridation etc. In contrast to the shape-invariant behaviour of the inert filler particles which do not change their morphology but only their interparticle distances upon polymer pyrolysis, the active filler particles may change their geometry by grain growth (Fig. 5). Hence, excess interparticle volume due to polymer shrinkage may be filled up with the filler reaction product and V_T^* in Equation 13 may be replaced by the maximum particle density of the free filler powder, V_T^{max}, which is only limited by the particle size distribution and particle geometry [33].

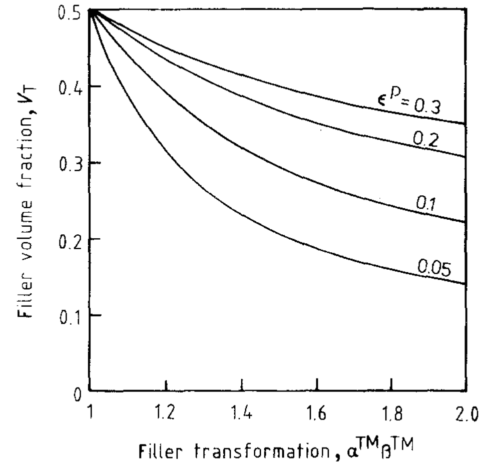

Figure 6 Critical volume fractions of active filler phases to achieve zero shrinkage upon reaction pyrolysis ($V_T^{max} = 0.5$).

Fig. 6 shows V_T versus $\alpha^{TM}\beta^{TM}$ for ε^P ranging from 0.05 to 0.2 and $V_T^{max} = 0.5$, which are typical values for a system of a high-yield polysiloxane [29] containing submicrometre-sized filler particles [34]. If the filler reacts with the solid carbon, K, only $\alpha^{TM} = 1$ and the abscissa value equals β^{TM}. If the filler is however carburized with carbon from the gaseous decomposition product, $m_{G'} = m_{H_2}$ in Equation 14 and $\alpha^{TM} > 1$. If the filler may react with a reactive atmosphere such as CH_4, NH_3 or N_2 to form a carbide or nitride, respectively, α^{TM} may be redefined as

$$\alpha^{TM} = 1 + \frac{m_{C,N}}{m_T} \qquad (19)$$

where $m_{C,N}$ is the mass of the carbon or nitrogen picked up from the reaction atmosphere. Table II summarizes the transformation properties of a variety of potential active filler systems which form stable carbides and nitrides, respectively. The majority of elemental fillers exhibit a volume shrinkage

TABLE II Volume changes upon reaction pyrolysis of potential active filler systems

Filler	$\alpha^{\mathrm{TM}}\beta^{\mathrm{TM}}$		
	Carburization (solid)[a]	Carburization (gaseous)	Nitridation (gaseous)
Elemental fillers			
Ti	0.76 (TiC)	1.14 (TiC)	1.08 (TiN)
V	0.79 (VC)	1.28 (VC)	1.27 (VN)
Cr	0.83 (Cr_3C_2)	1.25 (Cr_3C_2)	1.50 (CrN)
Zr	0.79 (ZrC)	1.09 (ZrC)	1.03 (ZrN)
Nb	0.85 (NbC)	1.27 (NbC)	1.35 (NbN)
Mo	0.95 (Mo_2C)	1.22 (Mo_2C)	[b]
Hf	0.83 (HfC)	1.17 (HfC)	1.04 (HfN)
Ta	0.86 (TaC)	1.27 (TaC)	1.25 (TaN)
W	0.84 (WC)	1.32 (WC)	[b]
Al	1.09 (Al_4C_3)	1.53 (Al_4C_3)	1.26 (AlN)
B	0.93 (B_4C)	1.20 (B_4C)	2.42 (BN)
Si	0.70 (SiC)	1.07 (SiC)	1.13 (Si_3N_4)
Fe	0.88 (Fe_3C)	1.10 (Fe_3C)	1.39 (FeN)
Binary fillers			
TiB_2	1.00 (TiC, B_4C)	1.12 (TiC, B_4C)	2.14 (TiN, BN)
ZrB_2	1.02 (ZrC, B_4C)	1.46 (ZrC, B_4C)	1.95 (ZrN, BN)
HfB_2	1.00 (HfC, B_4C)	1.45 (HfC, B_4C)	1.95 (HfN, BN)
TaB_2	1.10 (TaC, B_4C)	1.72 (TaC, B_4C)	2.46 (TaN, BN)
$MoSi_2$	0.96 (Mo_2, SiC)	1.48 (Mo_2C, SiC)	
FeSi	0.97 (Fe_3C, SiC)	1.47 (Fe_3C, SiC)	
$TiSi_2$	0.90 (TiC, SiC)	1.47 (TiC, SiC)	1.53 (TiN, Si_3N_4)
$CrSi_2$	0.93 (Cr_3C_2, SiC)	1.54 (Cr_3C_2, SiC)	1.23 (CrN, Si_3N_4)

[a] $\alpha^{\mathrm{TM}} = 1$.

[b] Mo and W nitrides decompose at temperatures > 700 °C; volume change $\Delta V/V_0 = \alpha^{\mathrm{TM}}\beta^{\mathrm{TM}} - 1$; densities of the filler and filler reaction products for calculating $\alpha^{\mathrm{TM}}\beta^{\mathrm{TM}}$ were taken from Kieffer and Benesovsky [35].

($\alpha^{\mathrm{TM}}\beta^{\mathrm{TM}} < 1$) upon carburization with solid carbon only. Depending on the polymer composition, reaction with the gaseous decomposition products of the polymer phase (G), however, may increase α^{TM} according to Equation 15, and hence the values for $\alpha^{\mathrm{TM}}\beta^{\mathrm{TM}}$ given in Table II may increase. The monoatomic fillers show a significant volume expansion when carburized or nitrided in a reactive gas atmosphere. For the reaction of Ti with excess solid carbon, for example, a minimum shrinkage of only 0.04 would be estimated for a polymer with $\varepsilon^{\mathrm{P}} = 0.2$ at a maximum possible filler content $V_{\mathrm{T}} = V_{\mathrm{T}}^{\max} = 0.5$. Zero shrinkage, however, should be possible at a filler content of approximately $V_{\mathrm{T}} = 0.4$ when the Ti is nitrided in a reactive gas atmosphere during pyrolysis. Using binary TiB_2 as a reactive filler, zero shrinkage is calculated for internal carburization at $V_{\mathrm{T}} = V_{\mathrm{T}}^{\max} = 0.5$, but at only $V_{\mathrm{T}} = 0.29$ for reaction with external nitrogen resulting in the formation of TiN and BN. An even lower filler volume fraction of $V_{\mathrm{T}} = 0.26$ should be sufficient to achieve zero shrinkage in the case of external nitridation of TaB_2.

Combining both inert and active filler compounds in the same polymer–matrix system offers the possibility of tailoring the shrinkage and residual porosity in a very broad region. In a system with an inert filler the residual porosity after pyrolysis is composed of the retained porosity in the polymer pyrolysis product, V_{v}, and the unfilled interparticle void volume as described by Equations 9 a and b. Therefore a minimum porosity was predicted at a certain polymer/filler ratio [34] which was confirmed by experimental observation of a density maximum in a pyrolysed polysilazane–Si_3N_4 mixture at a polymer/powder ratio of 30 wt % [36]. This ratio corresponds to a volume fraction of polymer which is equal to the volume fraction of voids in a dry-pressed body, $V_{\mathrm{F}}^{\max}$, of the same powder [34].

In contrast to a system with inert fillers, where the general pyrolysis profile was found not to be changed by the filler phase [17], the residual porosity in an active filler-containing system will be dominated by the porosity due only to entrapment of gaseous decomposition products in the polymer pyrolysis product. The porosity is suggested to depend on the fragment size of the gaseous species and the polymer packing density. Typically, the retained porosity was found to be of the order of 0.3–0.4 in the pyrolysis product [9]. While an inert filler will not influence the chemistry of the pyrolysis reaction, an active filler phase is suggested to react with solid and gaseous decomposition products [22]. Thus, the temperature range of polymer decomposition may be changed and large gaseous hydrocarbon species may eventually be cracked, and the gaseous species of smaller molecular size and high diffusivity such as H_2 can escape without forming large pores. In contrast to the polymer systems containing an inert filler, where a finite value of retained porosity was suggested to be necessary to provide transport paths for the volatiles to be removed and to prevent damage of the polymer–filler body during pyrolysis [34], systems containing an active filler may potentially yield dense pyrolysis products of the polymer-derived matrix. A dense Si–O–C–glass forming the matrix phase between TiC particles was obtained by reaction pyrolysis of a polysiloxane–Ti-powder system in argon atmosphere at 1200 °C [22]. Because of the low packing density of the glass network the volatile may migrate as molecules through the structure without forming large pores [29].

Two main strategies for microstructure development of polymer-derived bulk ceramic bodies may therefore be defined with respect to shrinkage and porosity:

(i) fabrication of products with high density and minimized shrinkage seem to be possible with systems containing critical volume fractions of active filler phase(s), and

(ii) fabrication of products with low density but zero shrinkage should be possible with systems containing inert filler phase(s) up to volume fractions that form a rigid skeleton in the precursor mixture.

In addition to the use of pre-ceramic polymer compounds as binder systems to enhance the density and strengths of green ceramic bodies [16, 34, 36–38], new potential applications for ceramic products made of systems containing a high fraction of polymer phase (> 50 vol %) and an inert and/or an active filler phase(s) seem to be exciting. While ceramic materials with filler-controlled porosity which remains unchanged even at high temperatures offer high potential in environmental protection and energy conversion, polymer-derived ceramics of high density may become attractive for application as structural components particularly because of their excellent shaping properties and low reaction temperatures.

4. Conclusions

The volume change which results in pronounced shrinkage and porosity formation and in most cases in damage to bulk bodies is a key problem of polymer–ceramic conversion. In order to develop processing techniques that can be successfully used to fabricate ceramic bodies directly from pre-ceramic polymer compounds, a model has been derived which describes the volume contributions to shrinkage and porosity generation during the pyrolysis of filler-containing polymer precursor systems. Using active filler phases which may react with the decomposition products of the polymer pyrolysis, instead of or in addition to inert filler particles, provides a powerful tool to minimize shrinkage and porosity and to avoid cracking in the pyrolysed product. In addition to the improvement of ceramic yield of the polymer precursor, the use of active fillers (in particular multicomponent transition metal borides and silicides) may offer successful possibilities for near-net shape and low-temperature fabrication of ceramic components from a variety of easily shapable polymer pre-ceramic systems.

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