Journal of the European Ceramic Society **11** (1993) 105–113

Thermodynamics and Microstructural Development of Ceramic Composite Formation by Active Filler-controlled Pyrolysis (AFCOP)

Michael Seibold & Peter Greil*

Technical University of Hamburg-Harburg, Advanced Ceramics Group, D-2100 Hamburg 90, Germany

(Received 6 March 1992; accepted 7 July 1992)

Abstract

Pyrolytic conversion of silicon-containing preceramic polymers to oxycarbide matrix composites may significantly be changed in the presence of active filler dispersoids. The formation of novel oxycarbide composite materials from titanium- and chromium-containing polysiloxane precursors was predicted based on thermodynamic phase equilibria calculations and investigated up to temperatures of 1400°C. During heat treatment the transition metals react with gaseous and solid decomposition products of the polymeric matrix and facilitate the formation of carbide and silicide phases embedded in a silicon oxycarbide matrix. A variety of active fillers may be used to tailor microstructure formation of polymer derived ceramic composite materials in order to make bulk component fabrication with a broad range of compositions and properties possible.

Die pyrolytische Umwandlung von Silizium-haltigen vorkeramischen Polymeren zu einer oxykarbidischen Matrix kann durch die Präsenz von Dispersoiden aktiver Füllstoffe verändert werden. Die Bildung neuer oxykarbidischer Verbundwerkstoffe ausgehend von Titan- und Chrom-haltigen polysiloxanischen Prekursoren wurde auf der Grundlage thermodynamischer Berechnungen der Phasengleichgewichte vorhergesagt und bis zu Temperaturen von 1400°C untersucht. Während der Wärmebehandlung reagieren die Übergangsmetalle mit gasförmigen und festen Zersetzungsprodukten der polymeren Matrix und erleichtern damit die Bildung karbidischer und silizidischer Phasen, die in einer Siliziumoxykarbid-Matrix eingelagert sind, Um die Ausbildung des Gefüges von keramischen Verbundwerkstoffen, die von Polymeren abgeleitet wurden, maßzuschneidern kann eine Reihe verschiedener aktiver Füllstoffe angewandt werden. Auf diese Weise ist die Herstellung umfangreicher Komponenten in einem weiten Zusammensetzungsbereich und in einem weiten Bereich an Eigenschaften möglich.

La conversion pyrolytique de précurseurs polymères contenant du silicium en des composites à matrice oxycarbure peut être fondamentalement modifiée par la présence de dispersoïdes actifs. La formation de nouveaux matériaux composites à partir de précurseurs polysiloxane contenant du titane et du chrome a été prédite sur base de calculs thermodynamiques et étudiée jusqu'à la température de 1440°C. Durant le traitement thermique, les métaux de transition réagissent avec les produits gazeux et solides issus de la décomposition de la matrice polymère et favorisent la formation de phases carbures et siliciures, englobées dans la matrice d'oxycarbure de silicium. Une variété de dispersoïdes actifs peuvent être utilisés pour contrôler le développement de la microstructure de ce type de composites céramiques de telle façon que l'on peut fabriquer des composants massifs présentant une large gamme de compositions et de propriétés.

1 Introduction

Preceramic silicon-containing polymers such as polysilanes, polycarbosilanes, polysilazanes and polysiloxanes have attained particular interest for manufacturing ceramic materials in the system Si–C–N–O.[1] Tailoring of molecular structure and composition of the appropriate starting compound is highly attractive because of its potential to optimize the processing behavior and to fabricate new composite materials. Hence, carbon-rich oxycarbide 'black' glasses with a carbon content more than 10 wt%[2] or molecular TiC/SiC-composites[3] were prepared. Although a variety of silicon-containing polymeric preceramics with high ceramic yields exceeding 80 wt% could be developed,[4] only high strength ceramic SiC(O) fibers have attained greater significance.[5]

---

* To whom correspondence should be addressed.

Journal of the European Ceramic Society 0955-2219/93/$6.00

The tremendous density differences and corresponding shrinkages and/or porosity between the polymeric precursors ($\rho \sim 1\ g/cm^3$) and the desired ceramic products (amorphous C, $\rho \sim 1{\cdot}8$–$2{\cdot}1\ g/cm^3$; SiO_2, $\rho \sim 2{\cdot}2$–$2{\cdot}6\ g/cm^3$; Si_3N_4/SiC, $3{\cdot}2$–$3{\cdot}3\ g/cm^3$), however, still provide significant limitations for the use of polymer pyrolysis technology for the fabrication of bulk components and dense matrices in ceramic matrix composites. Weight loss upon heating of the polymer is associated with the evolution of small, mainly cyclic fragments at fairly low temperatures above ~200°C if the organometallic structure has not been sufficiently cross-linked.[6] With increasing temperature cleavage of chemical bonds with low binding energy[7] results in a maximum of gas evolution in the temperature range of 400–600°C even at low heating rates of ~1°C/min. During the conversion of polycarbosilanes, for example, a variety of gaseous species such as CO, H_2, hydrocarbons (CH_4, C_2H_6, C_6H_6, etc.) and silanes ($(CH_3)_4Si$, $(CH_3)_3SiH$, $(CH_3)_2SiH_2$, etc.) were observed which have to be removed from the precursor by diffusion through a network of pore channels.[8] Therefore, polymer derived bulk ceramic products generally consist of large pores and suffer from extensive cracking. Consequently, only ceramic products with specific dimensional limitations, such as powders, fibers, foams and coatings could be successfully fabricated, whereas bulk components were still not accessible.

The formation of bulk components from organosilicon polymer/active filler mixtures has recently been reported as a novel processing route for the fabrication of ceramic composite materials.[9,10] In the presence of a carbide forming transition metal, such as titanium (Ti) or chromium (Cr) and transition metal silizides and metal borides, the tremendous linear shrinkage encountered during pyrolysis of a pure polysiloxane polymer of typically more than 25% could be drastically reduced below 5%; hence, crack-free bulk components with controlled shrinkage and porosity could be prepared. Modelling of dimensional changes during the polymer–ceramic conversion[11] even shows the possibility to achieve zero shrinkage by adjusting both nature and volume content of active filler phases to the chemical reactions of the decomposition process during pyrolysis. Suitable preceramic polymers may be chosen out of a variety of available ceramic precursors; those with high ceramic yields >75 wt% seem to be favorable. Recently, polysilazanes and polycarbosilanes were also demonstrated to be suitable reactants for the active filler controlled process.[12]

The aim of the present work is to investigate the possibility to manufacture oxycarbide ceramic composites by the incorporation of active filler powders into polysiloxane preceramics. Polymers with Si–O backbone structures offer a broad variety of different molecular weights, commercial availability of both liquid and solid starting compounds and hence low cost. Thermodynamic criteria for the selection of appropriate filler candidates will be compared with experimental results obtained by X-ray diffraction, thermogravimetry and IR-spectroscopy in order to confirm the capability of this novel processing approach.

2 Experimental Procedure

Specimen preparation

Polysiloxane/metal filler composites with 20 vol% of filler loading were prepared from commercially available polysiloxanes (PR 6155 and PR 6163, Petrarch systems, ABCR GmbH, Karlsruhe, Germany) Ti-powders (00961, Alfa Ventron chemicals, Karlsruhe, Germany) and Cr-powders (00685, Alfa Ventron chemicals, Karlsruhe, Germany) (purities considering metallic content >99%). The mean grain sizes of the filler powders were 58 and 25 μm, respectively, as determined by laser granulometry (CILAS 715 E 564, Cilas Alcatel Instruments, Markoussis, France). Filler powders were ultrasonically cleaned in acetone and dispersed in glycerol by vigorous stirring at room temperature. The methylsilsesquioxane (MSS, PR 6155) polymer and phenylpropylsilsesquioxane (PPS, PR 6163) copolymers having a phenyl to propyl ratio of 7:3 were blended on a 2:1 weight ratio basis in order to adjust an initial molar C:Si ratio of >3·5:1 to provide sufficient carbon for the filler conversion, and then dissolved in trichloromethane. The polymer solution was added dropwise to the filler/glycerol suspension. The coated granules (Fig. 1) could be separated from the dispersing agent by filtration and the solvent was stripped off in vacuum at 10^{-1} h Pa. The polymer-coated filler powder was moulded in a die press at 150°C with 30 MPa for 30 min to obtain cylindrical

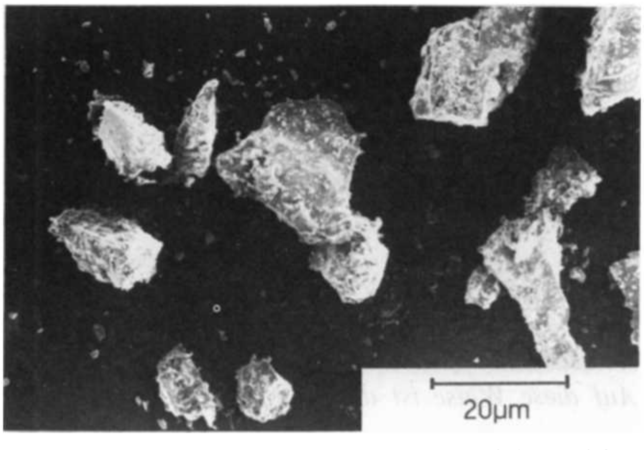


Fig. 1. Granules of polysiloxane- (MP-) coated Cr-particles.

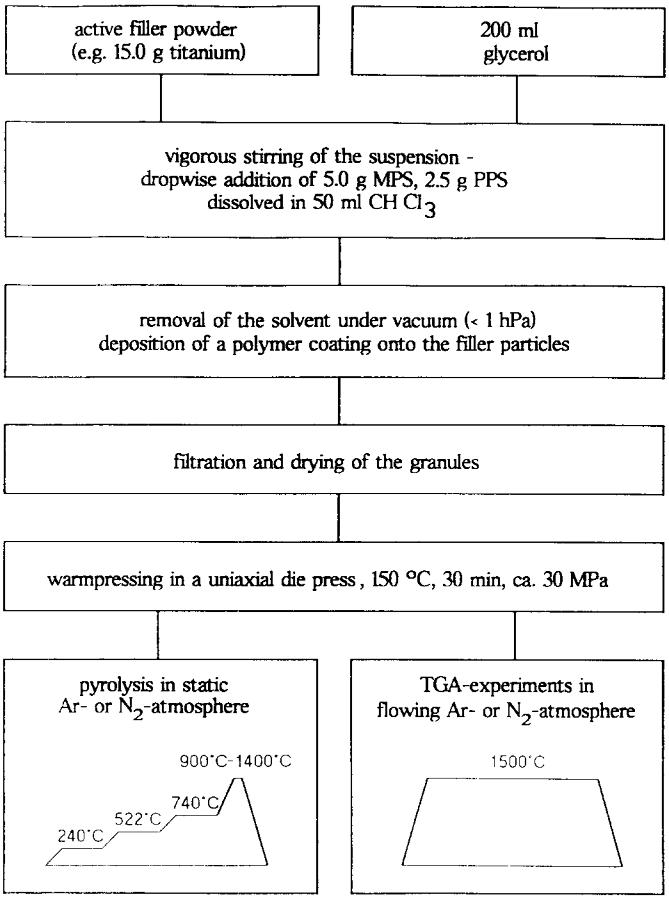


Fig. 2. Fabrication scheme of reaction pyrolyzed composite bodies.

pellets of 25 mm diameter and 2–3 mm height. The flow chart of the processing scheme is shown in Fig. 2.

Pyrolysis experiments were conducted in a resistance heated furnace (Hochtemperaturtechnik, Saarbrücken, Germany) with programmable supplies of both argon and nitrogen (99·999% N_2, used without further purification) in static atmosphere conditions. Prior to heating schedules the furnace was evacuated < 1 h Pa to ensure low oxygen and water contamination from pyrolysis atmosphere. Accurate temperature control was provided by an additional Pt/Pt-10% Rh thermocouple placed directly above the alumina crucibles. Pyrolysis was carried out at temperatures ranging from 900 to 1400°C/1 h with isothermal holds of 5 h at 240, 522 and 740°C and heating rates of 1 and 2°C/min (see Fig. 2).

Analytical methods

IR-spectrometry (Matson Polaris, Matson Instruments, Norwalk, CT, USA) and thermogravimetric analysis (STA 409, Netsch, Selb, Germany) were carried out according to standard procedures to evaluate pyrolysis mechanisms. FTIR-spectra were collected from KBr pellets, while runs in the thermobalance were performed with a heating rate of 5°C/min up to 1500°C, atmospheric conditions were slightly altered; instead of static atmosphere, a flow rate of 25 ml/min was adjusted. Pyrolysis and reaction products were analyzed by XRD (PW 1729, Phillips, Eindhoven, The Netherlands) using monochromated Cu-K$_\alpha$-radiation and examined by energy dispersive spectroscopy (LINK systems AN 10/55 S, High Wycombe, Bucks, UK).

Table 1. Gibbs energies at 927°C[13]

Condensed species	*G° (kJ/mol)*	*Gaseous species*	*G° (kJ/mol)*
C	−18·016	CH_4	−335·095
SiO_2	−1006·262	H_2	−179·352
Cr_3C_2	−282·282	CO	−370·973
CrSi	−165·231	Ar	−201·801
Cr	−49·007		
TiN	−409·413		
TiC	−228·026		
TiSi	−247·093		

Thermodynamic phase equilibria calculations

Prior to sample preparation, thermodynamic phase equilibria calculations of pyrolysis cycle were performed to obtain suitable filler candidates. Equilibrium phase compositions of pyrolyzed filler/polymer blends were calculated in order to estimate the influence of filler content and pyrolysis temperature. The microcomputer program EQUITHERM (VCH Verlagsgesellschaft, Weinheim, Germany) was used to predict a combination of stable phases with the aim to minimize the free energy of the entire system. Equilibrium phase compositions are found by systematic variation of species which are possible and permitted by using iterative methods of linear algebra. Results are presented as plane sections in the compositional space (phase content, filler content, temperature) at a fixed total composition as a function of temperature or at a fixed temperature with respect to the filler content. Thermodynamic data of eight condensed phases and four gaseous phases used in the calculations were taken from Ref. 13 and are summarized in Table 1.

3 Results and Discussion

Thermodynamic considerations

Active filler particles dispersed in the starting polysiloxane precursor may react with various constituents of the decomposing polymer phase during pyrolysis. Using, for example, transition metals as active fillers, carburization processes are facilitated even at low temperatures when carbon bearing species, such as hydrocarbons (CH_4, C_6H_6 . .) or alkyl-silanes ($(CH_3)_3SiH$, $(CH_3)_2SiH_2$. . .),[14] are released at temperatures above 400°C. Crystallization of polysiloxane derived silicon oxycarbide glasses above 1000°C showed the occurrence of C, SiC and SiO_2 as major solid constituents.[15] Hence, some of the simplified possible overall reactions of an active filler Me would be:

$$Me + xC + SiO_2 \rightarrow MeC_x + SiO_2 \quad (1)$$

$$Me + (3-x)C + SiO_2 \rightarrow MeO_x + SiC + (2-x)CO \quad (2)$$

$$Me + 2xC + xSiO_2 \rightarrow MeSi_x + 2xCO \quad (3)$$

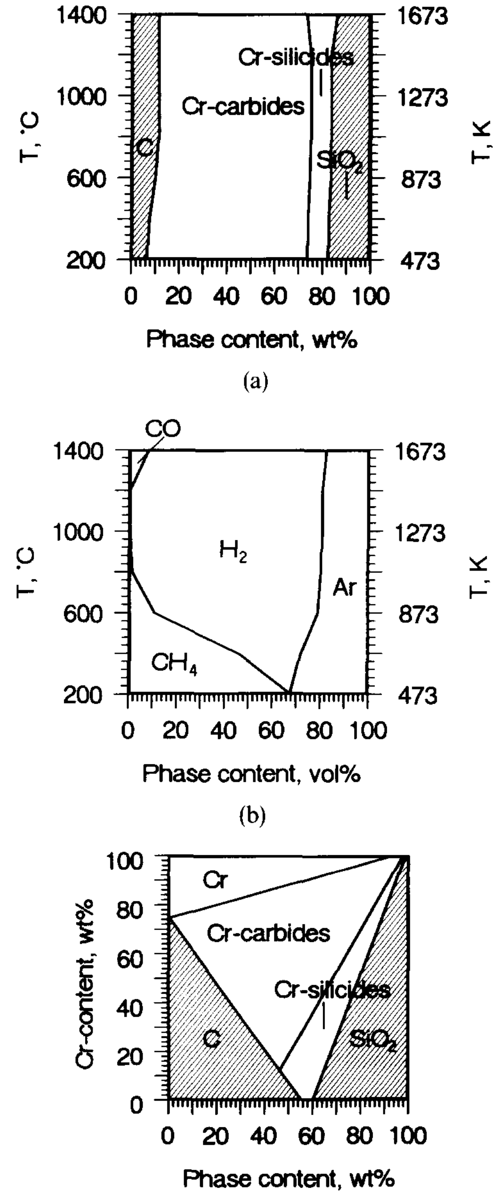
which result in the formation of binary carbides, oxides or silicides of various compositions and the additional release of gaseous CO. Additional ternary oxycarbides and carbosilicides may be formed as stable phases or metastable reaction layers at the filler/matrix interface. Nevertheless, thermodynamic stability criteria for specific filler reaction products may be derived from reactions (1)–(3), at least to a first approximation.

Due to their extremely high melting points, excellent high temperature strength, good corrosion resistance, high hardness and electrical properties,[16] a number of transition metal carbides such as TiC, NbC, Cr_3C_2, TaC and WC seem to be of particular interest for use as reinforcing compounds in carbide and oxycarbide ceramic matrices. In addition, carbide forming active fillers offer potential to gather excessive free carbon which is detrimental to high-temperature (HT) properties like oxididative stability. Thus, the stability of the transition metal carbides versus oxidation or silicate formation may serve as an important criterion to evaluate suitable filler materials to be used in reaction pyrolysis technology. Further conditions are the volume changes[11] or the reaction kinetics encountered during filler transformation.

Following the argument of relative thermodynamic stability at the greatest energy of formation concerning reactions (1)–(3), critical conditions for the filler-carbide or filler-silizide stability during pyrolytic reactions may be established. From the number of possible choices, two active fillers—Ti and Cr—were selected for further investigation. Ti-powders of high reactivity are commercially available at reasonable cost, and phase reactions in the system Ti–Si–C–O have been studied extensively.[17] Cr reveals the greatest energy of carbide formation ($Cr_{23}C_6$) at 1127°C of 413·964 kJ/mol and excellent stability towards thermal decomposition at ambient pressures. An exceptional oxidative stability close to that of SiC has been reported in the literature.[18]

To evaluate the influence of filler content and pyrolysis temperature on stable phase compositions, the pyrolytic reactions of a polysiloxane precursor plus 20 vol% Ti and Cr, respectively, were simulated in the temperature range 200–1400°C. Figures 3(a) and (b) show the calculated phase stability diagrams for an elemental composition of 1·140 mol Cr, 1·649 mol C, 1·881 mol H, 0·370 mol Si and 0·538 mol O which corresponds well to a composition of 20 vol% Cr dispersed in the polysiloxane blend as described in the Experimental Procedure section. To maintain pyrolysis conditions in static inert gas atmospheres, 0·223 mol Ar was added.

Figure 3(a) shows the stable condensed phases; their portions can be read with respect to different temperatures. The hatched area refers to matrix compounds resulting from polymer degradation during pyrolysis; the other phases result from filler reactions. At a temperature range between 200 and 1400°C, Cr-carbides can be expected as a stable phase of filler compound together with Cr-silizide.



(a)

(b)

(c)

Fig. 3. Phase stability diagrams of a bulk composition. (a) Condensed phases. (b) Gas phase: 1·140 mol Cr, 1·649 mol C, 1·881 mol H, 0·370 mol Si, 0·538 mol O. (c) Condensed phases at 1200°C.

SiO_2 and C are stable coexisting phases of a ceramic residue which would result from degradation of the polymeric matrix compound. Phase proportions remain almost constant with respect to pyrolysis temperature; silizide formation becomes more important at temperatures >1000°C.

SiC was not found as part of the stable phase assembly, which is not unexpected since the reduction of SiO_2 by C following reaction (4) is known to occur preferentially at temperatures above 1400°C:

$$SiO_2 + 3C \rightarrow SiC + 2CO \qquad (4)$$

The gas phase composition exhibits methane formation at lower temperatures of between 200 and 800°C and hydrogen contribution at all temperatures (Fig. 3(b)). These calculations correlate well with experimental results previously reported by Cooke.[19] Above 1200°C carbon monoxide was found to occur which is attributed to a decomposition reaction, such as that given in eqn (4) or:

$$SiO_2 + C \rightarrow SiO + CO \qquad (5)$$

To tailor the amount of residual carbon in the composite, one may wish to monitor stable phase assemblies at fixed temperatures with respect to different Cr-contents (Fig. 3(c)). An increase of Cr-filler content results in a lower amount of free carbon present in the matrix up to filler loadings of 75 wt% (corresponding to 33 vol%). Above this threshold value, free chromium remains in the pyrolyzed residue, whereas Cr-carbides and Cr-silizides are present regardless of chromium filler loadings. The amount of SiO_2, and consequently Cr-silizide formation, is reduced with respect to increasing Cr-content, while the amount of carbide formation increases above a threshold value of 12 wt% filler content (corresponding to 2 vol%) up to 75 wt%. Higher Cr-loadings result in residual excessive metal Cr as a stable phase.

Similar tendencies could also be predicted by thermodynamic modeling of a corresponding Ti/polysiloxane mixture, as shown in Fig. 4(a). A bulk composition of 1·01 mol Ti, 2·073 mol C, 2·376 mol H, 0·47 mol Si and 0·694 mol O which is equivalent to a precursor composition of 80 vol% polymer (MSS to PPS weight ratio 2:1) containing 20 vol% Ti was taken to calculate phase compositions during pyrolysis in argon atmosphere. TiC and Ti-silizides turned out to be in equilibrium with C and SiO_2 as matrix phases. If the calculations are performed in nitrogen gas atmosphere (50 mol N), however, the equilibrium conditions change significantly. Figure 4(b) shows the corresponding phase stability diagram where TiN and Ti-silizides are the only stable phases of the filler products at temperatures <1000°C. Above that temperature, TiC is found to occur additionally as an equilibrium phase.

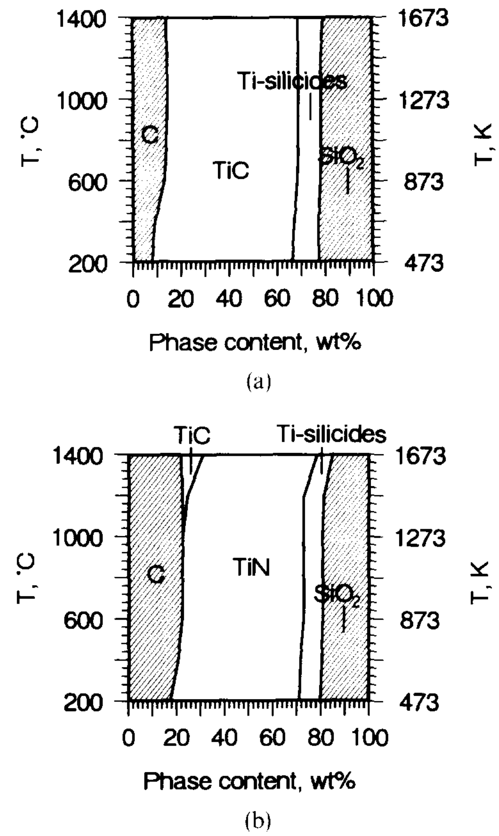


Fig. 4. Phase stability diagrams of a bulk composition. (a) Condensed phases: 1·010 mol Ti, 2·073 mol C, 2·376 mol H, 0·470 mol Si, 0·694 mol O, 0·223 mol N. (b) Condensed phases: 1·010 mol Ti, 2·073 mol C, 2·376 mol H, 0·470 mol Si, 0·694 mol O, 50 mol N.

Reaction pyrolysis and microstructural characterization

Pyrolysis of the polysiloxane precursor

During heat treatment the polymer undergoes the transformation into a ceramic product combined with continuous weight loss up to 1300°C as shown in Fig. 5. The MSS polymer reveals two distinct weight transitions at 230 and 740°C, while the PPS copolymer exhibits weight losses at 230 and 540°C which is accompanied by further continuous smooth weight loss up to 1300°C. These results correspond well with those reported for a polysiloxane mixture reported by Hurwitz *et al.*[20] Ceramic yields achieve

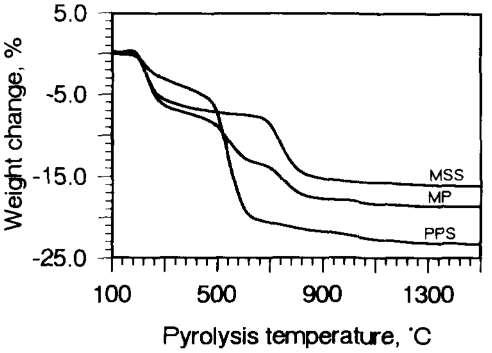


Fig. 5. Thermogravimetric analysis of the as-received polysiloxanes (MSS, PPS) and of the polysiloxane mixture MP in Ar-atmosphere.

81 wt% for the methyl polymer and 77 wt% for the phenylpropyl copolymer, respectively.

Major vibrational modes and bonding arrangements of the polymeric starting sources MSS and PPS are shown in Fig. 6(a),[21] while Fig. 6(b) reveals different IR-spectra of the corresponding polymeric blend of MSS and PPS on a 2:1 weight basis heat treated to different pyrolysis temperatures of 450, 700 and 900°C. Up to 450°C only a few fractions of the organic bonds seem to be broken; however, the Si–OH absorption peak has completely disappeared at the considered temperature. Obviously condensation of the silanol groups has taken place. Between 450 and 700°C absorption peaks associated with the aromatic configurations, such as the C_6H_5-ring, and the propyl groups, as indicated by the Si–C_3H_7 peak at 1219 cm^{-1}, almost completely vanish. Hence, the residue still contains bonds between hydrogen and carbon which are characteristic for the organic state. Drastic changes take place up to 900°C; only broad absorptions corresponding to Si–O and Si–C environments can be detected. A small peak at 1600 cm^{-1} might be assigned to amorphous carbon present in the char.

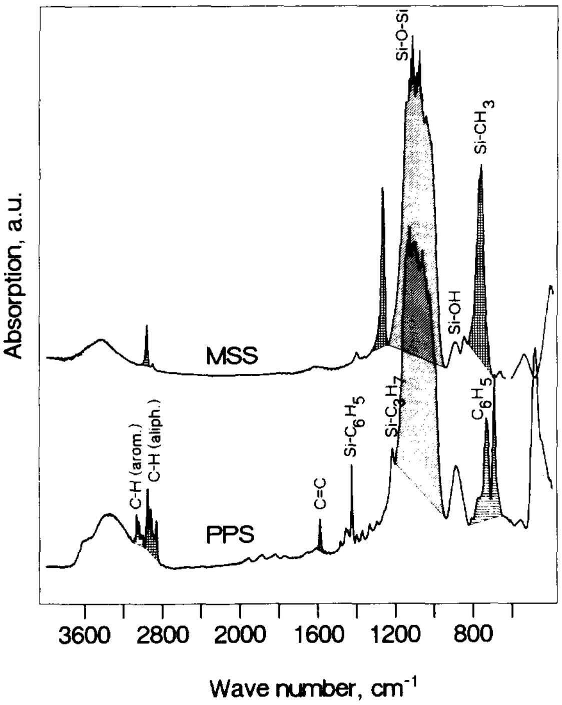


Fig. 6a. FTIR-spectra of the as-received polysiloxanes (MSS, PPS).

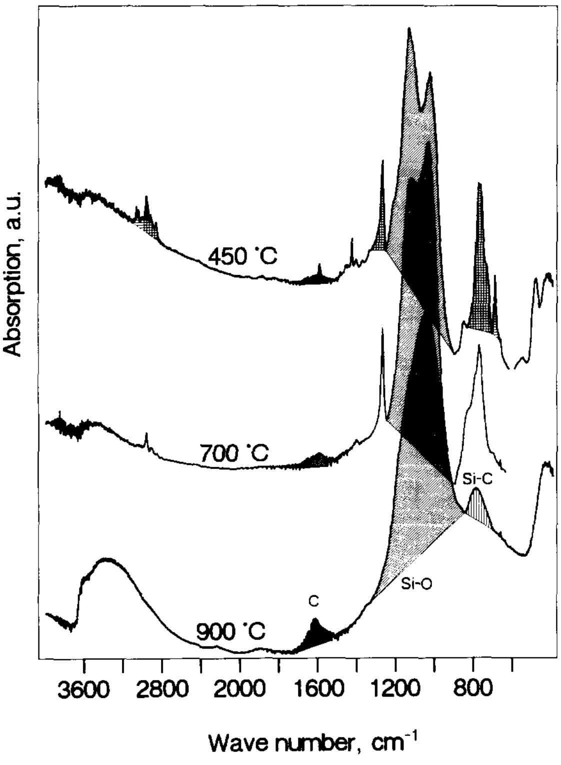


Fig. 6b. FTIR-spectra of the polysiloxane mixture MP pyrolyzed in Ar-atmosphere.

Reaction pyrolysis in the presence of an active filler
Figure 7 summarizes the carburization of Cr as an active filler incorporation into a polymeric polysiloxane precursor blend determined by X-ray diffraction. At a pyrolysis temperature of 900°C in static Ar-atmosphere considerable amounts of residual Cr can still be found. Formation of chromium carbides such as $Cr_{23}C_6$, Cr_7C_3 and Cr_3C_2 occurs simultaneously. At higher temperatures of 1100 and 1200°C the competing reactions of silizide formation become more important as indicated by the confirmation of a ternary

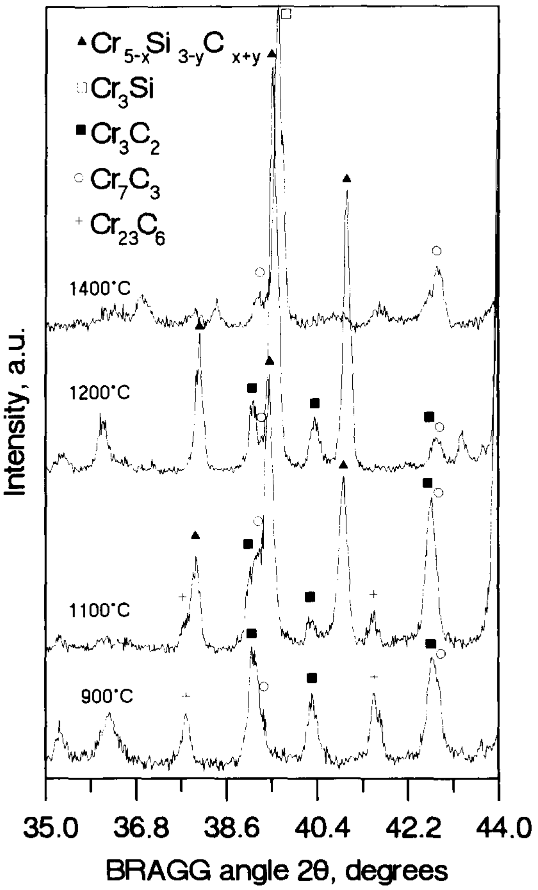


Fig. 7. XRD-spectra of the Cr-filled polysiloxane mixture MP pyrolyzed in Ar-atmosphere.

$Cr_{5-x}Si_{3-y}C_{x+y}$-phase.[22] At 1400°C a binary silicide phase of the Cr_3Si-type was found in the pyrolyzed residue.

Cross-sections as shown in the SEM-micrographs of 20 vol% composites, pyrolyzed at 1200°C in Ar (Fig. 8(a)), reveal the absence of major bubbles and craters in the pyrolyzed composite which usually arise during thermal treatment. Element mapping of Cr and Si (Figs 8(b) and (c)), respectively, derived from EDS-spectroscopy, indicates that the darker of the two phases can be assigned to a Si–O–C oxycarbide matrix phase whereas light phases primarily consist of Cr-compounds. The outline of the primary Cr-particles seems to be severely disintegrated which could be explained by decomposition reactions, especially silizide formation, with the matrix compound.

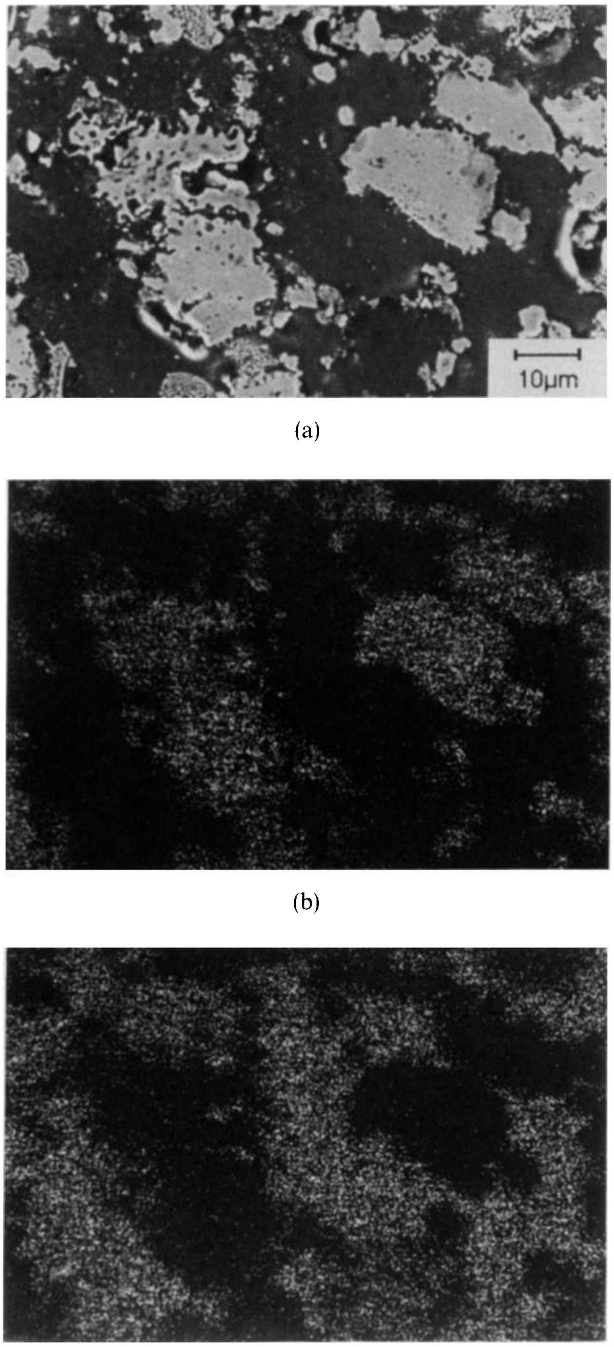


Fig. 8. (a) Electron micrograph of Cr-filled polysiloxane mixture MP pyrolyzed at 1200°C/1 h in Ar-atmosphere; (b) Cr element mapping; (c) Si element mapping.

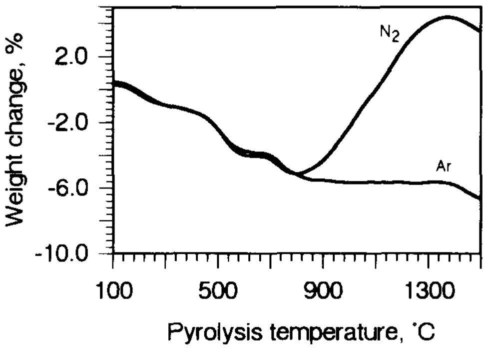


Fig. 9. Thermogravimetric analysis of the Ti-filled polysiloxane mixture MP, in Ar- and N_2-atmosphere.

Weight changes, as a function of temperature due to the incorporation of Ti-powder into the polysiloxane matrix in inert Ar-atmosphere or under the influence of reactive N_2-gas, are monitored in Fig. 9. In the case of the Ar-environment, similar weight loss transitions as compared to the pure polymer blend can be observed, indicating that degradation reactions during pyrolysis remain almost unchanged. Ti-carbide formation could be identified by X-ray diffraction (XRD), as shown in Fig. 10.

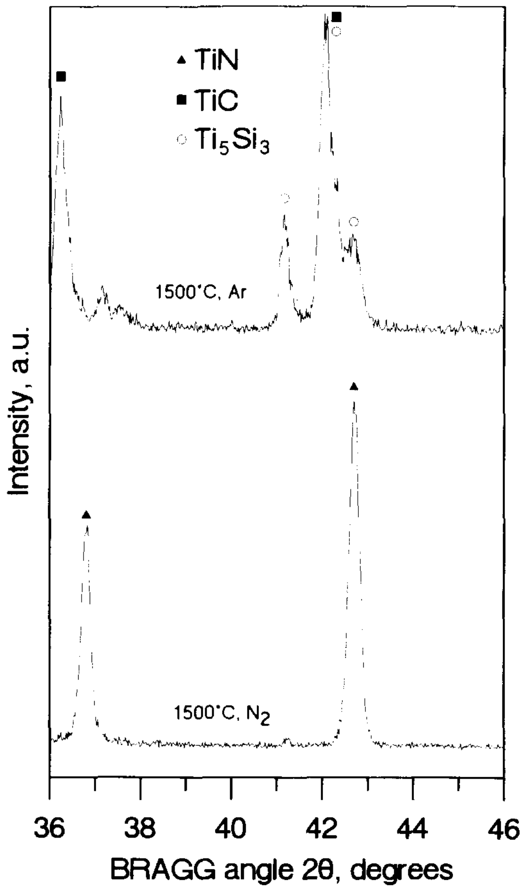


Fig. 10. XRD-spectra of the Ti-filled polysiloxane mixture MP pyrolyzed in Ar- and N_2-atmosphere.

Additional peaks in the XRD-spectrum could be assigned to Ti_5Si_3, indicating competing silizide formation which confirms the predictions of the phase equilibria calculations (see Fig. 4(a)). If nitrogen was used as the pyrolysis atmosphere, the X-ray diffraction pattern of the pyrolyzed residue only reveals intensities which can be attributed to the formation of TiN (Fig. 10). It is, however, not possible to distinguish between TiN and TiC formation since they tend to form solid solutions $TiN_{1-x}C_x$ at temperatures of interest.[23] In contrast to pyrolysis in Ar-atmosphere which seems to stimulate a predominant solid-state reaction during carburization of the filler compound, the analogous treatment in nitrogen which leads to the occurrence of TiN is based on a gas-phase reaction, as confirmed by a drastic weight increase as shown in Fig. 10 at pyrolysis temperatures above 800°C. The weight loss in both curves which occurs at temperatures $>1400°C$ is assigned to the reduction of SiO_2 by C, as outlined in eqns (4) and (5).

Thermodynamic calculations in the present study could be successfully focussed on the evaluation of possible filler elements for the reaction pyrolysis concept. Pyrolysis experiments not only revealed the postulated reactivity of transition metal filler particles with the decomposition products released during polymer degradation, but also differences with respect to the filler nature have to be noted. Concerning phase assemblies corresponding to equilibrium conditions in the ternary systems,[24] the formation of a ternary $Me_{5-x}Si_{3-y}C_{x+y}$ (Me = Ti, Cr...)-phase could be expected; however, it was only observed in the case of Cr-loading. Further investigations will thus have to enlighten the phenomena taking place during mass transport of C- and N-atoms into the metal structure.

4 Summary

The reaction pyrolysis of preceramic polymer/metal powder mixtures has significant potential to fabricate and tailor different microstructures in multiphase ceramic matrix composites with respect to filler nature and content. Preservation of complex shaped green parts can be achieved due to the incorporation of the active filler compound. Thermodynamic modeling revealed predictions for different stable phase assemblies depending on filler concentrations and pyrolysis atmosphere which were confirmed by the experimental preparation of polysiloxane derived carbide/Si–O–C materials. More detailed and progressive examinations will be necessary in the future to develop this novel processing approach, and to clarify the influence of the filler particles on the chemical and physical reactions which take place during pyrolysis in order to facilitate control of both shrinkage and porosity.

Acknowledgement

The authors are grateful to Dr Christian Rüssel, University of Erlangen, Institute of Materials Science III, Germany, who performed the IR-spectroscopy.

References

1. Seyferth, D., Wiseman, G. H., Schwark, J. M., Yu, Y. F. & Poutasse, C. A., Organosilicon polymers as precursors for silicon-containing ceramics. In *Inorganic and Organometallic Polymers.* ACS Symposium Series, Vol. 360, Denver, CO, 1987, p. 143.
2. Renlund, G. M., Prochazka, S. & Doremus, R. H., Silicon oxycarbide glasses: Part I. Preparation and chemistry; Part II. Structure and properties. *J. Mater. Res.*, **6** (1991) 2723.
3. Lee, B. I. & Hench, L. L., Molecular composites of SiC/SiO_2, SiC/Al_2O_3 and SiC/TiC. *Am. Ceram. Soc. Bull.*, **66** (1987) 1482.
4. Yu, Y. F. & Mah, T. I., Si–O–N ceramics from organosilicon polymers. In *Better Ceramics Through Chemistry II.* MRS Symposia Proceedings, Vol. 73, Palo Alto, CA, 1986, p. 559.
5. Yajima, S., Hayashi, J., Omori, M. & Okamura, K., Development of a silicon carbide fibre with high tensile strength. *Nature*, **261** (1976) 683.
6. Rice, R., Ceramics from polymer pyrolysis, opportunities and needs—A materials perspective. *Am. Ceram. Soc. Bull.*, **62** (1983) 889.
7. Wall, L. A., Pyrolysis of polymers. In *The Mechanisms of Pyrolysis, Oxidation and Burning of Organic Materials.* NBS Special Publication 357, Gaithersburg, 1970, p. 67.
8. Lipowitz, J., Rabe, J. A., Frevel, L. K. & Miller, R. L., Characterization of nanoporosity in polymer-derived ceramic fibres by X-ray scattering techniques. *J. Mater. Sci.*, **25** (1990) 2118.
9. Seibold, M. & Greil, P., Composite ceramics from polymer–metal mixtures. In *Advanced Materials and Processes, Proc. 1st Eur. Conf. on Advanced Materials and Processes*, Aachen, 1989, p. 641.
10. Greil, P. & Seibold, M., Active filler controlled pyrolysis (AFCOP)—A novel fabrication route to ceramic composite materials. In *Advanced Composite Materials, Ceramic Transactions, Vol. 19*, Orlando, 1990, p. 43.
11. Greil, P. & Seibold, M., Modelling of dimensional changes during polymer-ceramic conversion. *J. Mater. Sci.*, **27** (1992) 1053.
12. Seyferth, D., Bryson, N., Workman, D. P. & Sobon, C. A., Preceramic polymers as 'reagents' in the preparation of ceramics. *J. Am. Ceram. Soc.*, **74** (1991) 2687.
13. Barin, I., *Thermochemical Data of Pure Substances.* Verlag Chemie, Weinheim, 1989.
14. Bouillon, E. *et al.*, Conversion mechanisms of a polycarbosilane precursor into an SiC-based ceramic material. *J. Mater. Sci.*, **26** (1991) 1333.
15. Renlund, G. M., Silicon oxycarbide glasses. PhD thesis, Rensselaer Polytechnic Institute, Troy, NY, USA.
16. Toth, L. E., *Transition Metal Carbides and Nitrides.* Academic Press, London, 1971.
17. Wakelkamp, W. J. J., van Loo, F. J. J. & Metselaar, R., Phase relations in the Ti–Si–C System. *J. Europ. Ceram. Soc.*, **8** (1991) 135.
18. Kosolapova, T. Ya., *Carbides—Properties, Production and Applications.* Plenum Press, London, 1971.

19. Cooke, T. F., Inorganic fibers—A literature review. *J. Am. Ceram. Soc.*, **74** (1991) 2959.
20. Hurwitz, F. I., Hyatt, L., Gorecki, J. & Amore, L. D., Silsesquioxanes as precursors to ceramic composites. *Ceram. Eng. Sci. Proc.*, **8** (1987) 732.
21. Noll, W., *Chemie und Technologie der Silicone*. Verlag Chemie, Weinheim, 1968.
22. Parthe, E., Schachner, H. & Nowotny, H., Ein Beitrag zum Aufbau von Siliziden der Übergangsmetalle. *Mh. Chem.*, **86** (1955) 182.
23. Storms, E. K., *The Refractory Carbides*. Academic Press, London, 1967.
24. Wakelkamp, W., Diffusion and phase relations in the systems Ti–Si–C and Ti–Si–N. PhD thesis, Eindhoven, The Netherlands, 1991.