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Sol–gel-based carbon/silicon carbide

V. Liedtke*, I. Huertas Olivares, M. Langer, Y.F. Haruvy

ARC Seibersdorf Research GmbH, Aerospace Materials Technology, A-2444 Seibersdorf, Austria

Abstract

The current paper describes a novel approach to produce C/SiC composites via a fast-sol–gel process. Tailorable organo-silane liquid precursors are reacted, to produce a resin-like sol within tens of minutes. Carbon-fibre preforms, impregnated with this sol, construct intermediate composites after curing a few hours. These composites are easily converted, via high-temperature high pressure pyrolysis, to the desired C/SiC composites.

This facile route to high-performance materials offers not only more effective production and cheaper thereby, but also a highly versatile process: via simple modifications of the precursors, fillers, preforms and pyrolysis program, one can meet a wide variety of performance demands by tailor-making novel varieties of the C/SiC. Manufacturing, characterisation, performance and possible applications of these composite-materials will be discussed, as well as their comparison with commercial ones.

Keywords: Sol–gel processes; Composites; SiC; Structural applications; Re-entry

1. Introduction

1.1. Carbon-fibre reinforced silicon carbide composites

Carbon-fibre reinforced silicon carbide (C/SiC) composites provide excellent thermo-mechanical properties at temperatures up to 2000 °C.[1–3] Their high strength-to-weight ratio, which sustains at the high temperatures, makes them potential candidates for highly demanding engineering applications such as heat shields and structural components for re-entry space vehicles, high performance brake discs, and ultra-high temperature heat exchanger tubes. In space-flights, manned ones in particular, re-entry is the most risky stage since materials' failures during re-entry can become fatal. Future vehicles, replacing the outdated US Space Shuttle, are designed to be multiple-use and comprise heat-shields and heat-exposed elements which have to be re-entry-durable, reliable and fully reusable. For these elements, C/SiC ceramics have the most favourable properties and are, therefore, at the challenging front of the contemporary materials' research.

C/SiC composites can be fabricated by a CVD infiltration process, yet their high performance is attained at prohibiting costs for many applications. Liquid silicon infiltration processes, also a common fabrication route, offer some cost advantage, but require a very delicate process control. More cost-effective C/SiC composites fabrication could significantly broaden the scope of their applications, thus increasing the scope of experience, on reusable service in particular. This experience is a crucial key for increasing the reliability, of both production and use of C/SiC composites, which are particularly important for space missions.

At high temperatures and in the presence of oxygen, C/SiC composites necessitate a protective layer to prevent reinforcement burn-off and progressive degradation thereafter. Unfortunately, the functional reliability of such protective layers is often compromised by cracking, resulting primarily from thermo-mechanical induced stresses. CVD-produced protective layers are particularly prone to such cracking. We have found[4] that the durability, reusability and reliability of the protective layers and the C/SiC composites, under high mechanical loads and high temperatures, are bilaterally dependant and, hence, these two components should be developed hand in hand, tailored to match each other, in order to get the optimum performance for the envisaged application. The currently employed protective layers for C/SiC composites, like the composites themselves, exhibit satisfactory performance at a penalty of grave fabrication complexity, costs, and insufficient experience in use, thereafter. Increasing the reliability of these protective layers also necessitates novel, simpler and less costly routes, like the one facilitated by the fast-sol–gel route.

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* Corresponding author. Tel.: +43 50550 3346; fax: +43 50550 3366.
E-mail address: volker.liedtke@arcs.ac.at (V. Liedtke).

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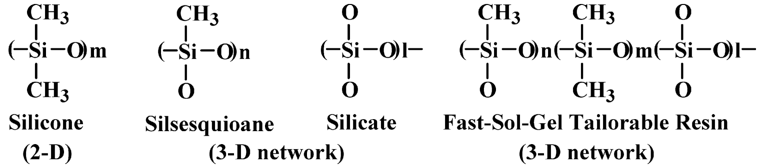
1.2. The sol–gel approach to ceramics



$(-\overset{CH_3}{\underset{CH_3}{Si}}-O)_m$ $(-\overset{CH_3}{\underset{O}{Si}}-O)_n$ $(-\overset{O}{\underset{O}{Si}}-O)_l-$ $(-\overset{CH_3}{\underset{O}{Si}}-O)_n(-\overset{CH_3}{\underset{CH_3}{Si}}-O)_m(-\overset{O}{\underset{O}{Si}}-O)_l-$

The fast-sol–gel process[5] involves rapid hydrolysis and polymerization of organo-silanes, with minimal water and no solvent, followed by removal of the by-products. This process allows facile fabrication of glassy materials within minutes of reaction and a few hours curing at 65–140 °C. These glassy materials are tailorable to a wide variety of specific objectives, monoliths, composites, coatings, sealants, and micro-optical elements and arrays.

Coatings made from such resins readily adhere to surfaces and furthermore, chemically bond to oxide ones.[6] Their 3D structure is durable to oxidative degradation in terrestrial and space applications[7,8] and, hence, these materials are less prone to produce silicone-based outgassing and permanent contamination.[8–10] The silisequioxane units – $CH_3SiO_{3/2}$ comprise, *ab initio*, a Si–C unit and the equivalent of 1.5 molecules water. Pyrolysis of these fast-sol–gel derived materials, under non-oxidative environment, produces silicon carbide (SiC) and silicon-oxy-carbide. This conversion most probably takes place via the schematic reaction: $(SiRO_{3/2})_n \rightarrow SiC + CO_2 + H_2O$. The innovative effort to convert a variety of carbon-reinforced sol–gel derived composites into C–SiC composites, free of C–C moieties and, hence, of improved performance, resulted in the development of both C/SiC composites and protective layers.[11,12]

The current paper describes the two approaches to produce the C/SiC composites via the fast-sol–gel process. The sequence of processes to convert SiC organo-silane precursors to a resin, to a carbon-reinforced glass, and then to the C/SiC are described, and the process versatility and tailorability merits are discussed. Further, a new dimension of tailoring is introduced, via ceramic fillers, alumina in particular, as μ-powders as well as nano-powders into the matrix. The new 'super-reinforcement' principle and results are discussed, in the context of composition/process/structure/properties-correlations. The combined approach to a composite/protective-layer orchestrated tailoring is further discussed, aiming at a harmonized design of application, performance and materials ensemble.

2. Experimental

2.1. Reagents

All reagents were utilized as received. Alkoxysilane monomers: tetramethylorthosilicate (TMOS, Fluka), methyltrimethoxysilane (MTMS, Aldrich), dimethyldimethoxysilane (DMDMS, Aldrich); catalysts: hydrochloric acid and hydrofluoric acid (Merck) solutions were prepared with deionized water; reinforcement: C-fabric, made of Tenax HTA 5131 400 tex f6000 t0 style 462 fibers (TOHO), via Köper 2/2 balanced weaving, 245 g/m^2; Alumina particles, ALCOA A 1656, ca. 500 nm, Zirconia particles, TOSOH TZ-8Y, ca. 100 nm; nano-alumina, neutral, ca. 50 nm, 35 m^2/g, #4/38, from Plasma & Ceramic Technologies GmbH, Latvia.

2.2. Fast sol–gel

2.2.1. Sol–gel/alumina resins (a) μ-powders

Into a 50 ml reaction bottle equipped with a stirring bar, 9 g alumina μ-powder and 5 g HF 1 M were introduced, sealed, shaken vigorously, then stirred 5 min at 100 °C to activate the alumina. Monomers were added: MTMS and DMDMS, 90/10 or 85/15% w, and the reaction bottle sealed. The mixture was reacted by shaking vigorously, then stirring 5 min at 100 °C. The reaction bottle was carefully opened, and 6 g methanol were out-distilled under gravimetric control.

2.2.2. Sol–gel/alumina resins (b) nano-powders

Into the above reaction bottle, 9 g alumina *n*-powder was introduced, then the monomers (same as above). The alumina and monomers were vigorously shaken. Then 5 g HF 1 M were added, the bottle sealed, vigorously shaken, and reaction continued at 100 °C same as above.

2.2.3. Sol–gel/alumina resins (c) micro- and nanohybrids

The μ-alumina–HF reaction – same as (a). Then the monomers added, the *n*-powder, and the reaction was continued same as (b).

2.3. Intermediate composites

2.3.1. Carbon-fabric activation

Carbon-fabric cut discs were sonicated in H_2O_2 3–6%, for 2–6 min, then dried 1 day at 80 °C. Special care was taken to avoid rupture of the carbon-fabric.

2.3.2. One step composite fabrication

In a $\Phi = 65$ mm 5 cm deep mold: (i) 1 ml freshly prepared resin was spread at the bottom; (ii) C-fabric disc was directionally placed. The (i) + (ii) sequence (2 g resin) was repeated four more times, with 45° fabric rotation each step. Step (i) then formed the top layer. The CMC objective thickness was 2 mm, suitable for mechanical and thermal testing. This layout is shown in Fig. 1 – left. Following 3 h 80 °C gelling, the composite was covered and loaded for 60 N before drying, 1 day at 80 °C.

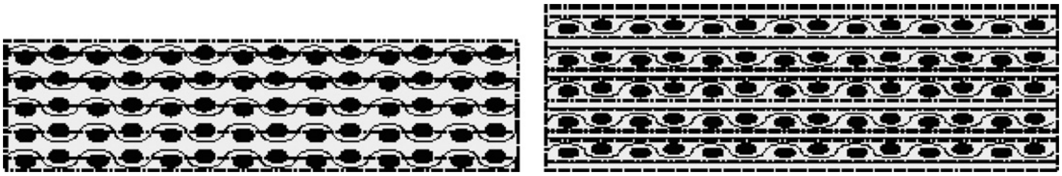


Fig. 1. Fabric-resin layout in a one-step (left) and a two-step (right) composite fabrication.

2.3.3. Two step composite fabrication

In a $\Phi = 65$ mm 5 mm deep mold 4 ml sol–gel/alumina resin was spread and C-fabric disc soaked therein. Five such ensembles were prepared and dried 1 day at 80 °C. In a $\Phi = 65$ mm 5 cm deep mold (i) 1 ml freshly prepared resin was spread at the bottom; (ii) C-fabric dry *prepreg* disc, with sol–gel/alumina resin, was directionally placed. The (i) + (ii) sequence (2 g resin) was repeated four more times, with 45° *prepreg* rotation each step. Step (i) then formed the top layer (cf. Fig. 1, right). Following 3 h 80 °C gelling, the composite was covered and loaded for 60 N before drying, 1 day at 80 °C.

3. Thermal processing

3.1.1. Pyrolysis

Dry intermediate were pyrolysed prior the hot-press stage, to prevent the contamination of the hot press. A multi-stage pyrolysis program, under Argon flow, was utilized, providing a slow ramp between 150 and 300 °C and a 4 h hold at 450 °C.

3.1.2. Hot pressing

The hot-press process of the pyrolysed composites took place under vacuum (0.2 mbar), via a sequence of matched T–P 11 h ramping to 1600 °C/30 MPa, and a 4 h hold at this T–P regime.

3.2. Mechanical testing

Mechanical properties were tested employing a universal testing machine (Shimadzu AGC-10/TC) with a max. load of 100 kN. Ultimate tensile strength (UTS) and residual tensile strength (RTS) were tested according to DIN ENV 658-3. Test conditions: ambient air and temperature; Crosshead speed 0.5 mm/min; sample dimension 50 mm × 10 mm × 2 mm (approx. values).

4. Results, observations and discussion

4.1. C-fabric sizing

The matrix-to-reinforcement bonding has a primary role in the integrity and performance of composites. Despite the seemingly excellent bonding of the sol–gel resins to the C-fabric, matrix-fabric interface delamination was sometimes observed upon pyrolysis. Hydrophilization of the C-fabric's epoxy resin sizing seemed advantageous in that respect, and that was carried out by sonication-aided oxidation with hydrogen peroxide solution. Extensive oxidation of the seizing resulted in fabric rupturing and, hence, oxidation under milder conditions was employed for the sizing activation. The oxidation regimes, and resulting composite's performance are shown in Table 1.

Table 1
Effect of C-fabric sizing oxidation on mechanical properties of composites

Sample code	C-fabric activation % H_2O_2; t (min)	Composite UTS[a,b]
J41	–	76
J42	–	103
J47	3% 2′	70
J48	3% 2′	45
J50	4.5% 4′	60
J51	4.5% 4′	58
J45	6%; 6′	44
J46	6%; 6′	49

[a] 3-point bending strength [MPa]—average of three tests.

[b] All samples have identical matrix composition, with 90:10 MTMS to DMDMS. Al_2O_3/Si ratio of the matrix is 0.45.

Contrary to the previous assumptions, the more substantial the sizing oxidation is, the smaller the composite's UTS becomes. This observation may manifest either damage to the carbon fibers per se, or a better bonding of the unoxidized sizing to the specific sol–gel recipe used in Table 1. Further studies with a different sol–gel recipe have shown that this finding is probably general for this family of fast sol–gel resins. The reason is however not yet completely understood, and a closer look to the fiber/matrix interface is essential.

4.2. Sol–gel composition

The sol–gel process facilitated tailoring the composition the resin to a wide variety of recipes. The effect of the various compositions studied on the thus produced C–SiC composites is shown in Table 2.

As can be clearly seen from Table 2, the TMOS component, which drives the post-pyrolysis matrix from almost pure SiC to silicone-oxy-carbide, endows a substantial strength to the C/SiC composites. Conversely, the DMDMS component, which

Table 2
Effect of sol–gel recipe on the produced composites

Sample code	M:D:T[a]	Composite UTS[b]
J52	9:0:1	235
J53	9:1:0	75
J54	10:0:0	168

All composites have similar C-fabric activation. No alumina added to the matrix.

[a] MTMS:DMDMS:TMOS weight ratio.

[b] 3-point bending strength [MPa]—average of three tests.

was found highly advantageous in fast-sol–gel resins employed for coatings and protection layers, strongly decreases the C/SiC strength. This puzzling observation calls for a further deciphering via microanalysis.

4.3. Sol–gel resins modified with Al_2O_3

4.3.1. μ-Alumina

Adding ceramic fillers to sol–gel-produced resins is a common route to decrease shrinkage and thus, to eliminate cracking upon drying. Adding alumina to the fast-sol–gel-produced resins resulted in poor stability of the mixture, no matter at what stage the admixing took place, and despite prolonged mixing and sonication. This phase separation was attributed to a mere physical bonding between the rather hydrophilic particles and the amphiphilic resin (cf. Fig. 2). The latter tends to coil with the polar moieties inwards.[13] This rationale suggests that the sol–gel process should rather commence from the surface of the filler surface, following its activation.

Thus, allowing the alumina μ-particles to react first with the water/HF and consequently with the silane monomers resulted in a sustained homogeneous resin. It is noteworthy that the alumina seemingly absorbed all of the aqueous reagents. Nevertheless, homogeneity was apparent when the monomers, added and shaken vigorously with the alumina, were reacted 5 min at 100 °C. A salient observation was a sol–gel reaction pattern regular for this synthetic route. These observations suggest that the alumina activation resulted in numerous Al–OH and Al–F groups at the surface of the alumina μ-particles. These groups could then react with the alkoxysilane monomers and the adsorbed water and bring forth the condensation/hydrolysis/condensation propagation:

$$\equiv\text{Al–OH} + \text{MeO–Si}\equiv \rightarrow \equiv\text{Al–O–Si}\equiv + \text{MeOH} \quad (2)$$

$$\equiv\text{Al–F} + \text{MeO–Si}\equiv + H_2O \rightarrow \equiv\text{Al–O–Si}\equiv + \text{MeOH} + \text{HF} \quad (3)$$

Thus, the sol–gel resin formation seems to have started mostly at the alumina particle-surface, which inevitably has become an integral part of the resin. Indeed, this way produced resins exhibited sustained homogeneity, resembling commercial painting lacquers. These resins could be facilely brushed onto surfaces, and were thus coherently applied onto the C-fabrics to fabricate the intermediate composites, as well as onto some resin-deficient spots after retrieving the composites from the molds. This property may suggest future applications of these resins, since their silicone nature provides a high UV and oxidation resistance, lacking in most organic paints.

4.3.2. Nano-particles

Nano-particles of alumina (n-Al_2O_3) were introduced into the sol–gel-produced resins in order to study their special effects on the resins' behavior and performance. To avoid dissolving of the nano-particles by the HF, in view of their small size, the n-Al_2O_3 was added after the HF was added to the silane monomers. Once again, the regular sol–gel reaction pattern was observed in all cases, as soon as the reaction mixture was shaken vigorously and stirred a few min at 100 °C.

An intriguing observation during these reactions, at high concentrations of n-Al_2O_3, was a rapid viscosity increase, foaming, and obstruction of the alcohol's out-distillation thereafter. This rapid viscosity rise probably manifests rapid conversion of the sol into the gel, via a multiple anchoring of the sol-chains onto the numerous anchoring locales at the huge surface area of the nano-alumina of 35 m^2/g, according to manufacturer's information.

An attempt to reduce the viscosity by decreasing the water-to-silane ratio resulted in resin disintegration upon drying. Hence, the water stoichiometry was retained and instead, resin dilution was practiced. The twofold benefit, of a lower viscosity and extended pot-life, facilitated sufficient pot-time for orchestrating the subsequent C-fabric layers in all the needed orientations (0/90°, +/−45°, 0/90°, +/−45°, 0/90°).

4.3.3. Micro–nano-hybrid resins

A three-fold chore of the alumina in the sol–gel resins can be envisaged: filler, a thermal insulator, and a super reinforcement agent for the matrix, onto which the matrix chains anchor. The first two are similarly carried out by both types of alumina. The third one strongly depends on the size. While pure nano-alumina in the sol–gel results in an excessive viscosity and a hardly workable resin, 10/90 wt.% nano/micro-alumina was found to provide both the desired workability and the necessary super-reinforcement effect. Nevertheless, these hybrids necessitated a special order of steps: reaction of the μ-alumina with the aqueous HF first, then adding the monomers and, last, adding the nano-alumina. Initiating the reaction via vigorous shaking and stirring, like before, completed the process.

4.4. Composites fabrication and performance

Fabrication data of C-fabric ceramic composites made via the fast-sol–gel/alumina resins are shown in Table 3, in which the J-

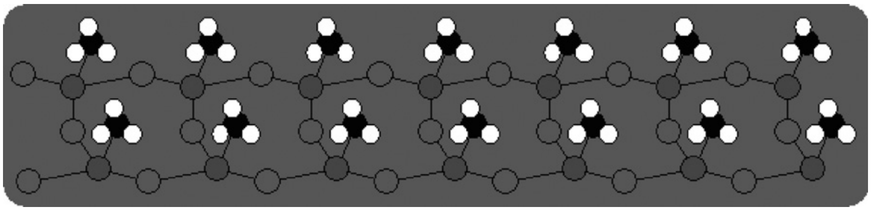


Fig. 2. A model of fast-sol–gel chain segment.

Table 3
Effect of filler content on C-fabric/sol–gel/Al_2O_3C/SiC composites

Sample code	C-fabric activation	M:D:T[a]	Al_2O_3 type	Al_2O_3:Si [b]	C_{HP} (%)	Strength[c] (MPa)
J53	4.5% 4′	90/10/0	None	0	42.2	75
J57	4.5% 4′	90/10/0	Micro	0.30	73.0	84
N2	4.5% 4′	90/10/0	Nano	0.27	58.4	90
N8	4.5% 4′	90/10/0	Nano	0.23	50.5	61
N10	4.5% 4′	90/10/0	90/10 μ/n	0.45	42.2	74
N11	4.5% 4′	90/10/0	80/20 μ/n	0.45	40.0	102

[a] MTMS:DMDMS:TMOS weight ratio.
[b] Al_2O_3 to silane-monomers weight ratio.
[c] 3-point bending strength—average of three tests.

series denote micro-alumina only, and the N-series denote pure nano-alumina, or hybrid composites with micro-particles and nano-particles. The salient observation from Table 3, in which the alumina content is the sole variant, is that within the up to ±20% variance in the samples themselves, there seems no clear correlation between amount and type of alumina powder and the composites' UTS.

It has however to be mentioned that the monomer composition of this series was found to give the weakest composites, when comparing different matrix compositions (cf. Table 2). Therefore, further investigations with matrix systems comprising of TMOS instead of DMDMS are currently under preparation. Additionally, the carbon fabric activation was also not beneficial for the mechanical properties (cf. Table 1).

4.5. Effects on development of advanced oxidation protection systems

The same base process as described for matrix preparation of composites can be transferred to the application of sol/gel-based oxidation protection systems (OPS). A first generation of these systems has already been successfully tested under re-entry relevant application conditions and was found to perform very competitive to other types of coatings[4]; the ease of process and significant cost advantages of the sol/gel process are however noteworthy.

Experiences with *n*-alumina have lead to preparation of new OPS, with tailored thermal expansion to meet the CMC base material requirements. First results are promising, and a thorough investigation is currently under way.

5. Conclusions

Summarising all the aforesaid, the effect of the resin constitution is the most significant one. It is noteworthy that the DMDMS constituent in the resin is a key factor in obtaining crack-free oxidation-protection-coatings, since it allows the coating the necessary flexibility to stay crackles during the curing stages. This constituent has no role in the composites but rather a mal-effect on the UTS. The effect of the type of ceramic filler, as well as the effect of the nano-particles are the focus of a further study currently en-route. This study is being carried out at the optimal orchestration of all other parameters deciphered in this study.

It is essential to evaluate the effect of alumina admixing to a matrix that has been prepared from the optimum monomer composition, i.e. containing TMOS rather than DMDMS. These investigations are currently being performed.

Surface activation of the fibres by sonicated oxidation does reduce the mechanical properties significantly and will therefore be discarded, though the reason is not yet fully understood. Additional investigations on the interfaces have to be carried out.

Finally, in the course of our studies, the fabrication of a flat CMC slab became a routine. Further, fabrication of curved CMC samples came out flawless as from the first attempt. Conic samples are awaiting their testing, and T shape samples are en-route. The one-step fabrication, which was found in the past inferior to the two-step one[14] has reached the stage of controlled resin concentration and distribution and hence utilized almost solely in this study, being more convenient for small samples of simple shape. Nevertheless, the two-step approach may become a more convenient route for larger and more complex CMC structures[15] once a mechanized fabrication of C-fabric prepreg is developed.

Last but not least, the materials, processes and resins that successfully create the C/SiC composites described above also successfully create SiC protective coatings. The latter require, of course, variation of the monomer composition yet a similar process and, hence, allow hand-in-hand development of both composites and their protective coatings, a unique feature which is cost-wise and performance-wise advantageous in research, development, engineering and application.

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