

## Review article

## High-temperature protective coatings for C/SiC composites



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## ABSTRACT

Carbon fiber-reinforced silicon carbide (C/SiC) composites were well-established light weight materials combining high specific strength and damage tolerance. For high-temperature applications, protective coatings had to provide oxidation and corrosion resistance. The literature data introduced various technologies and materials, which were suitable for the application of coatings. Coating procedures and conditions, materials design limitations related to the reactivity of the components of C/SiC composites, new approaches and coating systems to the selection of protective coatings materials were examined. The focus of future work was on optimization by further multilayer coating systems and the anti-oxidation ability of C/SiC composites at temperatures up to 2073 K or higher in water vapor.

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## 1. Introduction

In view of their low specific weight, excellent resistance to ablation as well as cost effective production, C/SiC composites represented an interesting material for high-temperature components of space propulsion systems [1].

At the same time, at higher temperatures (>1473 K), every oxidation process of the fiber, inter-phase and matrix cooperatively influences the mechanical behavior of C/SiC composites, which led to loss of strength and limited their potential applications for service under extreme conditions [2,3]. Consequently, C/SiC

composites needed anti-oxidation protection when exposed to oxidizing environment at higher temperatures.

The concept of high-temperature coating for C/SiC composites served as a structural link with stress compensation ability to the SiC matrix of C/SiC composites and such a coating acted as a diffusion barrier against oxygen.

The key aspects of protective coatings system were [4]:

- (1) The selection of coating technology and coating material.
- (2) Diffusion barrier function against liquids and gases.
- (3) Chemical compatibility (wetting angle, chemical stability, etc.) and thermo-physical compatibility (thermal expansion).
- (4) The thickness of high-temperature protective coating.

This review explained the current status of the problem of effective oxidation protection of C/SiC composites.

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## 2. Coating technology

Currently, the main coating techniques for C/SiC composites were:

- (1) Atmospheric plasma spraying (APS), which was a high-energy coating process with plasma temperatures in the region of 20,000 K and powder particle velocities of up to 450 m/s [5]. The powder, suspended in a carrier gas, was injected into the plasma. After melting and being accelerated, the powder particles impacted the substrate and built up the coating [6].
- (2) Preceramic-precursor-derived ceramic technology, which could fabricate ceramic coatings at low temperatures. The precursor could be cured to form a polymer coating at room temperature by UV light [7], or at temperatures below 373 K with thermal initiator [8].
- (3) Slurry method is one technique, which could be used to fabricate coatings on complex shaped components at low cost [9]. However, this technology required very high heat-treatment temperature to obtain dense coatings. The high temperature could damage the composites to some extent [10].
- (4) Reactive preparation is one technique, which could be used to fabricate coatings by reaction. For examples, ZrB<sub>2</sub> coatings upon C/SiC composites were prepared by pasting the slurry of zirconium powder, boron powder and phenolic resin, followed by high temperature sintering [11].
- (5) Sol–gel method, reported in recent literatures, was an easy way to produce oxidation-resistant coatings at low processing temperatures [12,13]. ZrO<sub>2</sub>–SiO<sub>2</sub> gradient multilayer oxidation protective coatings were prepared by a sol–gel technique using tetraethoxysilane (TEOS) and zirconyl chloride as source materials [14].
- (6) Chemical vapor deposition (CVD), which was one of the most popular solutions for coating technology [15–18]. CVD was a synthesis process: the chemical constituents react in the vapor phase near or on a heated substrate to form a solid deposit [19]. The CVD technology combined several scientific and engineering disciplines including thermodynamics, plasma physics, kinetics, fluid dynamics, and of course chemistry. For example, SiC–ZrC–SiC coating was prepared by CVD in order to improve their oxidation resistance at ultrahigh temperatures [20]. A multiple-layered structure of CVD SiC/a-BC/SiC was coated on 3D C/SiC composites by CVD [21].
- (7) Microwave sintering [22], as a novel and effective sintering method for ceramics, was adopted to prepare the coatings for C/SiC composites. A novel celsian/yttrium silicate coating was prepared by microwave sintering on the surface of C/SiC composites [23].
- (8) Molten salt reaction method is another one technique, which could be used to fabricate coatings on complex shaped components at low cost and low temperature. Titanium coating [24] and Zr–Si–C coating [25] were deposited on C/SiC composites by using this method.

These methods displayed their distinctive advantages. For example, CVD had the advantage of producing coating with dense structure; sol–gel process could enable preparation of the thin coating with high homogeneity; slurry painting possessed the attractive advantages of simple process and low operation temperature; plasma spraying was very much suitable for the preparation of high melting point ceramic material coating.

For the application of the dense top oxidation coatings of C/SiC composites, CVD technique [26,27] and slurry method from solution [28–30] were most suitable.

**Table 1**

Melting points of high-temperature coatings on C/SiC composites.

Materials	$T_m$ (°C)
TiO <sub>2</sub>	1670
ZrO <sub>2</sub>	2600–2800
HfO <sub>2</sub>	2900
HfB <sub>2</sub>	3250
TiB <sub>2</sub>	3225
TaB <sub>2</sub>	3037
ZrB <sub>2</sub>	3225
SiC	2730
TiC	3140
TaC	3985
ZrC	3530
HfC	3890
Ta <sub>4</sub> HfC <sub>5</sub>	4215
80% TiC + 20% HfC	4215

## 3. Coating materials

The requirements for a protective coating material were:

- (1) Chemical compatibility (wetting angle, chemical stability) and thermo-physical compatibility (thermal expansion), as high oxidation resistance as possible.
- (2) Diffusion barrier performance against liquids (water) and gases (O<sub>2</sub>, CO<sub>2</sub>, etc.) and diffusion stability in contact with chemical compounds.
- (3) Low oxygen permeability and low intrinsic oxidation.
- (4) Strong adhesion to C/SiC composites.
- (5) When considering both single-layer and multilayer coatings, they should take into account the thermal expansion coefficients (TECs) of the materials, which could cause interfacial stress, resulting in cracking [4].

The development of protective coatings on C/SiC composites generated the strong need for aeronautic application; different coating systems were tested, mainly consisting of refractory compounds containing boron, silicon, hafnium and zirconium. The melting points of the materials which were most widely used as high-temperature coatings were listed in Table 1.

The highest heat resistance, related to the melting and flow points, was offered by a number of inorganic compounds of a polymer nature and metals (Table 2) [4].

The most widely used protective coating materials include:

- (1) The carbides SiC, TiC, TaC, ZrC, and HfC.
- (2) The borides ZrB<sub>2</sub>, HfB<sub>2</sub>, B<sub>4</sub>C and TiB<sub>2</sub>.
- (3) The oxides SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, and HfO<sub>2</sub>.
- (4) The nitrides Si<sub>3</sub>N<sub>4</sub> and BN.
- (5) The silicides MoSi<sub>2</sub> and TiSi<sub>2</sub>.
- (6) The combinations, such as SiC + TaC, Si<sub>3</sub>N<sub>4</sub> + SiC, ZrC + SiC, HfC + ZrC, ZrB<sub>2</sub> + SiC, and so on.

**Table 2**

Melting points of inorganic compounds and metals that are used in high-temperature materials [4].

Compounds	$T_m$ (°C)	Compounds	$T_m$ (°C)
Oxides	250–2900	Zr	1855
Silicides	1540–2400	Ti	1933
Borides	1960–3250	Hf	2222
Nitrides	1900–3300	Nb	2500
Carbides	2600–4010	Mo	2620
		Re	3180
		W	3410

Thus, using coatings based on five classes of compound and their mixtures: carbides, oxides, borides, nitrides, and silicides.

### 3.1. Carbides

SiC coating on C/SiC composites had been grown using CVD [31]. Methyltrichlorosilane (MTS,  $\text{CH}_3\text{SiCl}_3$ ) with a molar ratio of 10 between  $\text{H}_2$  and MTS, which was carried by bubbling hydrogen and argon as the dilute gas to slow down the chemical reaction rate during deposition. The deposition temperature was maintained at 1373 K for 5 h at a reduced pressure of 3 kPa. The surface of the coating was smooth and the coating was rather uniform in thickness, 40  $\mu\text{m}$ . The coating process was shown to raise the strength of the composites [31].

A SiC/Mo-Si multilayer coating was prepared on the surface of C/SiC composites by CVD combined with slurry painting. The coating was composed of a dense CVD SiC coating alternating with a porous Mo-Si layer. From inside to outside the coating consisted of CVD SiC, Mo-Si, CVD SiC, Mo-Si and CVD SiC [32]. The coating showed excellent anti-oxidation ability and thermal shock resistance, and then it could effectively protect the C/SiC composites at 1673 K for a long time.

Multilayer coatings of SiC-ZrC-SiC were deposited on the composites [20]. SiC was deposited by the process carried out at 1273 K using MTS and  $\text{H}_2$  as precursors. ZrC layer was deposited using  $\text{ZrCl}_4$ ,  $\text{CH}_4$ , and  $\text{H}_2$  as precursors. The deposition temperature was 1573 K [33,34]. The SiC-ZrC-SiC coatings greatly improved the oxidation resistance of C/SiC composites. The formation of  $\text{ZrO}_2$  layer and the deflection of intrinsic cracks in the composites by the ZrC interlayer were the reasons for the enhanced oxidation resistance [20].

ZrC-SiC coating was immersed in the PCS-xylene solution, then immersed the composites into ZrC-PCS-xylene solution, and subsequently pyrolyzed at 1473 K under Ar atmosphere [28,30]. The composites with ZrC-modified SiC coating exhibited best anti-ablation resistance.

An amorphous boron carbide (BC) coating was prepared by low pressure CVD process from  $\text{BCl}_3$ - $\text{CH}_4$ - $\text{H}_2$ -Ar system [21]. The deposition conditions for CVD BC coating were as follows: temperature 1173 K, pressure 1.0 kPa, time 20 h,  $\text{BCl}_3$  flow 50 ml/min,  $\text{H}_2$  flow 60 ml/min,  $\text{CH}_4$  flow 20 ml/min, Ar flow 60 ml/min [21]. The surface and cross-section morphologies of the BC coating were homogeneous and amorphous.

HfC protective coatings with different structures were deposited by CVD.  $\text{HfCl}_4$ - $\text{CH}_4$ - $\text{H}_2$ -Ar system was applied to deposit HfC coating. HfC coatings were prepared on the surface of C/SiC substrates at a total pressure of 5 kPa in the temperature range of 1773–1873 K [35].

Zr-Si-C coating was prepared by molten salt reaction using KCl–NaCl, sponge Zr, and  $\text{K}_2\text{ZrF}_6$  [25]. As for Zr-Si-C coating process, a mixture of KCl–NaCl, sponge Zr, and 20 wt.%  $\text{K}_2\text{ZrF}_6$  was put in the alumina crucible and heated to 1373 K under an Ar atmosphere. The samples were immersed in the bath of molten salt for 3 h. The average diameter of Zr-Si-C coating was 10  $\mu\text{m}$ .

Additions of metal carbides, such as TaC, TiC and WC, increased the bending strength and thermal shock resistance of composites, their strength at 1973 K far exceeds that of graphite materials [36].

### 3.2. Borides

Borides were difficult to use as high-temperature coating materials as a single coating because of their low oxidation capability [37]. Thus, heavy-metal borides often mixed with carbides, which could offer higher thermal stability.

$\text{ZrB}_2$ /SiC coating was used by slurry in order to increase the oxidation resistance. In this process,  $\text{ZrB}_2$  powders with PCS-xylene

solution (mass ratio 4:5:6) were painted on the composites and subsequently pyrolyzed at 1473 K under argon (purity: 99.99%) atmosphere [29].  $\text{ZrB}_2$ /SiC coating could provide long time protection for C/SiC composites at higher temperature (1973 K).

$\text{ZrB}_2$  coatings were prepared by painting the slurry of zirconium powder, boron powder and phenolic resin, followed by high temperature sintering [11]. The coating was composed of mainly  $\text{ZrB}_2$ , small amount of ZrC and  $\text{ZrO}_2$ . Due to the  $\text{ZrO}_2$  formation from  $\text{ZrB}_2$  oxidation, C/SiC composite with  $\text{ZrB}_2$  coating showed a linear recession rate of zero [11].

A coating made of  $\text{HfB}_2$ /SiC composites (20% weight SiC) was tested as an oxidation protection on C/SiC composites [38]. The coating was applied by painting slurry on the surface of the composites and then by heat treating.  $\text{HfB}_2$ /SiC composites seemed to effectively protect the underlying C/SiC composites, with a mechanical strength reduction of only 20% after 30 min at 1873 K [38].

Ultra high temperature ceramics (UHTCs) particulate composite coatings are made of  $\text{ZrB}_2$ /SiC and  $\text{ZrB}_2$ /ZrC/SiC compositions; these coatings, which have a thickness of 100  $\mu\text{m}$ , could be processed by slurry approaches combining polymeric precursors to silicon carbide and carbon [39]. This approach had the potential to become a generic coating approach for composite coatings containing SiC phase ( $\text{Si}_3\text{N}_4$  phase was also feasible).

A borosilicate glass was successfully used as a coating on C/SiC composites, because it presented good oxidation resistance, good wetting, self-healing ability, and a low thermal expansion coefficient [40,41].

The self-healing coating for oxidation protection of C/SiC braiding materials was prepared by the sol–gel method using TEOS and TEOB. The coating was homogeneous and dense [42]. The coating showed good thermal shock resistance, excellent seawater corrosion resistance, and self-healing ability at 1073 K [42].

### 3.3. Silicides

SiC [31] and  $\text{S}_3\text{N}_4$  [43] were promising materials for fulfilling the thermo-physical requirements of C/SiC composites.

Different kinds of C/SiC modified with Si-B-C coating were fabricated by CVD [44]. Si-B-C ceramic as self-healing component had a remarkable effect on improving the oxidation resistance for C/SiC, which showed better residual mechanical property below 1273 K.

Borosilicate glass formed from oxidation of Si-B-C ceramic, which sealed cracks effectively in composites, was the reason for excellent oxidation resistance of C/SiC [44].

Three types of Si-Mo-SiO<sub>2</sub> coatings had been fabricated on the surface of C/SiC composites [45]. The coatings were composed of SiC,  $\text{MoSi}_2$ , Si and SiO<sub>2</sub>. Two single Si-Mo-SiO<sub>2</sub> coating (100  $\mu\text{m}$  and 300  $\mu\text{m}$  thick) prepared by slurry, then followed by a final sintering (sintered at 1773 K for 10 min in a carbon tube furnace with argon atmosphere), which had little protection for C/SiC composites. While three-layered Si-Mo-SiO<sub>2</sub> coating (100  $\mu\text{m}$  thick) prepared by triple paintings followed by sintering each time can effectively provide for 100 h protection at least at 1473–1673 K, and no peeling or burst was observed during oxidation test and thermal cycling between 1673 K and 373 K by water cooling. The good anti-oxidation ability and thermal shock resistance of triple Si-Mo-SiO<sub>2</sub> coating can be attributed to its microstructure with fewer defects and the self-sealing of micro-cracks during oxidation.

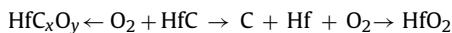
$\text{MoSi}_2$  exhibited excellent properties such as higher rigidity (8.5 GPa) and better oxidation resistance (>1873 K), which were potential candidates for coating materials of C/SiC composites [46,47]. Research progress on oxidation properties of high temperature oxidation resistant coating  $\text{MoSi}_2$  was reviewed [48,49]. It was the future development trend of  $\text{MoSi}_2$  coating technology on the surface of C/SiC composites, then researched and developed the

high-temperature, long-life and highly reliable oxidation resistant coating and ultra-high temperature oxidation resistant coating to satisfy the use requirements of aero-engines and space shuttles in the challenging and harsh working conditions [50].

### 3.4. Oxides

C/SiC composites exhibited better oxidation resistance in dry air due to the formation of a dense silica layer on their top [51]. However, the water vapor containing in combustion environments would remove the formed silica quickly, resulting in the mass loss and failure of the C/SiC composites [52,53]. Therefore, environmental barrier coatings (EBCs) were applied in order to protect the C/SiC composites from corrosion in combustion gas [54,55].

Oxides, especially those of light metals, had relatively low stability because they reacted with carbon at high temperatures: SiO<sub>2</sub> at 1473 K [48], TiO<sub>2</sub> at 1673 K [56], ZrO<sub>2</sub> at 1803 K, and HfO<sub>2</sub> at 1825 K [48]. Hafnium coatings offer similar thermal stability (1973 K). The associated chemical changes can be represented by the following scheme [57]:



So, it was reasonable to using oxides as a top layer (oxygen barrier) in multilayer coatings [48].

A new coating with Er<sub>2</sub>SiO<sub>5</sub> as inner layer and LaMgAl<sub>11</sub>O<sub>19</sub> (LMA) as top layer was designed and deposited on C/SiC composites by atmospheric plasma spraying to improve the oxidation resistance of the substrate at high temperature. The coating was attractive for the short-term applications (e.g. tens of minutes) of C/SiC composites exposed to gas flame with high temperatures (e.g. 2273 K) [5].

Yb<sub>2</sub>SiO<sub>5</sub>/LaMgAl<sub>11</sub>O<sub>19</sub> coatings were fabricated by plasma spray to improve the oxidation resistance of C/SiC composites. The Yb<sub>2</sub>SiO<sub>5</sub> and LMA feed powders were then plasma sprayed by using a Sulzer Metco plasma spraying unit with the F4-MB gun onto the C/SiC substrates to produce the coatings of Yb<sub>2</sub>SiO<sub>5</sub>, LMA and Yb<sub>2</sub>SiO<sub>5</sub>/LMA, respectively [6].

SiCN-Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> environmental barrier coatings were fabricated on the surface of C/SiC composites at low temperatures [58]. The Sc<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> powders were prepared using a sol-gel process. Sc(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and TEOS were used as the raw materials in this process.

Mullite coating was deposited on C/SiC composites by a hydrothermal electrophoretic deposition process using mullite powder as source material [59]. The mullite coating prepared at 180 V exhibits excellent anti-oxidation property, which can effectively protect C/SiC composites from oxidation in air at 1773 K for 164 h with weight loss of 1.75%.

Barium aluminosilicates (BAS) were coated on the C/SiC composites by dip-coating method [12]. The BAS sol was prepared using the following materials: BaCO<sub>3</sub>, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, TEOS, and citric acid. The results indicated that the BAS coatings could resist the attack of molten Na<sub>2</sub>SO<sub>4</sub> to C/SiC composites in dry air.

Polysiloxanes polymer coatings were formed on C/SiC composites at 1273 K in air with barium-strontium aluminosilicate (BSAS) as fillers. After the polymeric coatings were pyrolyzed at 1623 K under argon, a dense SiOC-BSAS-coated C/SiC composite was obtained [60]. Even after having corroded for 200 h in water vapor, the coated C/SiC composites showed little weight loss and high residual flexural strength.

Celsian/yttrium silicate coating was prepared by microwave sintering on the surface of C/SiC composites [23]. Celsian crystallizes from BaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (BAS) glass in the coating and yttrium silicate was formed through the reaction of yttrium oxide and molten BAS glass at high temperatures. The coating was dense and pore-free

by microwave sintering. The celsian/yttrium silicate coatings can protect C/SiC composites for no less than 90 min at 1773 K.

BaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (BAS) glass ceramic coatings were prepared on C/SiC composites by in situ sintering [61]. The sample sintered at 1473 K had an obvious transition layer of 40 μm in thickness between the coating and the composites, which could enhance the adhesion strength. The weight loss of the composites with BAS coatings was decreased with the increase of the sintering temperature.

The SiO<sub>2</sub>/ZrO<sub>2</sub> and ZrO<sub>2</sub>/SiO<sub>2</sub> bilayer films with good optical characteristics were prepared on glass substrates by sol-gel dip-coating method [62]. TEOS and zirconium oxychloride (ZrOCl<sub>2</sub>·8H<sub>2</sub>O) were used as SiO<sub>2</sub> source and ZrO<sub>2</sub> source, respectively. The surfaces of ZrO<sub>2</sub> monolayer film and SiO<sub>2</sub>/ZrO<sub>2</sub> bilayer film were smooth and compact relatively, and the nano-grains structured surfaces of the SiO<sub>2</sub> monolayer film and ZrO<sub>2</sub>/SiO<sub>2</sub> bilayer film were observed.

## 4. Thickness of coatings

This was not exact definition on the oxidation performance of C/SiC composites. According to the definition of C/C composites, it is known that one of the parameters used to quantify the effect of thermal load on structural materials is thermal stability of three terms: short, medium, and long, which was defined as the time taken for a 3% weight loss, accompanied by strength loss for 15 min, 15 h, and 100 h, respectively [48].

Coatings should be neither too thick, in order to retain good mechanical properties, nor too thin, in order to ensure effective protection of C/SiC composites from oxidation.

At the same time, thin layer meant good adhesion to the substrate; thick layer increased the peel off ability between the substrate and the coating.

Based on the above data, it is also shown that the thickness of coatings on C/SiC composites by various techniques could be usually introduced in the range of 10–200 μm.

## 5. Future work

It can be expected in the future that C/SiC composites, as the aero-engines and space shuttles materials, will suffer the harsh working conditions, such as ultra-high temperature, high pressure and high speed.

It is going to be the future development trend to research and develop high-temperature resistant, highly durable and greatly reliable oxidation resistant coating to satisfy the use requirements of the future.

The main employment is shown as follows:

- (1) Multilayer coatings seem to be a promising strategy for the protection of C/SiC composites in various applications.
- (2) The highest service temperatures reported in the data were 2273–2550 K. The most effective materials are carbide-boride combinations, such as ZrC-ZrB<sub>2</sub>, HfC-HfB<sub>2</sub>, and the thermal expansion coefficients of the materials should be taken into account.
- (3) It is not yet fully clear about the anti-oxidation ability of C/SiC composites at temperatures up to 2073 K or higher in water vapor.

## 6. Conclusions

Literature data were used to examine the current status of the problem of effective oxidation protection for C/SiC composites, materials capable of protecting C/SiC from oxidation.



Various advanced technologies were suitable for the application of coatings on the surface of C/SiC composites; among those, CVD technique and slurry method were most suitable.

The key coating materials of C/SiC composites were carbides, borides, silicides, oxides and their combinations. The most effective materials are carbide-boride combinations.

Multilayer coatings seemed to show better anti-oxidation performance for C/SiC composites in various applications, but thermal expansion coefficients of the materials should also be taken into account.

The focus of future work is on optimization by further multilayer coating systems and the anti-oxidation ability of C/SiC composites at temperatures of up to 2073 K or higher in water vapor.

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