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Review
Oxidation protection for carbon fibre composites

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Carbon fibre-reinforced ceramic matrix composites are promising candidate materials for high-temperature structural applications such as gas turbine blades. In oxidizing environments at temperatures above 400 °C, however, carbon fibres are rapidly oxidized. There is, therefore, a need to coat the composite in order to protect it against oxidation. This review identifies the requirements of an effective oxidation protection system for carbon fibre-reinforced ceramics and summarizes the work which has been carried out towards this goal over the last 50 years. The most promising coatings are those composed of several ceramic layers designed to protect against erosion, spallation and corrosion, in addition to possessing a self-healing capability by the formation of glassy phases on exposure to oxygen.

1. Introduction

Ceramic matrix composite materials reinforced with carbon fibres have received an increasing amount of attention in recent years. Much of the attention has been focused on developing these materials for use as high-temperature structural components in advanced gas-turbine engines. The driving force behind this research is the desire to increase the efficiency of these engines which dictates that they must operate at higher temperatures. Thus new materials must be found that can withstand this hostile, reactive environment.

The high strength and exceptional fracture toughness of these composites, combined with their refractory properties and their resistance to erosion, corrosion and wear, make them ideal candidates for this application [1]. In an inert atmosphere or in vacuum, carbon fibres retain their strength, modulus and other mechanical properties to temperatures in excess of 2000 °C which is much higher than those tolerated by other materials. A major problem arises, however, when composites containing carbon fibres are exposed to an oxidizing environment. Once the temperature is above 400 °C, the carbon fibres react with oxygen and are rapidly burnt away. Regardless of exposure time, successful operation in an oxidizing environment therefore requires the composite to have a protective coating of an appropriate combination of refractory materials in order to prevent oxygen attacking the substrate.

The development of an effective oxidation protection system for carbon has been in progress for more than 50 years and many different materials have been tried. The most promising systems include functionally active layers which are designed to react with any oxygen which penetrates through cracks in the outer layer to form a glass which flows and seals these cracks. This enables the oxygen to be consumed before it can reach the substrate and the system is intended to be self-healing.

This paper is a review of the literature which discusses the fundamentals of oxidation protection and the various protection systems for carbon fibre-reinforced ceramic matrix composites (CMCs) and summarizes developments which have been made in recent years.

2. Requirements of integrated oxidation protection systems and their components

The factors which must be considered when designing an oxidation protection system are well established. They are summarized in Fig. 1.

The primary function of an oxidation protection system is to isolate the substrate material from the oxidizing environment. To achieve this, the system must perform a number of functions.

At least one component of the system must form an effective barrier to the ingress of oxygen. This

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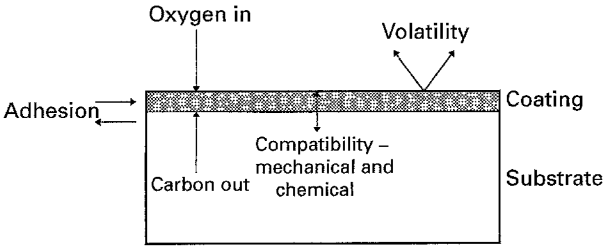

Figure 1 Considerations when designing an integrated oxidation protection system [2].

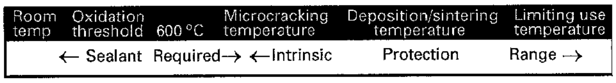

Figure 2 General oxidation behaviour of coated CMCs with carbon fibre reinforcement [4].

component of the system must therefore have a low oxygen permeability. Ideally, a material can be used which forms an adherent *in situ* oxide. In addition, it is equally important to minimize the diffusion of carbon outwards from the substrate. This is specially vital if some layers in the system contain oxides because these may be reduced by carbon.

In service, it is inevitable that cracks will form in the outer layer of a coating because the coefficient of thermal expansion (CTE) of the substrate is so low compared to the coating materials. This mismatch causes microcracks to form on cooling down from the coating deposition temperature. For the system to protect against oxidation for long periods of time, it must possess a self-healing capability [2]. At least one of the internal layers must be either a glass or a glass-forming compound which can flow into and seal any cracks which develop. In order to create an oxidation protection system capable of providing protection over a large range of temperatures, it is necessary to seal the cracks which develop in the temperature range from the oxidation threshold of the composite (400 °C for C/SiC) to the microcracking temperature of the protective coating [3]. The microcracking temperature is the temperature at which the coating was originally flaw free, i.e. the deposition temperature for chemical vapour deposited (CVD) coatings or the sintering temperature for slurry coatings. This general oxidation behaviour of coated CMCs with carbon fibre reinforcement is represented schematically in Fig. 2.

It is necessary to establish a good adherence between the substrate and the coating, and between the different layers of the system. This requires good wetting properties and use of the correct manufacturing route. A suitable bond layer may provide the necessary resistance to the outward diffusion of carbon as well as forming a strong bond at the surface of the substrate. The bond layer should not penetrate excessively into the substrate.

Mechanical and chemical compatibility must be ensured between the coating system and between the various layers of the system. The coefficients of thermal expansion of layers in contact with each other should be matched as closely as possible to avoid the generation of large stresses during heating and cooling. It is also important that the components of the system do not react with each other to form undesirable phases, dissociate at high temperatures, or undergo phase transformations involving large volume changes during heating or cooling in the temperature range of interest.

To avoid non-uniform attack of the protection system, the homogeneity of the material must be ensured. The number of defects allowing the passage of oxygen through the coating should be minimized. The volatility of components of coatings should be as low as possible to minimize coating degradation. Coating degradation can also be reduced by the application of an outer erosion protection layer. If a suitable material is selected, this function can be combined with the requirement for a primary oxygen barrier.

The mechanical properties of the coating must not be neglected. The coating must be able to withstand any stresses generated at the surface of the component. A low modulus is desirable in order to accommodate strains generated by thermal expansion coefficient mismatches during thermal cycling.

This combination of properties cannot be met by any single material. It is necessary, therefore, to develop multi-layer coatings where each layer performs a specific function, allowing the coating as a whole to provide the required oxidation protection.

3. Fundamentals of multi-layer oxidation protection systems

It is generally accepted that in order to protect a ceramic matrix composite from oxidation over a range or high temperatures, a multi-layer system is required. The protection mechanisms of single layers of multilayers of the same material do not work over wide ranges of temperature and may not protect against the various oxidation mechanisms which exist over such temperature ranges. The main advantage in the development of a multi-layer coating is the possibility of associating complementary specific properties and of gaining the advantages of each layer while limiting their drawbacks [1].

In a multi-layer system, the individual layers should be strategically stacked with respect to the substrate. In this way, protection can be provided over the whole temperature range of interest. Various layers are activated at different temperatures or under certain conditions such as the opening of a crack. The stacking order of the layers must also take into account thermal expansion coefficients and chemical compatibility.

3.1. Erosion protection layers/primary oxygen barriers

If coated composites are to be used in aerospace gas turbines they will be exposed to high-velocity hot particles and reduced ambient pressures where vaporization becomes a threat to lifetime. It is apparent, therefore, that hard ceramic outer coatings with low vapour pressures are required for these applications.

TABLE I Temperatures for oxide vapour pressures of 10^{-3} mm [8, 9]

	HfO_2	Y_2O_3	ThO_2	ZrO_2	BeO	Al_2O_3	CaO	TiO_2	SiO_2	MgO
Temp. (°C)	2475	2250	2239	2239	2027	1905	1875	1780	1770	1695

By far the most common primary oxygen barriers are silicon carbide, SiC and silicon nitride, Si_3N_4. They are both refractory and oxidation-resistant due to the formation of a slow-growing silica, SiO_2, scale upon oxidation. Silica exhibits a relatively low vapour pressure to temperatures as high as 1650 °C as well as low oxygen diffusivity [2]. The silica-based ceramics also exhibit the most attractive thermal expansion compatibility with the substrate.

The oxidation of Si_3N_4 differs from that of SiC in that its oxidation rate is two to three orders of magnitude lower in the well-studied temperature range of 1100–1400 °C. Also, while SiC yields SiO_2 as the only product of oxidation, Si_3N_4 oxidation produces an inner layer of silicon oxynitride, Si_2N_2O beneath the outer silica scale. It has been proposed that this inner Si_2N_2O layer constitutes a better barrier than SiO_2 to oxygen diffusion by virtue of a tighter network structure, and hence is responsible for the slower oxidation rate of Si_3N_4 [5]. Silicon oxynitride is considered to be one of the most stable nitrides in oxidizing atmospheres at high temperature and could therefore be an excellent candidate material for a primary oxygen barrier in a protection system [6].

Many hard oxide ceramics have also been considered as potential outer layers. Sheehan [7] has calculated that a value of 10^{-3} mm is an appropriate maximum vapour pressure for a material to be used as an erosion protection layer. Table I shows the temperature at which various oxides have a vapour pressure of 10^{-3} mm [8, 9].

It can be seen from Table I that all of these materials appear to be suitable for use as an erosion protection layer, having vapour pressures below the critical value of 10^{-3} mm at temperatures up to a minimum of 1695 °C. However, most of these materials have features which are undesirable for coating use. CaO and BeO are both sensitive to moisture. The high toxicity of BeO is a further disadvantage, as is the radioactivity of ThO_2. Titanium oxide is very sensitive to the oxygen concentration of the environment and may suffer from phase instability and the formation of suboxides which are less refractory than TiO_2. In order for HfO_2 and ZrO_2 to be useful as erosion protection layers, they must be stabilized against undesirable phase changes which occur during heating and cooling. It has been shown that an outer HfO_2 layer has less tendency to crack than Y_2O_3 [10]. Vitreous SiO_2 is a good barrier to oxygen but lacks the hardness required of an erosion protection layer. The usefulness of silica is, therefore, limited to that of a scale formed on a silicon-containing non-oxide ceramic. The thermal expansion coefficients of oxide ceramics are generally higher than the corresponding borides or carbides, meaning that there is a greater mismatch in CTE between the coating and substrate for an oxide coating than a non-oxide coating. This mismatch can lead to coating spallation. Hence it is advantageous to coat the substrate with a non-oxide material which forms an appropriate oxide scale on exposure.

A disadvantage of non-oxide outer layers which form oxide scales is the erosion of the scale by vaporization and excessive flow in high-velocity gas streams. These problems may be overcome by the use of overlay coatings. Such overlayers are discussed later. A more serious problem with oxide scales is the buildup of gaseous oxidation products between the scale and the non-oxide ceramic. Equlibrium gas presssures at the scale/ceramic interface increase with increasing temperature. When a temperature is reached where the gas pressure at the interface is greater than the ambient pressure, the scale becomes frothy and porous. This allows very rapid attack of the underlying ceramic.

Because it is desirable to combine the requirement for an erosion protection layer with that for a primary oxygen barrier, the oxygen permeability of candidate materials must be considered. HfO_2, ZrO_2, and ThO_2 can be ruled out on the grounds that their oxygen permeabilities are too high [11–13]. These materials may, however, be useful as erosion protection layers when the primary oxygen barrier requirement is fulfilled by another layer. The permeabilites of Al_2O_3 and Y_2O_3 are lower, but are still higher than that of vitreous silica, suggesting that SiC and Si_3N_4 may well possess the best combination of properties for use as an erosion protection layer/primary oxygen barrier.

In the past, iridium has been tried as an outer erosion layer for protecting CMCs from oxidation at very high temperatures. Iridium is attractive because of its 2440 °C melting point and its extremely low oxygen permeability at temperatures as high as 2200 °C [7]. Although excellent protection has been demonstrated for short times in the 2000–2100 °C range, difficulties in fabricating high-quality coatings and the cost and availability of iridium were deterrents to further development. Other major drawbacks for the use of iridium are the high thermal expansion mismatch between the metal and the coating and erosion problems due to the formation of volatile IrO_3 [14]. The thermal expansion mismatch is probably more significant because IrO_3 formation can be controlled by the application of a thin oxide overlayer [7].

To summarize, it is apparent that SiC and Si_3N_4 are the most attractive materials in terms of the combination of properties required, due to their formation of a glassy silica scale. Outer coatings of these materials are primary barriers to oxygen, provide a hard erosion-resistant outer surface, and act to resist erosion and vaporization of glasses used in other layers for crack sealing. Oxides such as Al_2O_3 and Y_2O_3 are worthy of consideration as oxygen barriers, whilst other oxides such as HfO_2, ZrO_2, and ThO_2 may be of use as erosion-protection layers. Iridium may offer useful oxygen barrier properties but exhibits a large thermal expansion mismatch with the substrate, potentialy causing spallation problems.

Unfortunately, silicon-based ceramics have poor environmental durability in atmospheres containing molten salts, water vapour, or hydrogen. Molten salts such as Na_2SO_4 or Na_2CO_3 are formed from impurities in an engine's fuel and air intake and dissolve the protective silica scale that exists on the surface of SiC and Si_3N_4. Water vapour reacts with the silica scale to form gaseous $Si(OH)_4$, and hydrogen reduces the silica scale to gaseous SiO [15]. All of these reactions can lead to an accelerated or catastrophic degradation, and thus limit the lifetime of the protection system. SiC and Si_3N_4 erosion layers therefore require an overcoat to ensure environmental protection if their full potential is to be realized.

It has been proposed that a tantalum pentoxide overcoating could protect silicon-based outer erosion layers from the various forms of corrosion [16]. An additional outer layer of a material such as Ta_2O_5, Si_2N_2O or ZrO_2 may also be used to minimize erosion and excessive flow of vitreous silica. Mullite ($3Al_2O_3 2SiO_2$) appears most promising as an overcoating because of its chemical compatibility with silicon-based ceramics, low CTE, and relatively high chemical stability. Mullite coatings applied by conventional plasma spraying are amorphous but then tend to crack on thermal cycling due to a volumetric contraction associated with crystallization. Lee *et al.* [15] have now developed a fully crystalline, plasma-sprayed mullite coating which has dramatically improved adherence and thermal shock resistance. The superior coating adherence is obtained by first roughening the SiC surface prior to deposition of the mullite overlayer. The precipitation of amorphous mullite is prevented by decreasing the cooling rate. This is achieved by heating the SiC layer above the crystallization temperature. This new mullite coating has been applied to an SiC substrate and subjected to cyclic oxidation between room temperature and 1200–1400 °C in air. For a 20 h cycle oxidation test, the weight gain was half that of an uncoated substrate. In contrast, conventionally sprayed mullite coatings did not render any oxidation protection to the substrate because of severe cracking of the coating. Preliminary tests have shown that these novel mullite coatings are promising for protection against molten salt corrosion, and mullite–yttria-stabilized zirconia (YSZ) dual layer coatings are promising for protection in oxidizing/reducing gases and water vapour [15].

3.2. Functionally active layers

In order to provide effective oxidation protection over long periods of time and under conditions of thermal cycling, it is necessary for a coating system to be capable of preventing any oxygen which penetrates the primary oxygen barrier from reaching the substrate, and to be capable of sealing cracks which will inevitably form during service. Both these functions can be performed by one or more functionally active layers. The use of glassy materials for such purposes has been considered for many years. In 1934, a patent was issued to the National Carbon Company for a coating method to render carbon articles oxidation resistant at high temperatures [17]. The coating described in the patent consisted of a SiC inner layer and an outer glaze based on B_2O_3. Glazes on P_2O_5 and SiO_2 are also mentioned.

The use of borate glasses has been extensively studied. Borate glasses have many properties which make them useful materials in oxidation protection applications. The viscosity of B_2O_3 in the temperature range 600–1100 °C is such that it will form thin protective films. The tendency of B_2O_3 to wet SiC and Si_3N_4 and flow into coating cracks makes it an excellent sealant material for extended-life applications. In systems where the outer coating is a non-oxide ceramic which forms a silica scale, B_2O_3 forms an excellent sealant in the temperature range 600–1100 °C where the viscosity of silica is too high to allow crack-sealing behaviour. The usefulness of borate glasses is limited, however, by vaporization at temperatures above 1000 °C [18] and moisture sensitivity [19]. Hydrolysis of B_2O_3 when exposed to ambient moisture causes the glass to swell and crumble. This can cause coating spallation at room temperature due to glass swelling or spallation during heating due to moisture release [4]. Hydrated borates are highly volatile and so there may be glass depletion at relatively low temperatures in moist environments [2]. These properties, together with the comparatively high vapour pressure and oxygen diffusivity, mean that B_2O_3 is generally used as a secondary oxidation barrier beneath the outer coating which acts to minimize the glass depletion.

In order to provide protection at temperatures above 1100 °C, it is necessary to use a sealant with superior high-temperature properties to those of B_2O_3. Silica is stable up to approximately 1800 °C, but at lower temperatures is too viscous to close cracks effectively. Glasses must, therefore, be modified in order to protect the composite over the full temperature range.

Volatilization can be reduced by increasing the viscosity of borate glasses. This may be achieved by adding up to 25 mol % of a refractory oxide to the B_2O_3 sealant. Suitable oxides include TiO_2, ZrO_2, HfO_2, Al_2O_3, Y_2O_3, Sc_2O_3, La_2O_3, SiO_2 and CeO_2. The choice of oxide is determined by the temperature range over which the effect is required. For example, alumina is a suitable addition in the 550–900 °C range, titania for intermediate temperatures, and either zirconia or hafnia for a high-temperature regime in the range 1200–1600 °C [20]. The moisture sensitivity of borate glasses can be reduced by the use of Li_2O additions, but unfortunately lithia has the disadvantage of reducing viscosity and so increasing volatilization. This may be corrected, however, by the addition of a third oxide such as silica.

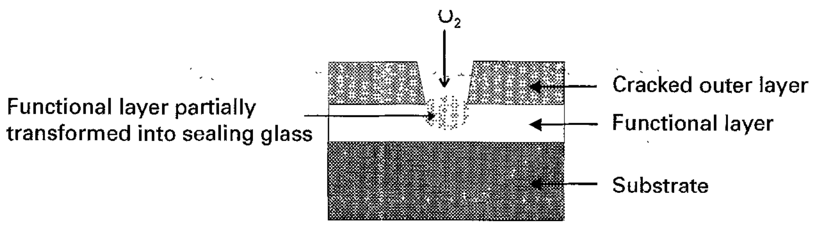

Figure 3 Conversion of functional layer material to glass sealant on exposure to oxygen.

The crack-sealing properties of silica-based glasses may be improved by the addition of alkali oxides such as Li_2O or B_2O_3. However, the downside to this approach is that both these additions compromise the advantages pure silica presents over borate glasses because both the moisture sensitivity and oxygen permeability of the glass are increased. This could result in damage due to moisture uptake, chemical incompatibility with outer coatings, or accelerated oxygen transport to the substrate. Both Li_2O and B_2O_3 have significantly higher vapour pressures than SiO_2 and thus may present volatility problems over long periods at high temperatures [2].

To summarize, silica-based glasses offer a temperature advantage over borates, but do not perform as well at the lower end of the temperature range. Low-temperature performance can be improved by fluxing with oxide additions but this is at the expense of high-temperature performance. The upper temperature limit for the use of borate or silicate glasses in contact with carbon is 1500 °C [2], so if a ceramic matrix composite reinforced with carbon fibres is to be used at higher temperatures, a refractory carbide interlayer is required to prevent a carbothermic reduction reaction occurring.

In order to overcome the deficiencies of binary systems, a sealant of composition $10TiO_2$–$20SiO_2$–$70B_2O_2$ has been developed [21]. The SiO_2 and TiO_2 additions have the effect of increasing the moisture resistance of the glass, reducing volatility at high temperatures, increasing the viscosity of the sealant, and preventing corrosion of any SiC layers in contact with the sealant. Increasing the TiO_2/B_2O_3 ratio reduces the high-temperature viscosity of the sealant, whereas increasing the SiO_2/B_2O_3 ratio causes the low-temperature viscosity to increase rapidly which is detrimental to oxidation performance in the 500–800 °C temperature range.

A glassy sealant belonging to the system P_2O_5–SiO_2–Al_2O_3 has been developed to protect CMCs reinforced with carbon fibres [22]. The coating is formed by either spraying with a gun or by brush application of a liquid suspension. After drying, the mixture is heat treated at a temperature sufficient to transform the layer into an insoluble, self-healing silica glass.

A more recent approach to the use of glass sealants in functionally active layers is to use glass-forming compounds which, when oxidized, form glasses. This method has the advantage that oxygen which penetrates the outer layers is actively absorbed rather than simply slowed down. Fig. 3 shows schematically the way in which such layers work.

Several boron- and silicon-containing compounds have been suggested for use in functionally active layers. Boron carbide, B_4C, is of interest for such an application because it oxidizes much more rapidly than silicon-based materials, thus giving faster sealing. On exposure to oxygen, B_4C undergoes the reaction

$$B_4C + 4O_2 \rightarrow 2B_2O_3 + CO_2 \qquad (1)$$

This occurs between 700 and 900 °C and is accompanied by a 250% volume increase which ensures excellent crack-sealing properties [7]. The main disadvantage of B_4C is the formation of a gaseous oxidation product. Gas buildup underneath a coating can cause spallation or reduce the effectiveness of the B_2O_3 sealant by causing it to become frothy and porous.

Several borides have been considered for functional layer use. The most common are titanium and silicon borides. TiB_2 exhibits exceptional hardness and chemical stability and therefore offers considerable promise for use in highly erosive and corrosive environments such as those found within gas turbine engines. The oxidation of TiB_2 produces a two-phase mixture of B_2O_3 glass and TiO_2:

$$2TiB_2 + 5O_2 \rightarrow 2B_2O_3 + 2TiO_2 \qquad (2)$$

Courtois *et al.* [3] have deposited titanium diboride by CVD as a sealant layer underneath an SiC outer layer to protect C/SiC composites and found it to be a promising material for crack sealing in the temperature range 700–1100 °C. The silicon borides have an advantage over other potential functional layer materials because they oxidize to form a borosilicate glass with no other products. Also, the composition of the resulting glass can be determined by altering the composition of the boride. This means that sealants can be produced for specific temperature ranges.

Another candidate material for use as a crack sealant is molybdenum disilicide, $MoSi_2$. The initial oxidation of $MoSi_2$ in air is strongly dependent on O_2 partial pressure and temperature. At high temperature and high oxygen partial pressure, for example, 1420 °C and $> 10^4$ Pa, $MoSi_2$ oxidizes to form volatile MoO_3 and vitreous SiO_2. As the silica layer coarsens it becomes more difficult for oxygen to diffuse through the SiO_2 scale and the specimen becomes resistant to further oxidation. This process is referred to as passive oxidation. At low partial pressures, gaseous SiO_2 forms and no protective layer exists, this is active oxidation. Below 600 °C, MoO_3 is not volatile, which, in turn, prevents the formation of a continuous amorphous SiO_2 layer. This results in a spalling of layers from the surface, referred to as $MoSi_2$ pest [23]. It should also be noted that $MoSi_2$ undergoes a ductile to brittle transformation at approximately 1000 °C [24]. Molybdenum disilicide is not, therefore, as straightforward a crack sealant as borosilicate glasses and the pesting problem must be solved if effective protection is to be achieved.

3.3. Bond layers

The main functions of the bond layer are to reduce the thermal expansion coefficient mismatch between the substrate and the functionally active layers, prevent the outward diffusion of carbon from the substrate, and prevent chemical reactions between the functional layer materials and the substrate.

In designing protection systems for long-term use at high temperatures, the avoidance of coating spallation is vital. This is therefore the primary function of the bond layer, and is achieved by matching the thermal expansion coefficient of the bond layer as closely as possible to that of the substrate.

The most commonly used bond-layer materials are SiC and Si_3N_4 can be applied using either CVD or slurry techniques. The thermal expansion coefficient of Si_3N_4 more closely matches that of carbon fibre-reinforced CMCs. It would therefore be expected that Si_3N_4 bond layers would perform better than SiC. It has been found, however, that the better CTE match of Si_3N_4 to the substrate affords no major improvement over SiC in terms of oxidation protection [25]. The thermal expansion coefficient of the bond layer may be reduced by depositing a coating of SiC or Si_3N_4 containing a dispersion of low-expansion particulates such as silica or boron nitride [7].

The second function of the bond layer is to prevent the reduction of oxides in the outer layers by carbon. This is highly undesirable, because not only does it involve degradation of the carbon fibres and, therefore, the mechanical properties of the composite, but also consumes oxide sealant material, reducing the lifetime of the coating. Both SiC and Si_3N_4 perform this function acceptably, but SiC may itself react with oxides to form SiO and CO gases during prolonged exposure to high temperatures [7].

4. Performance issues

Currently, the best oxidation-protected carbon fibre-reinforced CMCs have quite variable service lifetimes. Although variability is often associated with the practical issues of coating quality and reproducibility, typical failure mechanisms can be identified as:

(i) coating erosion;
(ii) coating spallation due to CTE mismatches;
(iii) reactions between substrate and/or coating components;
(iv) reactions between erosion layer and the surrounding atmosphere; and
(v) the moisture sensitivity of borate glasses.

Coating spallation is often a problem because very few coatings can match the ultralow CTE of CMC composites made with high-performance carbon fibres. The traditional ways of avoiding spallation are to minimize the thermal expansion mismatch between the coating and the substrate, minimize coating thickness, and maximize coating adherence.

A multi-layer coating with a CTE graded configuration ranging from high at the surface to low at the substrate, invariably develops cracks at the tensile-loaded high CTE surface which propagate towards the substrate. However, if the graduation is interrupted by a low CTE intermediate layer, cracks initiated at the surface terminate at the low CTE component which is loaded in compression [10]. Kehr *et al.* [26] have proposed that a ZrO_2 filled CVD-SiC bond layer created by SiC deposites on a diluted ZrO_2 slurry layer will reduce crack formation because of stress-releasing microcracks that form in this process.

The one desirable feature that is not present in the current generation of coating systems is minimal coating thickness. This is principally due to the problem of glass-sealant corrosion of the outer coatings. Corrosion of the outer SiC and Si_3N_4 coatings is as a result of destructive oxidation of the protective SiO_2 that is normally maintained on the silicon-based ceramics. Glass-forming inner layers are generally thin, no more than approximately 50 μm. Thin outer coatings have been tried, but because of rapid degradation by the borate sealant glasses, such outer coatings are usually at least 200 μm thick [27]. Coatings of this thickness have an increased tendency to spall under rapid thermal cycling conditions and are still subject to corrosive failure over long periods at high temperatures [7].

5. Systems described in the current literature

The simplest systems consist of either a single layer or several layers of the same material. These systems provide only limited protection because they are prone to failure by spallation and oxygen penetration, and have no internal sealing capability. An example is a single layer of SiC deposited by slurry dipping [28]. Such coatings are not worthy of further consideration as viable oxidation protection systems except in low-temperature, short-term applications.

The protective properties of refractory coatings such as SiC can be dramatically improved by covering with a glassy layer. The glassy layer usually consists of a borate-based glass, applied either as a slurry [29] or by dipping in molten B_2O_3 [30]. These systems provide some self-healing capability up to around 1000 °C but are limited by borate volatility at higher temperatures, the major volatile being HBO_2 [31]. Hoffmann *et al.* [32] have protected C/C composites with a SiC coating applied by CVD and an outer layer of silica. Problems associated with this system are the lack of low-temperature crack sealing due to the high viscosity of silica and the poor erosion resistance at high temperatures where the lower viscosity of silica allows excessive flow and some volatilization.

One system which shows some promise for possible incorporation into a more complex coating is a borate glass containing particles of a refractory material, for example $ZrSiO_4$ [33]. The zirconium silicate particles make the borate phase more effective at high temperatures or moisture contents by holding the glass in pores between particles, thus reducing evaporation. Borides of zirconium and hafnium could also be used as particles.

5.1. Multi-layer systems

A multi-layer protection system has been developed for C/SiC composites and consists of a SiC bond layer, an inner sealant layer of B_4C, and an outer erosion layer of SiC [1]. In this example, shown in Fig. 4, all three layers were deposited by CVD. It was found that the layer thicknesses affected both the spallation behaviour and the temperature range over which the coating is effective.

The best results have been achieved using a thick inner SiC layer (120–140 μm), a thin sealant layer (10–15 μm), and an outer SiC layer of intermediate thickness (40–60 μm) so that the total thickness of the trilayer coating is in the range 160–200 μm.

Franc and Macret [34] have developed an oxidation protection system for C/SiC composites designed for use in structural components on space vehicles which are exposed to extreme temperatures during re-entry. This system, shown in Fig. 5, consists of a SiC bond layer, an adaption layer, and a primary oxygen barrier.

The purpose of the adaption layer is to prevent oxide–carbide reactions and improve the mechanical compatibility of the layers. Promising results up to 2000 °C have been obtained using the system shown in Fig. 5 but alternative materials may be used. It is claimed that the outer layer may be Al_2O_3, HfO_2 or ZrO_2 while the adaption layer may be composed of TiB_2, AlN, HfN, ZrC, Pt or Ir.

Bentson *et al.* [35] have patented a complex four-layer protection system for C/C composites which comprises inner and outer glass sealant layers covered with inner and outer ceramic layers, as shown in Fig. 6. The inner sealant layer is applied by painting and is a boron-rich layer which comprises elemental boron or B_4C, and a zirconia source which may be zirconia itself, zirconium diboride or possibly zircon sand. This particulate is preferably bimodal, with the large particles being at least ten times larger than the small particles. An ideal composition is 60 wt % B_4C, 30 wt % pitch and 10 wt % ZrO_2 (to level the viscosity of the borate glass over a wide temperature range). The outer sealant layer is composed of precursors to a ternary or quaternary borate glass, and a granular refractory material. A particularly preferred composition is 30 wt % B_4C, 5 wt % SiO_2, 15 wt % Li_2ZrO_3, 30 wt % SiC particles and 20 wt % pitch. The zirconia is included to provide viscosity stabilization of the borate glass. Lithium reduces loss of the boron from the borate glass upon exposure to atmospheric moisture through cracks. Li_2ZrO_3 is preferred as a source for lithium and zirconium because of its high melting point. The inner ceramic layer of the outer coating is composed of B_4C and is 5–25 μm thick, whereas the outer ceramic layer is 100–300 μm thick and is SiC. Both layers are applied by either CVI or CVD processes. This coating proved successful when the C/C composite was subjected to thermal cycling up to 1460 °C [35].

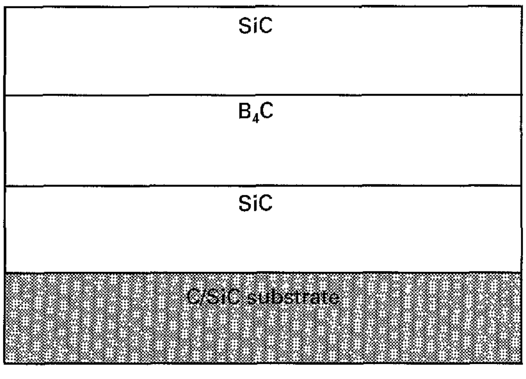

Figure 4 The multi-layer oxidation protection system developed by Goujard *et al.* [1].

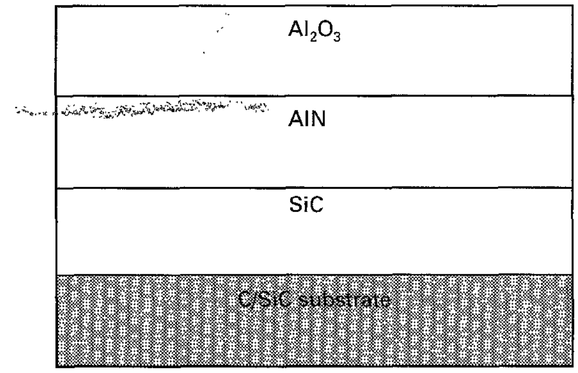

Figure 5 The multi-layer oxidation protection system developed by Franc and Macret [34].

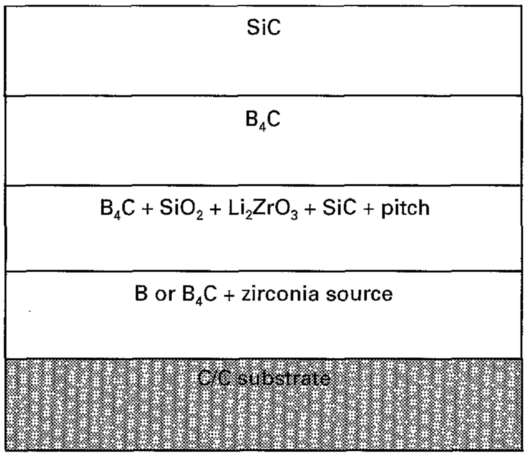

Figure 6 The multi-layer oxidation protection system developed by Bentson *et al.* [35].

Another promising coating system which has recently been developed by Dietrich [36] involves hot-wall CVD reactor technology to deposit multiple SiC layers on to a C/C substrate at lower temperatures than conventional high-temperature, cold-wall processes. The advantages of using a low deposition temperature are that the crack network which develops within the coating on cooling down to room

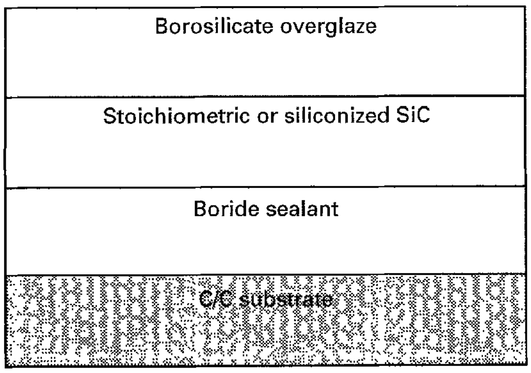

Figure 7 The multi-layer oxidation protection system developed by Dietrich *et al.* [36].

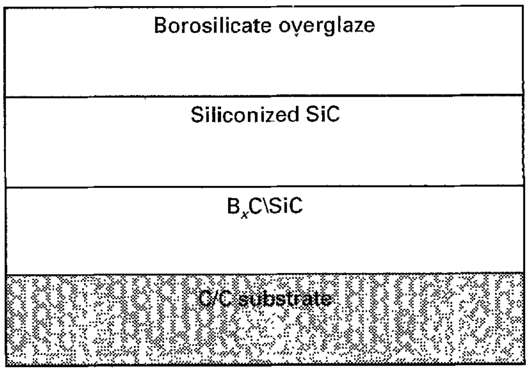

Figure 8 The multi-layer oxidation protection system developed by Barrett *et al.* [25].

temperature tends to be very tight in terms of crack width. Also the crack network is closed at a temperature considerably below the maximum use temperature. The coating itself is a three-part system as shown in Fig. 7.

The protection system consists of an initial boride sealant layer applied to the substrate by either slurry painting, spraying or CVD. This is covered with the primary oxygen barrier, applied by CDV, consisting of near-stoichiometric SiC or siliconized SiC. The last step is an optional borosilicate overglaze applied by painting, spraying or impregnation. A multiple CVD deposition process is used to apply the SiC layer in order to obtain a uniform thickness. Depositing the sealant layer by CVD ensures a more compact, denser, and more oxygen-impermeable layer compared to one applied by a slurry. Also, thickness is difficult to control when using slurry sealants.

The coating with a siliconized SiC primary oxygen barrier (containing 80%–90% silicon) has been extensively evaluated and found to be satisfactory for applications up to around 1400 °C. The free silicon in the coating is believed to reduce oxidation due to its lower CTE compared to SiC and also due to its plasticity, which develops above 1000 °C. On testing above 1400 °C under atmospheric conditions, however, silicon metal has been observed sweating out of the coating. For applications above this temperature, the protective coating with a near-stoichiometric SiC primary oxidation barrier (containing 60%–75% silicon) has been used.

The purpose of the glassy overcoat is to fill the existing crack network with a sealer that enhances oxidation protection and moisture resistance. The glaze is applied as an aqueous sol of borosilicate composition which can be either painted, sprayed or dipped. It is even possible to use a gas turbine engine's heat for final firing of the coating. While considering a gas turbine engine application, it would be expected that the glaze would become fluid and be wiped away by the high-velocity gases, but it has been found that sufficient glass stays in the crack network to provide necessary protection. A potential advantage of the glaze is that it can be renewed periodically without the need to remove the composite component [36].

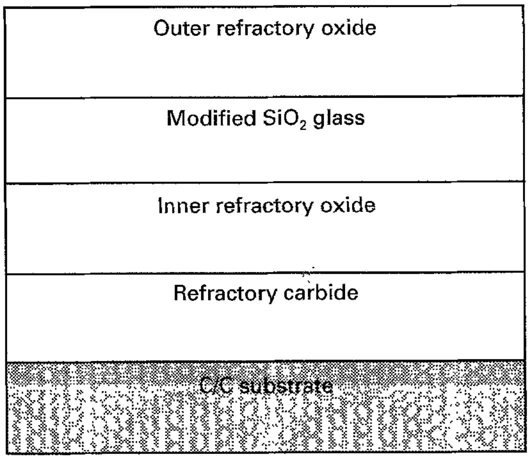

Figure 9 The idealized coating system proposed by Strife and Sheehan [4].

Barrett *et al.* [25] have evaluated the oxidation performance of coated C/C composites tested with and without external glassy overcoats. The protection system which gave the best results is shown in Fig. 8. This oxidation protection system consists of a non-stochiometric boron carbide/silicon carbide (B$_x$C/SiC) layer which is covered with a siliconized SiC layer. Finally, a glassy overcoat is applied. It has been found that coated samples with externally applied glazes have appreciably longer oxidative lifetimes. This is because this overcoat seals coating cracks prior to the formation of B_2O_3 from boron-bearing constituents within the coating. This increases the lifetime of the available boron reservoir in the component by reducing volatilization and hydration of the internal sealant. When diffusion of oxygen occurs through the glaze to the underlying coating, B_2O_3 counterdiffusion and mixing with the glaze slows the depletion of the boron reservoir [25].

An idealized four-layer coating for protecting C/C composites at temperatures in excess of 1800 °C has been proposed by Strife and Sheehan [4] and is shown in Fig. 9. This system has a refractory oxide as an outer layer for erosion protection with a modified SiO_2 glass inner layer to provide an oxygen barrier and as a sealant for cracks in the outer coating. The inner layer has to be isolated from the substrate and carbide inner layer by a second layer of refractory oxide. A refractory carbide inner layer serves as a diffusion barrier between the C/C and oxides to prevent carbothermic reduction. Candidate materials for such a system include ZrO_2, HfO_2, Y_2O_3, ThO_2 for the refractory oxide layer, while TaC, TiC, HfC, or ZrC could be possible selections for the carbide layer because they all have low carbon diffusivities. A multilayer system such as this possesses the required chemical stability, but there would certainly be problems in producing coatings of consistent quality. In addition, the high CTE of the protection system compared to the substrate will create severe problems of mechanical compatibility in thermal shock situations.

6. Conclusion

SiC and Si_3N_4 are the leading candidate materials for the erosion and bonding layers of an oxidation protection system for carbon-fibre composites. When functioning as an erosion layer, these silicon-based materials require an overcoat to ensure environmental protection if their full potential is to be realized. Effective oxidation protection can only be achieved if the coating system has a self-healing capability. A functional layer containing boron and/or silicon phases is therefore necessary to seal cracks. Silica-based glasses offer a temperature advantage over borates, but do not perform as well at the lower end of the temperature range. Low-temperature performance can be improved by fluxing with oxide additions but this is at the expense of high-temperature performance. This literature review shows there are many different coating systems that have been tried; however, when selecting a system, costs should always be considered and compared with the savings introduced as a result of increased lifetimes.

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