

High-Temperature Protective Coatings on Carbon Composites

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Abstract—Research on high-temperature coatings for the protection of heat-proof carbon composites from oxidation and ablation in high-speed high-enthalpy fluxes of oxygen-bearing gas is analyzed. A promising coating architecture with excellent protective properties is established.

Keywords: carbon composites, oxidation, erosion, ablation, high-speed fluxes, protective coatings, oxide films

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Carbon composites are very promising heat-proof materials, with distinctive properties suitable for use in thermally stressed aerospace components [1, 2]. However, the use of carbon composites in oxygen-bearing atmospheres is limited by the rapid oxidation of carbon and silicon carbide at around 400 and 1200°C, respectively [1–3]. That impairs the mechanical properties of such composites.

In high-speed high-enthalpy fluxes of oxygen-bearing gas, the structural degradation of carbon composites is worsened by thermochemical processes (oxidation or catalysis), mechanical wear (erosion), and ablation [4–6]. By ablation, we mean endothermal entrainment of material from the surface by a gas flux (by melting and flow, evaporation, sublimation, or thermolysis). It is of great importance to expand the range of operational temperature and duration of carbon composites.

Current approaches to the protection of carbon composites include inhibition of the matrix by antioxidants; and application of preventive coatings to prevent the oxidation of reinforcing fibers. The most effective, however, is the application of heat-proof protective coatings at the surfaces in contact with oxidative materials [2–6].

In the present work, we analyze existing approaches to the protection of carbon composites from oxidation or ablation, with a view to selecting a coating architecture that ensures effective protection.

MULTILAYER COATINGS BASED ON ULTRAHIGH-TEMPERATURE CERAMIC

Single-layer coatings cannot be regarded as promising means of protecting carbon composites (with rare exceptions [7]), because they are not gas-tight and

their thermal linear-expansion coefficients are inconsistent with those of the substrate. Defects formed in single-layer coatings in the course of production or operation will affect the preventive properties. Therefore, at present, attention focuses on the development of multilayer heterophase coatings—in particular, those whose main structural component is ultrahigh-temperature ceramic based on highly refractory transition-metal borides (ZrB_2 , HfB_2 , TiB_2) with added carbides (SiC , ZrC , HfC , TiC , TaC) and silicides ($MoSi_2$, $TiSi_2$, $ZrSi_2$, $TaSi_2$, WSi_2) [5, 6].

Usually, the inner layer in the coating system consists of silicon carbide SiC , characterized by high thermal stability and chemical compatibility with carbon composites; their thermal linear-expansion coefficients are also similar. Accordingly, SiC may effectively provide barrier and compensation functions [3, 5].

At the surface of a carbon-bearing composite, a multilayer coating based on HfC , with an SiC inner layer, was obtained in [8]. The coating's protective properties are due to the combined action of all the layers (including an outer layer based on refractory erosion-resistant hafnium dioxide HfO_2 , formed by the oxidation of HfC). In addition, the rate of heat transfer declines on account of the gaseous oxidation products (CO , CO_2 , SiO) at the boundary layer.

Since HfO_2 is highly catalytic, the coating's effectiveness may be decreased on additional surface heating by heterogeneous recombination of the atoms and ions in the gas flux to form molecules. Therefore, better resistance to oxidation and ablation is provided by three-layer $SiC/HfC/SiC$ [9] and $SiC/ZrC/SiC$ [10] coatings.

In the general case, the outer layer of multilayer coatings must include the oxides of refractory metals,

oxide-forming compounds (such as borides, carbides, and silicides), or pure metals capable of forming gas-tight surface films on oxidation. The following coatings are characterized by high resistance to ablation, on account of their laminar structure, which serves as a thermal barrier and inhibits oxygen diffusion to the carbon composite: MoSi₂/SiC [11], TaC/SiC [12], ZrC/SiC [13], HfC–SiC/SiC [14], HfC–HfO₂/SiC [15], HfC–ZrC–SiC/SiC [16], and HfC–TaC–SiC/SiC [17].

Compounds of rare-earth elements (most often, lanthanum) may be introduced to stabilize the oxides ZrO₂ and HfO₂ in tetragonal or cubic modifications or in compounds with phase stability from room temperature to the proposed operating conditions [18]. For example, the resistance to heating in ablation may be improved if the coatings on carbon composites are modified with La₂O₃ [19] and La₂Zr₂O₇ [20].

Multicomponent oxide films formed when complex coatings react with oxygen are the most promising. For example, the protective properties of the HfC–ZrC–SiC/SiC coating are due to the formation of a gas-tight oxide layer on the surface, according to [16]. In addition, the reaction of SiO₂ with HfO₂ and ZrO₂ forms orthosilicates HfSiO₄ and ZrSiO₄, which are relatively impermeable to oxygen and also prevent crack propagation (by pinning) [21, 22]. With increase in the duration of ablation, the silicon content gradually declines, and the coating structure becomes laminar, thanks to phase transitions of HfO₂ and ZrO₂. Analogous behavior is observed for the HfC–TaC–SiC/SiC system, at whose surface the ablation is accompanied by the formation of oxides HfO₂, HfSiO₄, and Hf₆Ta₂O₁₇ with high melting points [17].

We know that there is less evaporation of oxides formed in the oxidation of refractory carbides at high temperature thanks to the lack of boron. Nevertheless, diborides are assumed to be more resistant than carbides to oxidation and ablation [5, 6]. In addition, although the melting points is significantly higher for refractory carbides than for diborides, thanks to the higher thermal conductivity, boride–carbide coatings are regarded as more promising for the creation of heat-proof coatings on carbon composites, because the borosilicate glass formed on the surface prevents oxygen diffusion within the coating. In addition, refractory oxides with low saturated vapor pressure are formed on the surface [18].

Thanks to research on the resistance to ablation, multiphase boride–carbide coatings with various modifiers have been created: ZrC–LaB₆/SiC [23], ZrB₂–SiC–ZrC/SiC [24], SiC–MoSi₂–ZrB₂/SiC [25], TaB₂–SiC–Si/SiC [26], ZrB₂–CrSi₂–Si/SiC [27], TaB₂–TaSi₂–SiC–Si/TaC–SiC [28], and ZrC–SiC/ZrC–LaB₆/ZrC/SiC [29]. For example, the ZrB₂–SiC–Si/SiC–B coating forms a heterogeneous layer based on borosilicate glass and ZrO₂ on the sur-

face [30]. That effectively protects the carbon-bearing composite from ablation thanks to the evaporation of B₂O₃, which decreases the surface temperature by increasing the heat absorption.

MULTIPHASE COATINGS WITH UNOXIDIZED LIQUID PHASE

In high-speed high-enthalpy fluxes of oxygen-bearing gas, we note the intensification of local gas corrosion and selective oxidation of individual coating components. Surface microrelief in the form of roughness, corrosive and erosive pitting, and cavities is also more developed. That, in turn, increases the turbulence of the gas in boundary regions and the erosive failure of the coatings. If unoxidized liquid phase is introduced in the coatings, random defects (including those inaccessible to viscoplastic oxide phase) are more effectively sealed. The range of possible coating-production methods is considerably increased, and their structural continuity is improved.

A SiC–ZrB₂–ZrSi₂ coating for C_f/C composites was described in [31]. The ZrSi₂ phase fills the pores and cracks in the structure typical of coatings based on ultrahigh-temperature ceramic. Together with the initial ZrB₂ phase, zircon ZrSiO₄ formed on oxidation of the coating permits pinning, thereby absorbing much of the energy in crack propagation, which is therefore slowed. Crack propagation is also impaired by the compressive stress due (probably) to the formation of elemental silicon as a result of the selective oxidation of the zirconium in ZrSi₂ by molecular oxygen. The coating is highly stable in thermocycling: it withstands 50 cycles of the type 20°C → 1500°C (5 min) → 20°C; the final density is 15.2 g/m².

A method of producing a heat-proof coating at the surface of C_f/C composites was described in [32]. The coating includes a barrier layer (tantalum carbide), an intermediate layer (tantalum silicide), and a base layer (consisting of a eutectic mixture of silicides such as WSi₂, W₅Si₃, MoSi₂, Mo₅Si₃, and HfSi₂). In an air flux, the coating withstands 15 thermocycles of the type 100°C → 1900°C (10 min) → 100°C.

A promising approach to the protection of carbon composites from oxidation is to create complex alloy coatings of the type Si–TiSi₂–MoSi₂–TiB₂–SiC_w [33, 34]. These coatings differ fundamentally from the familiar coatings in that a dendritic–cellular structure of disilicide phases Ti_xMo_{1–x}Si₂ (0.1 < x < 0.87), TiSi₂, and MoSi₂ is formed. The space within this structure is filled by fusible ($T_{me} \sim 1320^\circ\text{C}$) eutectic (Si + Ti_xMo_{1–x}Si₂ + TiSi₂), refractory TiB₂ particles, and SiC_w whiskers.

On oxidation, the coating is converted to a multi-layer structure with the formation of heterogeneous oxide film. Random defects are rapidly filled with eutectic and the protective film develops more rapidly

than for traditional coatings, through the liquid phase (eutectic). High resistance to erosion is ensured by the presence of a branched thermostable silicide framework, reinforced by refractory TiB_2 particles and SiC_w whiskers.

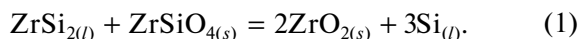
The coating effectively protects the carbon-bearing composite from oxidation and erosion in hypersonic high-enthalpy fluxes of air plasma at surface temperatures $T_w = 1680^\circ\text{C}$ (for at least 3600 s); 1740°C (for at least 1200 s); 1800°C (for at least 900 s); 1900°C (for at least 200 s); 2000°C (for at least 60 s); and 2100°C (for at least 20 s). The coating is characterized by high catalytic activity (constant rate of heterogeneous recombination of nitrogen and oxygen atoms, $K_w = 3\text{--}5$ m/s); satisfactory emissivity ($\epsilon \approx 0.7$); healing of technological and operational defects (diameter no greater than 0.6 mm); and protection of the sharp edges of components ($R \geq 0.5$ mm).

In hypersonic plasma fluxes, when T_w is around $1850\text{--}1860^\circ\text{C}$, coating failure occurs by erosional entrainment of the oxide film and the generation and growth of cavities at the interface between the unoxidized coating layer and the oxide film; the cavities are filled with volatile compounds (SiO , CO) [34]. When the saturated vapor pressure of the oxidation products exceeds the atmospheric pressure, the integrity of the oxide film is lost, and oxidation passes to the active stage.

Building on the work in [33, 34], promising $\text{ZrSi}_2\text{--MoSi}_2\text{--ZrB}_2$ ceramics were proposed in [35]. The matrix in such systems consists of ZrSi_2 ($T_{\text{me}} = 1620^\circ\text{C}$) or even more fusible $\text{Si--ZrSi}_2\text{--MoSi}_2$ eutectics. In addition to their structural value, such materials may be used in slip-firing modification of carbon-composite matrices and the production of heat-proof coatings. This is associated with their ability, when heated, to form considerable quantities of liquid phase, which is available for steeping of the composite matrix and sintering of applied powder layers in compact coatings. Materials based on ultrahigh-temperature ceramic are not suitable for such applications.

On oxidation at 1650°C in air, a multilayer oxide film is formed on the ceramic. It consists of an outer layer of complex silicate glass and a lower layer based on ZrO_2 and SiO_2 . Zircon ZrSiO_4 is formed and partially dissociates, while secondary refractory phases MoB and Mo_5Si_3 appear.

Within the ceramic, we observe a physicochemical reaction in the $\text{ZrSi}_2\text{--ZrSiO}_4$ system, leading to the reduction of elemental silicon and simultaneous oxidation of zirconium, to form the phase ZrO_2 , which is thermodynamically stable. With a shortage of molecular oxygen or its complete absence, the reaction above 1620°C takes the form



This is a multistage reaction; as it proceeds, more products are formed. On the one hand, that produces compressive stress in the ceramic, thereby hindering oxygen diffusion. On the other, it results in the upwelling of silicon and the eutectic ($\text{Si} + \text{ZrSi}_2$) toward the surface. On oxidation, they replenish the glassy film as it is entrained from the surface.

PROMISING COATING ARCHITECTURE

On the basis of our analysis of current approaches to the protection of heat-proof carbon composites against oxidation and ablation in high-speed high-enthalpy fluxes of oxygen-bearing gas, we may identify a promising coating architecture.

An effective coating must be heterophase and must include predominantly unoxidized refractory components. In the course of operation (oxidation), the coating must be converted to a multilayer system, with an external thermally stable layer in the form of a complex multicomponent oxide film. Refractory structural phases of type $\text{Zr}(\text{Hf})\text{O}_2$ should increase the resistance of the oxide film to erosional entrainment in the high-speed flux and create a temperature gradient in the coating. The glassy phase (ideally heterogeneous) around this framework is intended to decrease inward oxygen diffusion, to mend defects, and to damp the surface's catalytic activity.

To ensure thermal stability of the internal structure in the coating's basic (unoxidized) layer, a framework of refractory phases—such as $\text{Zr}(\text{Hf})\text{B}_2$ and/or MoSi_2 —is required. However, the layer based on refractory phases is itself inclined to defect formation, especially on thermocycling (because of the difference in thermal linear-expansion coefficients of the coating and the carbon-bearing composite).

To permit mending of the internal defects and to relax the thermal stress due to heat transfer, the coating must include not only a refractory framework but also a relatively fusible component, which will be in the liquid or viscoplastic state during coating operation—for example, TiSi_2 , ZrSi_2 , or a eutectic of type $\text{Si--TiSi}_2\text{--MoSi}_2$ [33, 34] or $\text{Si--ZrSi}_2\text{--MoSi}_2$ [35]. We also assume that the unoxidized components reacting with oxygen will replenish the oxide phases in the outer layers; in other words, it will play a regenerative role. By varying the composition and regulating the structural and phase transformations in the formation of the basic layer, broad scope is available for adjusting the functional properties of the coatings.

To protect the carbon base from the oxygen that unavoidably diffuses through the external oxide layer, it is expedient to use a barrier layer (based on SiC , say) applied to the substrate before the basic coating is formed. That layer may also ensure compatibility of the coating and carbon-bearing composite in terms of thermal properties (primarily the thermal linear-expansion coefficients), decrease the opposing diffu-

sion of carbon and coating elements, and increase the thermochemical stability of the coating structure as a whole and the adhesive strength within the system.

In our view, $ZrSi_2$ – $MoSi_2$ – ZrB_2 composites best correspond to the proposed coating architecture. Accordingly, we need to test their suitability as initial materials in slip-firing technologies for the production of protective coatings on carbon composites.

CONCLUSIONS

(1) We have analyzed existing methods of producing high-temperature coatings for the protection of heat-proof carbon composites from oxidation and ablation in high-speed high-enthalpy fluxes of oxygen-bearing gas. Globally, there is great interest in coatings based on highly refractory transition-metal borides (ZrB_2 , HfB_2 , TiB_2) with added carbides (SiC, ZrC, HfC, TiC, TaC) and silicides ($MoSi_2$, $TiSi_2$, $ZrSi_2$, $TaSi_2$, WSi_2); refractory oxides (HfO_2 , ZrO_2); or complex synthetic composites based on oxide ceramic.

(2) A promising coating architecture with excellent protective properties has been established.

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