

# Oxidation Protection Coatings for C/SiC Based on Yttrium Silicate

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## Abstract

*The factor which currently precludes the use of carbon fibre reinforced silicon carbide (C/SiC) in high temperature structural applications such as gas turbine engines is the oxidation of carbon fibres at temperatures greater than 400°C. It is, therefore, necessary to develop coatings capable of protecting C/SiC components from oxidation for extended periods at 1600°C. Conventional coatings consist of multilayers of different materials designed to seal cracks by forming glassy phases on exposure to oxygen. The objective of this work was to develop a coating which was inherently crack resistant and would, therefore, not require expensive sealing layers. Yttrium silicate has been shown to possess the required properties for use in oxidation protection coatings. These requirements can be summarised as being low Young's modulus, low thermal expansion coefficient, good erosion resistance, and low oxygen permeability. The development of protective coatings based on a SiC bonding layer combined with an outer yttrium silicate erosion resistant layer and oxygen barrier is described. Thermodynamic computer calculations and finite element analysis have been used to design the coating. C/SiC samples have been coated using a combination of chemical vapour deposition and slip casting. The behaviour against oxidation of the coating has been evaluated. © 1998 Elsevier Science Limited. All rights reserved*

## 1 Introduction

The last 30 years have seen a steady development in the range of ceramic materials with potential for high temperature engineering applications. One such application is the use of ceramic matrix com-

posites (CMCs) as structural hot section components of propulsion systems for the next generation of commercial supersonic aircraft. The inclusion of these materials in gas turbine engines would allow significantly higher operating temperatures than is possible with conventional nickel based superalloy materials. Such utilisation of CMCs offers improvements in thermal efficiency which can be translated into decreased specific fuel consumption, decreased weight and consequently lower stresses in rotating components and higher thrust to weight ratios. Raising the operating temperature would increase the thermodynamic efficiency of the engine and reduce the level of pollutant emission. These effects are achieved by moving closer to stoichiometric combustion of the fuel and reducing the amount of air which must be diverted through the turbine components for cooling purposes.

The combination of high strength and damage tolerant fracture behaviour of carbon fibre reinforced ceramics makes them candidates for this application. In non-oxidising environments, the mechanical properties of carbon fibre reinforced ceramics are retained to temperatures in excess of 2000°C.<sup>1</sup> The factor which currently inhibits the application of such materials in gas turbine engines is the oxidation of carbon fibres at temperatures above 400°C. To prevent oxidation requires eliminating access of oxygen to the carbon fibres. Hence there is a need for external coatings capable of preventing oxidation of carbon fibre reinforced ceramics for extended periods at temperatures in the region of 1600°C. Such coatings have been reviewed by Westwood *et al.*<sup>2</sup> These coatings are extremely prone to cracking, particularly when used under conditions of thermal cycling on a CMC substrate with a substantially lower thermal expansion coefficient. Thus, conventional coatings consist of multilayers of different materials designed to seal cracks by forming glassy phases on exposure to oxygen.

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Carbon fibre reinforced silicon carbide composite manufactured by Daimler-Benz Aerospace (Dornier Research) was used as the substrate for the coating layers. Yttrium silicate,  $\text{Y}_2\text{SiO}_5$ , has been suggested as a suitable outer coating layer and promising oxidation protection results have been reported.<sup>3</sup> Figure 1 shows the architecture of the coating.

Previous work in this area has typically been based on a 'trial and error' approach with minimal theoretical input to the design of coatings. The use of thermodynamic modelling and finite element analysis at the design stage was intended to act as a filtering process for potential coatings, allowing experimental work to be concentrated on the most promising coatings. Oxidation studies were carried out on the coated composite samples using continuous mass measurement during isothermal exposure to air at 1600°C.

## 2 Thermodynamic Calculations

The software which has been used is the MTDATA package<sup>4</sup> supplied by the National Physical Laboratory, UK. A methodology has been developed to apply thermodynamic modelling to oxidation protection coatings.<sup>5</sup> The chemical compatibility between coating components and reactions of the coating with an oxidising environment have been investigated.

The chemical compatibility between  $\text{Y}_2\text{SiO}_5$  and SiC has been assessed by performing calculations on the Y–Si–O–C system. The equilibrium phases for the composition 2Y–2Si–5O–1C (corresponding to  $\text{Y}_2\text{SiO}_5$ –SiC) have been calculated as a function of temperature (Fig. 2). The calculated amounts of  $\text{Y}_2\text{SiO}_5$  and SiC do not change between 0 and 1750°C, indicating that the two compounds will not react with each other over that temperature range.

The exposure of the coating to oxygen has been simulated by calculating the equilibrium species at 1600°C as a function of increasing oxygen concentration for the composition 2Y–2Si–(5 + x)O–1C

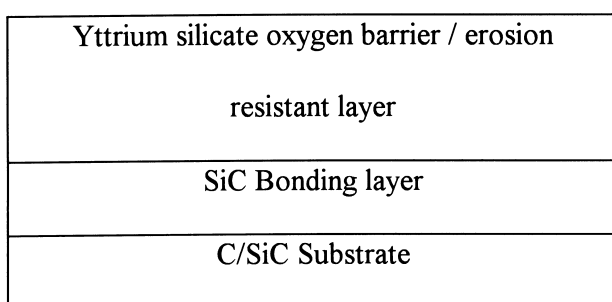


Fig. 1. Yttrium silicate-based coating architecture.

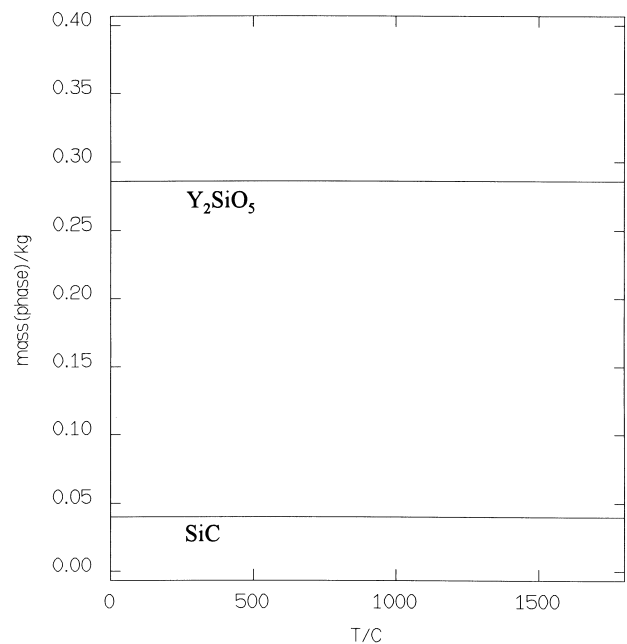


Fig. 2. Calculated equilibrium phases up to 1700°C for the composition 2Y–2Si–5O–1C.

( $\text{Y}_2\text{SiO}_5 + \text{SiC} + x\text{O}_2$ ). The results of these calculations are shown in Fig. 3. The reactions involved in the oxidation of a  $\text{Y}_2\text{SiO}_5 + \text{SiC}$  coating are thought to be:

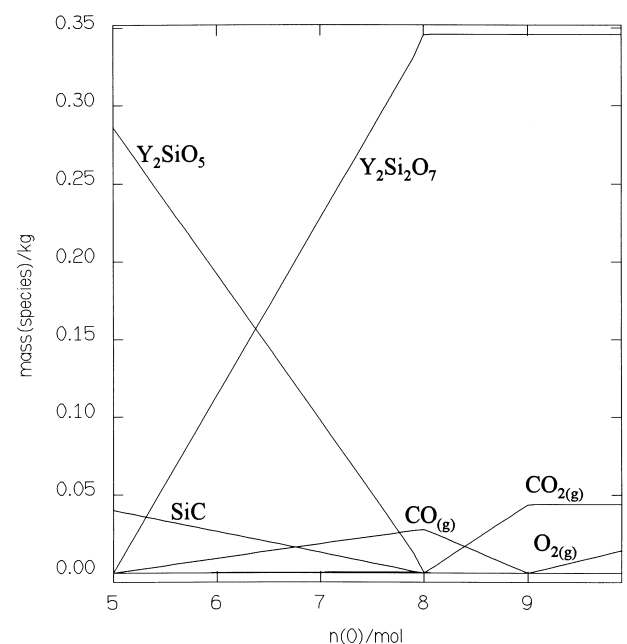
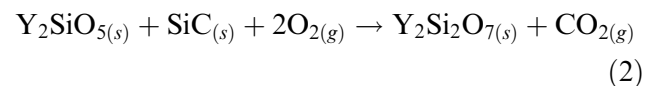
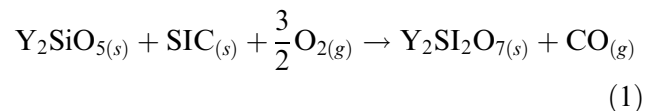


Fig. 3. Calculated equilibrium species at 1600°C as a function of oxygen concentration for the composition 2Y–2Si–(5 + x)O–1C.

### 3 Finite Element Analysis

A finite element analysis methodology<sup>6</sup> has been developed using the LUSAS software to determine the stresses in the coating which develop on thermal cycling due to the thermal expansion coefficient mismatch with the substrate. Hence it is possible to estimate the degree of cracking likely to occur. Figure 4 shows the stresses which are generated in the coated composite on cooling from 1200°C to room temperature.

Figure 4 shows that the 50 µm SiC bond layer is under a tensile stress of approximately 1.5 GPa and so will definitely crack. However, the outer Y<sub>2</sub>SiO<sub>5</sub> layer is only under a tensile stress of approximately 100 MPa and so is not expected to crack. This is because Y<sub>2</sub>SiO<sub>5</sub> has an extremely low coefficient of thermal expansion ( $4.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ )<sup>3</sup> and it also has an exceptionally low Young's Modulus (approximately 20 GPa).<sup>3</sup> It is these two mechanical property parameters which have to be minimised in order to reduce the stresses generated in a coating layer and thus minimise the degree of cracking.

### 4 Coating Manufacture

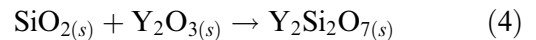
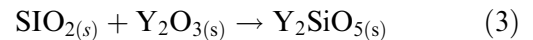
C/SiC substrate material with a CVD (20 µm) SiC bond layer was supplied by Daimler-Benz Aerospace (Dornier Research), Germany. The yttrium silicate layer was then deposited by slip casting and sintering.

Aqueous Y<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> slips were prepared from Y<sub>2</sub>O<sub>3</sub> powder of mean diameter 3.5 µm, and microcrystalline SiO<sub>2</sub> powder of mean diameter 2.5 µm. Two homogenising procedures were used: ball milling with Al<sub>2</sub>O<sub>3</sub> balls and jar for 4 h, and high speed shear mixing limited to short times (up

to 4 min). An alkali-free strong base, tetramethylammonium hydroxide (TMAH), was selected as a dispersant to achieve slip stability based on the results of isoelectric point measurements for Y<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. Viscosities as low as 8–10 mNsm<sup>-2</sup> were obtained for these slips. Two slip compositions were selected to give coatings with different compositions. One coating was composed of principally Y<sub>2</sub>SiO<sub>5</sub> while the other was a mixture of Y<sub>2</sub>SiO<sub>5</sub> and Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>.

Yttrium silicate coatings were obtained on C/SiC substrates with SiC bond layers by slurry dipping. Four layers of yttrium silicate were required to achieve a thickness of 100 µm on CVD SiC bond layers.

The sintering process is complex since the simultaneous presence of oxide and non-oxide materials seriously limits the compatibility conditions. The selected sintering parameters were 3 h at 1600°C in flowing argon ( $P_{\text{O}_2} = 10^{-3}$  bar). The possible reactions between SiO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> during sintering are:



The XRD pattern shown in Fig. 5 for the mixed Y<sub>2</sub>SiO<sub>5</sub>/Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> coating confirms that these reactions have occurred, indicating the presence of Y<sub>2</sub>SiO<sub>5</sub> as the main phase, along with a considerable amount of Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>.

### 5 Oxidation Studies

Oxidation behaviour has been investigated by continuous isothermal mass change measurements in

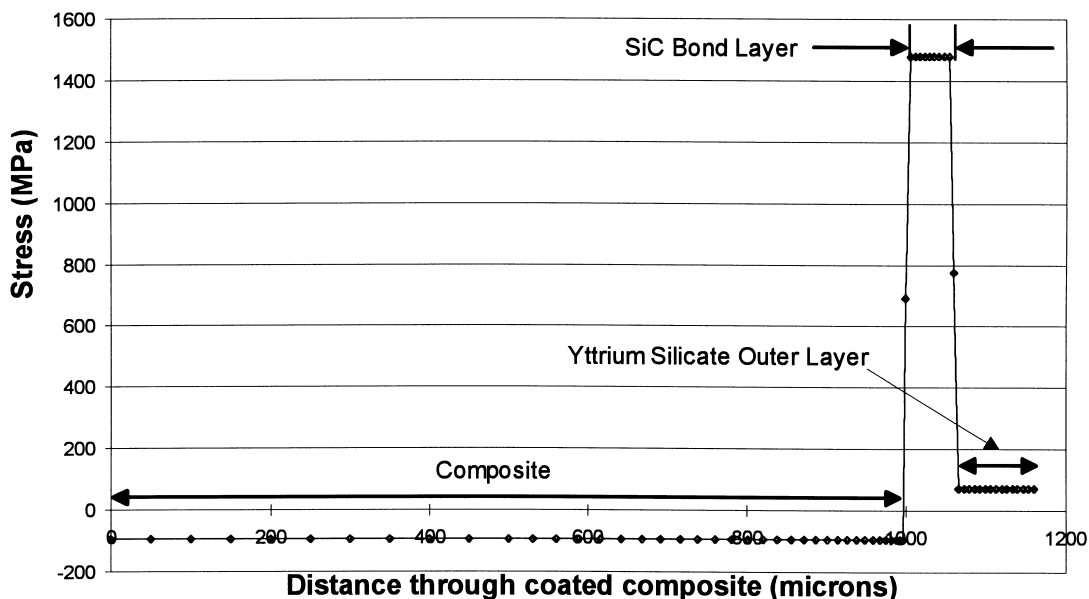


Fig. 4. Calculated stresses in SiC/Y<sub>2</sub>SiO<sub>5</sub> coated C/SiC on cooling from 1200°C to room temperature.

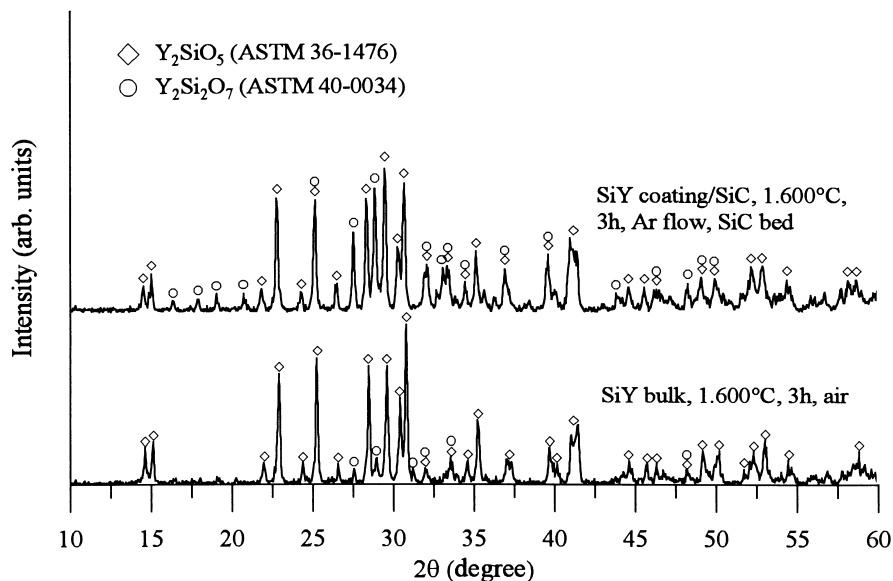


Fig. 5. Mixed XRD pattern for the mixed  $Y_2SiO_5/Y_2Si_2O_7$  coating after 3 hours at  $1600^\circ C$ .

air at  $1600^\circ C$ . Details of the experimental setup can be found elsewhere.<sup>7</sup> The results of oxidation tests on the two types of coating are shown in Fig. 6.

Work at Daimler-Benz Aerospace (Dornier Research) has shown that the critical mass loss at which the mechanical properties of the C/SiC composite used in this work are degraded sufficiently to cause failure is 3%. It can be seen from the results in Fig. 6 that the SiC/ $Y_2SiO_5$  coating provides negligible protection from oxidation. The mixed SiC/ $Y_2SiO_5 + Y_2Si_2O_7$  coating, however, protects the composite for 53 h. The reason for this difference becomes apparent in examination of samples by scanning electron microscopy. Figure 7 shows the surface of the  $Y_2SiO_5$  coating. It is clear

that this layer is extremely porous, explaining the rapid oxidation of the underlying composite. The surface of the mixed  $Y_2SiO_5 + Y_2Si_2O_7$  coating is shown in Fig. 8. It is clear that the degree of porosity in this coating is much lower, thus explaining the enhanced protective effect. The effect of the additions  $Y_2Si_2O_7$  is to lower the temperature at which effective sintering can be achieved. The sudden mass loss of the  $Y_2SiO_5 + Y_2Si_2O_7$  coated sample shown in Fig. 6 after approximately 50 h has been attributed to the oxidation of the SiC bond layer causing spallation of the outer coating. This is shown in Fig. 9. The relatively crack free appearance of the coatings and the absence of any evidence of phases other than SiC,  $SiO_2$ ,  $Y_2SiO_5$ ,

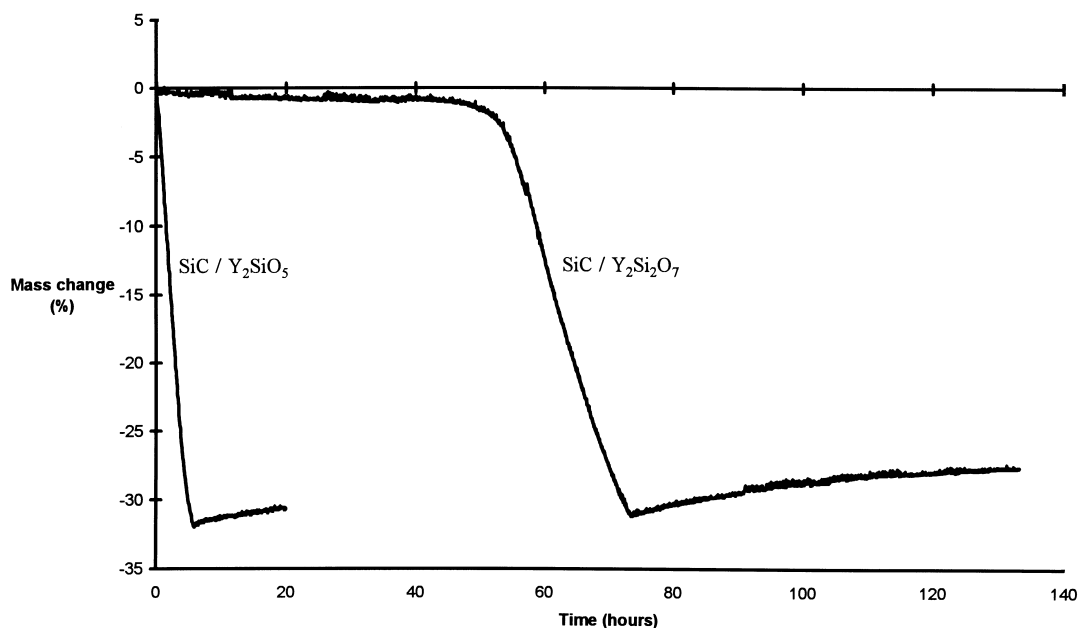


Fig. 6. Isothermal oxidation behaviour of C/SiC with coatings based on yttrium silicate at  $1600^\circ C$ .

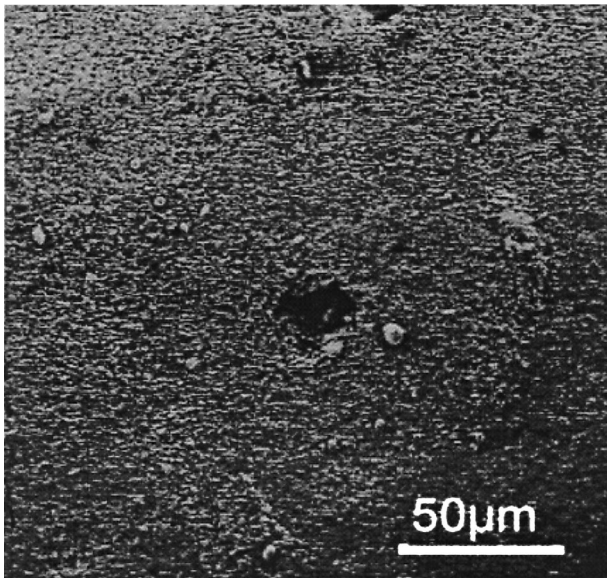


Fig. 7. SEM micrograph of the surface of the  $Y_2SiO_5$  coating.

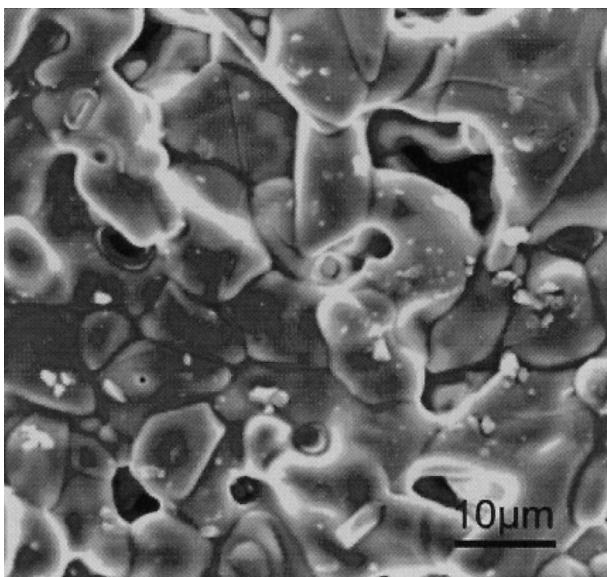


Fig. 8. SEM micrograph of the surface of the  $Y_2SiO_5/Y_2Si_2O_7$  coating.

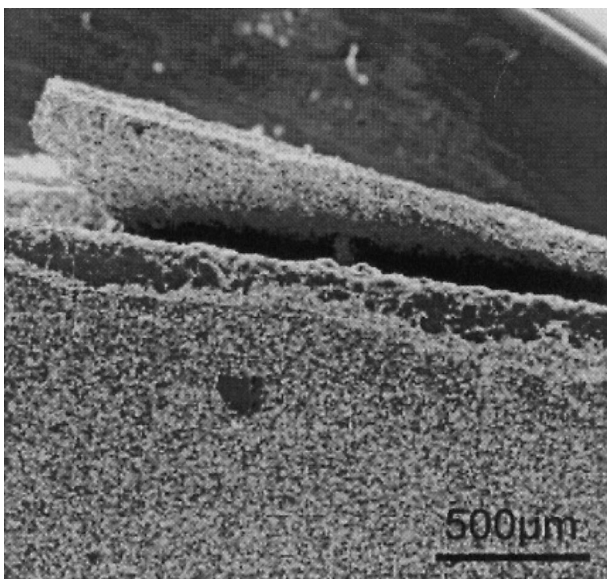


Fig. 9. Spallation of  $Y_2SiO_5 + Y_2Si_2O_7$  coating layer.

and  $Y_2Si_2O_7$  verifies the results of finite element analysis and thermodynamic calculations.

## 6 Conclusions

It has been shown that thermodynamic calculations and finite element analysis can be successfully used to predict the performance of oxidation protection coatings for C/SiC. A method has been developed to deposit  $Y_2SiO_5$  based coatings on SiC coated C/SiC by slip casting and sintering. The process variables have been investigated and the optimum parameters determined. It has been found that the coating must be of a high quality in order to provide significant protection against oxidation. This can be achieved by using a mixed  $Y_2SiO_5 + Y_2Si_2O_7$  outer layer. These coatings provide protection against oxidation at  $1600^\circ C$  as evidenced by isothermal mass change measurements and scanning electron microscopy. The failure mechanism of such coatings has been found to be spallation caused by the oxidation of the SiC bond layer.

## Acknowledgements

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