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Oxidation behaviour of SiC/SiC ceramic matrix composites in air

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ABSTRACT

Oxidation of silicon melt infiltrated SiC/SiC ceramic matrix composites (CMC) was studied in air at 1200–1400 °C for 1, 5, 24 and 48 h. Weight gain and oxide layer thickness measurements revealed the oxidation follows parabolic reaction kinetics with increase in temperature and time. XRD showed the extent of oxide layer (SiO_2) formation was greatest after 48 h at 1400 °C: an observation confirmed by X-ray photoelectron spectroscopy (XPS), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM) analyses. Oxide layer thickness varied from 1 μm after 48 h at 1200 °C to 8 μm after 48 h at 1400 °C. Oxidation of SiC/SiC composites is both temperature and time dependent with an activation energy of 619 kJ mol^{-1}. BN coatings around SiC fibres showed good resistance to oxidation even after 48 h at 1400 °C.

1. Introduction

The need to increase the cycle efficiency and reduce noise and NO_x emissions from jet engine turbines has promoted development of ceramic matrix composites (CMC) such as silicon carbide fibre-reinforced silicon carbide (SiC-SiC) [1–3]. Use of CMCs will lead to a significant improvement in fuel consumption and thrust-to-weight ratio compared to metal alloys. In addition, the low density of CMCs allows weight savings of up to 30% compared to Ni-based super alloys equating to about 1000 kg/engine thus leading to vastly improved fuel consumption [4]. At high temperature >900 °C, SiC may undergo either active or passive oxidation [5]. At low oxygen pressures (<1 atm), active oxidation occurs due to the formation of volatile products as follows:

$$SiC(s) + 2SiO_2(s) \rightarrow 3SiO(g) + CO(g) \quad (1)$$

$$SiC(s) + O_2(g) \rightarrow SiO(g) + CO(g) \quad (2)$$

During passive oxidation a protective film of SiO_2 is formed on the surface according to:

$$SiC(s) + \frac{3}{2}O_2(g) \rightarrow SiO_2(s) + CO(g) \quad (3)$$

$$SiC(s) + 2O_2(g) \rightarrow SiO_2(s) + CO_2(g) \quad (4)$$

Castello and Tressler [6] studied the oxidation behaviour of sintered SiC and chemical vapour deposition (CVD) SiC at 1200–1500 °C in dry oxygen. They observed a parabolic behaviour and suggested that oxidation is controlled by permeation of oxygen ions through the growing oxide film. However, the oxidation rates of CVD SiC were higher than those of sintered SiC due to the presence of free silicon. Schiroky [7] studied oxidation behaviour of CVD SiC at 1200–1800 °C. At >1500 °C, growth of uniform films of amorphous silica was observed and with bubble formation between 1700 and 1800 °C due to the high CO pressure at SiC-SiO_2 interfaces. Oxidation of CVD SiC was also investigated by Narushima et al. [8] at 1550–1700 °C. They observed that the parabolic oxidation behaviour of CVD SiC consists of stage I and stage II as a result of a change in diffusion rate of oxygen in the SiO_2 film due to crystallization from amorphous silica to β-cristobalite. However, in both stages, the parabolic rate constant (k) depends on the oxygen partial pressure meaning that the rate controlling process for oxidation is diffusion of the oxygen ions in the SiO_2 film. They obtained activation energies of 345 and 387 kJ mol^{-1} for stage I and stage II respectively at 1550–1700 °C in reasonable agreement with values obtained by Sucov (420 kJ mol^{-1}) at 700–1200 °C [9].

Only a few reports on the oxidation of SiC/SiC composites are available in the literature. Kleykamp et al. [10] were the first to investigate the influence of carbon-coated SiC fibre reinforcement on the oxidation behaviour of SiC at 550–1520 °C in air. They observed that at 870–985 °C, the amorphous SiO_2 transforms to tetragonal cristobalite and oxidation kinetics follow a quadratic rate law above 1000 °C. Moreover, no apparent improvement in corrosion resistance of SiC fibre-reinforced SiC compared to dense monolithic SiC was observed due to the high porosity (10 vol%) of the SiC matrix and the free carbon in the interlayers that is burnt out over the lower temperature range. Sheldon et al. [11]

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studied the oxidation behaviour of boron nitride (BN) coated SiC fibres in CMC at 1000–1450 °C. They suggested that oxidation of this material undergoes three different stages, where stage I represents oxidation of SiC to form SiO_2 and solid carbon according to:

$$SiC(s) + O_2(g) \rightarrow SiO_2(s) + C(s) \tag{5}$$

After all the available SiC has oxidised, stage II is active where the oxidation of solid carbon takes place to produce CO, where stage III corresponds to oxidation of the BN coating as follows:

$$2BN(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(l) + N_2(g) \tag{6}$$

They observed that formation of SiO_2 takes place before formation of B_2O_3 meaning that BN-coated SiC fibres will not necessarily lead to formation of a low melting oxide phase such as borosilicate glass, in agreement with Jacobson et al. [12].

Based on the above discussion, this work focuses on the oxidation behaviour and kinetics of BN-coated SiC-reinforced SiC composites at 1200–1400 °C in dry air for different periods of time. The main aim was to investigate the influence of several parameters (temperature and time) on the oxidation behaviour of SiC/SiC composites and to characterise formation of SiO_2 as a function of time.

2. Experimental methods

BN coated SiC/SiC composites were manufactured through chemical vapour infiltration (CVI) and slurry infiltration of SiC and then impregnated with liquid silicon. The SiC matrix and fibres are bonded together via a boron nitride fibre coating on the fibres, details are given elsewhere [13]. The samples were cut to 10 × 10 × 4 mm, then cleaned with acetone in an ultrasonic bath and dried in a vacuum oven for 24 h prior to testing. Oxidation experiments were conducted at 1200–1400 °C for 1, 5, 24 and 48 h in a lift furnace under static air and samples were quenched in air after each hold. Samples were placed on high purity >99.99% alumina boats (Almath crucibles, Newmarket, UK) in contact with their two edges to minimize the contact area between samples and crucible and then placed inside a chamber lift furnace (Lenton, Hope, UK) at a heating rate of 10 °C min^{-1}. The weight and dimensions of all samples were recorded before and after the experiment with precision of ±0.001 g and ±0.01 mm respectively.

Oxidation kinetics were analysed using a parabolic power law as follows [14]:

$$\left(\frac{\Delta w}{A}\right) = \sqrt{k.t} \tag{7}$$

where, Δw is the weight change before and after oxidation, A is the total surface area, k is the parabolic rate constant and t is the oxidation time. The activation energy (E) needed for oxidation was determined according to the Arrhenius equation [5]:

$$k = A.e^{(-E/RT)} \tag{8}$$

where, A is a constant, R is the gas constant and T is absolute temperature.

Samples before and after oxidation were characterised using XRD (Bruker instrument, Coventry, UK). XRD measurements were carried out in 2θ range of 10–80°. Phases were identified using Xpert High Score Plus software utilising the ICDD (International Centre for Diffraction Data) database.

Samples oxidised at 1400 °C for 1, 5, 24 and 48 h were analysed using XPS (K-Alpha, Thermo scientific, Warrington, UK) to determine the nature of the oxide layer through their binding energies. XPS measurements were conducted using Mg X-rays of 1253.6 eV. Photoelectrons from Si-2*p*, C–1s and O–1s core levels were collected using a hemispherical analyser with 50 eV pass energy, a 200 ms integration time and 0.1 eV steps. The analysis was performed using CasaXPS software. Shirley or two point linear background subtractions were employed depending on background shape. Scofield cross-sections were used as relative sensitivity factors in the calculation of the atomic percentages with relative sensitivity factor (RSF) of C 1s = 1.000. Peaks were fitted using GL(30) lineshapes; a combination of a Gaussian (70%) and Lorentzian (30%). All XPS spectra were charge corrected by referencing the fitted contribution of C—C graphitic like carbon in the C 1s signal to 284.6 eV.

Microstructures were examined in back scattered and secondary electron imaging (BSI and SEI, respectively) modes using a scanning electron microscope (SEM) JEOL (JSM 6010LA, Tokyo, Japan) also equipped with an energy dispersive spectroscopy (EDS) JOEL silicon drift detector (SDD) with ultra-thin window (UTW). Samples were mounted in epoxy resin and cut at 90 ° using diamond blade and polished to 1 μm and 0.06 μm suspensions of diamond and silica colloidal respectively. Samples were cleaned in an ultrasound acetone bath for 1 min to remove any contamination during polishing. Prior to SEM, samples were coated in gold to avoid electrical charging. The average oxide layer thickness (±0.5 μm) was obtained based on 200 points of both oxide faces from SEM micrographs using Image-J software.

The crystalline structures and chemistry of the as-received and oxidised samples of SiC/SiC CMC were characterised by Transmission Electron Microscopy (TEM). Cross-sectional TEM samples were prepared by focused ion beam (FIB) milling (Helios NanoLab 600). TEM bright field and Scanning Transmission Electron Microscopy (STEM) imaging was carried out on a JEOL (JSM 2100F, Tokyo, Japan)

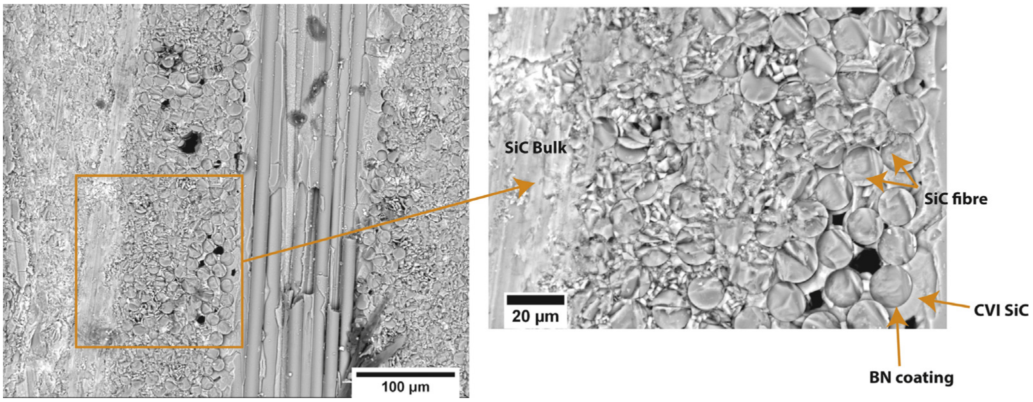

Fig. 1. SEI microstructure of BN coated SiC/SiC composites as received from supplier revealing the SiC bulk and fibres.