Surface & Coatings Technology 287 (2016) 119–128

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Phase and strain mapping of a protective coating on carbon–carbon

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ARTICLE INFO

Article history:
Received 5 November 2015
Revised 22 December 2015
Accepted in revised form 29 December 2015
Available online 30 December 2015

Keywords:
Carbon–carbon
Protective coatings
Synchrotron radiation
Residual stress

ABSTRACT

Carbon–carbon (C/C) is used in high temperature structures. To prevent rapid oxidation of the carbon, protective coatings are applied. This paper examines such a protective coating with high energy X-ray diffraction. The coating consisted of a 0.02 mm outer layer of sodium silicate glass on a 0.2 mm layer of silicon carbide (SiC) with a 0.1 mm transition layer into the C/C of carbon fibres surrounded by a SiC matrix. It was examined in its pristine state and after heating with an oxy-acetylene torch. An area X-ray detector was used to obtain phase and strain information as a function of depth through the coating. In-plane tensile strains were observed in both a crystalline SiO_2 phase and within the SiC of the transition layer. Oxidation protection was compromised by through-thickness cracks in the SiC layer caused by the large tensile cooling strains in the layer. The strains and the density of the cracking increased after heating. However, several mechanisms were identified that moderated the strains. Based on two of these mechanisms a buffer layer of graphite between the C/C and the SiC was proposed to improve oxidation resistance. The low elastic modulus of the graphite reduces the strains in the SiC coating, which reduces the crack density, which in turn improves oxidation resistance. Adding SiC fibres to the graphite and SiC was also proposed to further reduce cracking.

1. Introduction

The low density, high strength at very high temperatures (>2000 °C), and toughness of carbon–carbon (C/C) make it attractive for aerospace applications where high temperatures are experienced e.g. rocket nozzles and leading edges on re-entry vehicles [1,2]. However, it is susceptible to oxidation [1,2]. Oxidation resistance can be provided by replacing the carbon matrix with silicon carbide (SiC) [1] or by providing a protective coating [1,2,3], and [4]. The protective coating may have the benefit of allowing the bulk of the C/C to retain its high strength at high temperatures [5]. However, because the thermal expansion coefficient of C/C is lower than most oxidation resistant materials [6], in-plane residual strains will be formed in the coatings; either tensile strains when they cool from their formation temperature or compressive strains when they are heated during service (e.g. during re-entry). Such strains can limit the ability of the coatings to protect the underlying carbon from oxidation. Tensile strains can result in through thickness cracks in the coating that will allow any surrounding oxygen to penetrate directly to the carbon and thus burn it away at high temperatures. Compressive stresses can lead to spalling of the coating which again exposes the carbon to any surrounding oxygen and thus oxidation at high temperatures. Therefore the measurement of the strains in such coatings is an important factor in assessing their fitness-for-purpose. It is also important to map any variations of the strain in such coatings with depth, particularly as variations are likely at the outer surface and at the coating's interface with its substrate. Such strain measurement and mapping may indicate how oxidation protection might be improved by modifying the composition and structure of the coating and substrate system to reduce strains. High energy X-ray diffraction has been used to study the depth profile of residual strain in coatings [7,8].

We have studied C/C with a SiC conversion coating with and without heating with an oxy-acetylene flame. The coating contained through-thickness cracks generated by the thermal expansion mismatch between the coating and the C/C [2] and was therefore expected to contain residual strains. High energy X-ray diffraction was used to map the phase and residual strains as a function of depth. These maps were complemented with an analysis of the microstructures using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The type of C/C and coating system studied was employed successfully on the leading edges of the Space Shuttle Orbiter [2,9], thus this system, and the strain distributions measured here, provide a baseline against which alternative coatings [3] or improvements can be compared. In the discussion we analyse the origin of the observed residual strains and, based on this analysis, propose methods for reducing the level of strain and the number of through-thickness cracks with the intention of further improving the oxidation resistance. We also discuss how to improve the strain mapping technique and extend it to the carbon substrate.

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http://dx.doi.org/10.1016/j.surfcoat.2015.12.084
0257-8972/

2. Experimental

2.1. Samples

The 30 × 30 × 4.8 mm samples studied were cut from a 4.8 mm thick plate of C/C coated with a conversion coating of SiC and vacuum infiltrated with TEOS (tetra-ethyl orthosilicate) [9]. An example cross-section of the C/C is shown in Fig. 1. The C/C plate consisted of a two-dimensional lay-up of sheets of woven carbon fibre bundles. The orientation of the bundles in successive sheets alternated between +45°/−45° and 0°/90°, with the formation of the SiC consuming the surface +45°/−45° sheet. Within the C/C the bundles of carbon fibres had an elliptical cross-section approximately 0.13 mm high × 1 mm wide. The individual fibre diameter was about 8 μm. The manufacturing method is propriety but the C/C and coating are similar to the reinforced C/C with its SiC conversion coating that protected the wing leading edge of the Space Shuttle Orbiter [9]. The processing temperature of the SiC coating was 1650 °C, the TEOS is reportedly transformed to SiO_2 after a mild heat treatment, and an additional sodium silicate glass coating is applied to the top of the SiC coating [9]. This glass also contains SiC particles. The thermal expansion coefficient of this type of 2D C/C is 1.1×10^{-6} [6].

The strain mapping was performed on a pristine sample and a heated sample. The heating was performed using an oxy-acetylene flame to heat a circle of about 5 mm diameter in the centre of the 30 mm × 30 mm square samples. The peak temperature at the surface was measured as (1500 ± 100) °C by a pyrometer. The difficulty in aligning the pyrometer's line of sight exactly with the peak of the surface temperature distribution was responsible for the large temperature error. The heat flux was 920 Wm^{-2}. Following exposure to the flame, the heat affected region was visible to the naked eye. A 3 mm wide strip was cut from each sample so that the strip contained the bulk of the heat affected region at its centre as shown in Fig. 2. These strips were used for the high energy diffraction measurements. The visibility of the heated affected region enabled the X-ray beam to be positioned at its centre. A diamond cutting wheel was used to produce the strips and produced little damage. As the damage was limited to less than 0.1 mm from the cut it was unlikely to have affected the strain distribution through the bulk of the strips.

The chosen 3 mm width of the strips was a compromise between maintaining representative residual stresses, which required a wide sample, and strain sensitivity, which required a thin sample. Previous strain mapping and finite element calculation work [7] indicated that the strain relaxation would be limited in range to the order of the twice the coating thickness. However, the width could not be increased much beyond 3 mm without compromising the strain resolution as a wider strip would have broadened the diffraction rings on the X-ray detector. Thus, the 3 mm width was adequate for measuring representative residual stresses in the 0.2 mm thick coating and the adjacent 0.2 mm of substrate, but it was anticipated that any stress measurements from the central portion of the 4.8 mm thick substrate would be substantially below that found in the centre of a wider sample.

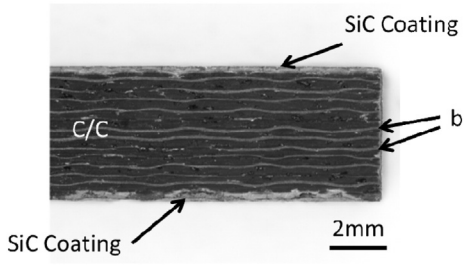

Fig. 1. Optical image of the C/C plate in cross-section. Two of the carbon fibre bundles running across the page are labelled b.

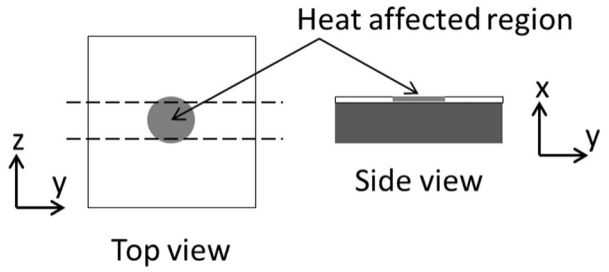

Fig. 2. Schematic diagrams of a 3 × 3 cm C/C sample viewed from the top, and the side view of the strip cut from the sample after exposure to the flame. The cut lines are shown as dashes and the heat affected region as mid-tone grey. The axes enable the relationship with the X-ray beam and detector to be visualised when compared to Fig. 3.

The strips were held in the X-ray beam by clamping them lightly at one end to minimise any disturbance to the stress field measured at the centre of the strips. This did not produce any visual damage to the strips such as extra cracking of the coating.

2.2. Apparatus

The strain mapping was performed using high energy X-ray diffraction at the A2 beamline at CHESS at Cornell University in New York State [10]. Fig. 3 shows a schematic of the experimental rig; the arrangement is similar to that developed at other synchrotrons [7,8]. A 60 keV X-ray beam was passed through the strip producing diffraction cones which were registered on a large area X-ray detector as diffraction rings (Fig. 4). Strain free material produced circular diffraction rings (solid circle on the detector in Fig. 3). Strains in the strip distorted the diffraction rings; for instance, a compressive strain in the y-direction would have reduced the atomic spacing in this direction causing the diameter of the rings to increase in this direction (the dotted ellipse in Fig. 3). The Poisson effect will have caused a complementary increase in the atomic spacing and a decrease in ring diameter in the x-direction (also the dotted ellipse in Fig. 3). Measurement of the distortion allowed the strains in the plane parallel to the detector and perpendicular to the X-ray beam to be determined.

It was also possible for the diffraction rings to be distorted by slight tilts in the detector relative to the incident X-ray beam direction. To enable these tilts to be determined and the images adjusted for this systematic distortion a powder sample of ceria [11] was also exposed. Kapton tape was used to fasten the ceria standard on the top of the analysed strips. The ceria spanned the strip in the direction of the X-ray beam which ensured that it covered the same span of distance from the detector. The powder did not sustain a macro stress and

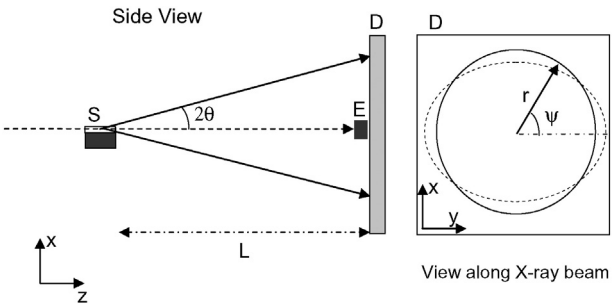

Fig. 3. Schematic diagram of the experimental layout where the incident and transmitted X-ray beam is shown as a dotted line, the diffracted X-ray beams are shown as solid arrows, S is the strip, θ is the Bragg angle, L is the sample to detector distance, E is the end stop for the X-ray beam, D is the detector, r is the radius of the diffraction ring, ψ is the azimuthal angle around the diffraction ring. The directions x, y and z are defined here. The vertical direction was x. Diffraction rings are shown on the detector; a solid circle for the strain free material, and a dotted ellipse from material compressed in the y-direction.