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Preliminary study of iridium coating on carbon/carbon composites

K. MUMTAZ, J. ECHIGOYA, M. TAYA
Department of Materials Processing, Faculty of Engineering, Tohoku University, Sendai 980, Japan

Iridium coating was deposited on as-received, polished and chemical vapour deposited (CVD) pyro carbon-coated carbon/carbon composite by d.c. sputtering. The as-received surface of the carbon/carbon composite was not fully covered by an iridium coating up to 12 μm thick, whereas better deposition and surface coverage with the iridium coating were obtained on the polished surface and CVD pyro carbon-coated carbon/carbon composite surface. After heat treatment at 2000 K for 1.2 ks, interconnected islands of iridium were formed on three surfaces of the carbon/carbon composite. Iridium neither reacted with nor dissolved the carbon/carbon composite, it had some penetration but did not react to form an interfacial compound, and the boundary between the iridium and carbon/carbon composite was distinct.

1. Introduction

Knowledge of the behaviour of metals or ceramics coating on carbon/carbon composite is necessary for the understanding of the protection of the composite from oxidation at high temperature [1, 2]. Major factors affecting performance of the coating include coating adherence, cracking/spallation, erosion and permeability to oxygen, in addition to chemical stability and compatability with carbon [3, 4]. Silicon carbide and various oxygen diffusion barrier coatings have been investigated which offer protection to the carbon/carbon composites up to 2000 K for several hours [5], but other materials will be required for higher temperature protection. The refractory platinum group metals, iridium, rhodium, ruthenium and some of their intermetallic compounds, offer possible candidates [6].

Iridium (m.p = 2520 K) has a very low oxygen permeability, good chemical compatibility and low carbon solubility below the eutectic temperature of 2373–2573 K. Contemporary engineering design requirements for very high-temperature structural materials have stimulated interest in iridium-based coating for carbon/carbon composites [3]. Good adherence of the homogeneous coating on the carbon/carbon composites surface will result in elimination of most of the problems such as inward diffusion of oxygen and will prevent outward diffusion of carbon during oxidation at high temperature. During coating, the carbon/carbon composite substrate surface is sensitive and it affects the structure and physical properties of the as-grown film.

A thicker coating of iridium will be required to cover the surface of the as-received carbon/carbon composite because cross-weave carbon/carbon composites contain a variety of macro and micro voids, gaps in the interstices of the weave and a variety of cylindrical voids in the matrix, which is uneconomical and results in many problems, while a thin thoroughly covered iridium coating on polished and CVD pyro carbon-deposited carbon/carbon composite will result in a reduction of coating defects. If the coating has pores, voids and irregularities, oxidation of the matrix and fibres will occur, with oxygen penetration into the materials, resulting in severe excavation of the carbonaceous matrix from between the fibre bundles and degradation of the fibres. The purpose of this study was to investigate the effect of iridium deposition on different surfaces of carbon/carbon composite using d.c. sputtering, and after heat treatment the surface morphology and interaction characteristics of iridium on carbon/carbon composite surfaces.

2. Experimental procedure

2.1. Material preparation

The composite materials used in this study were made from high-modulus carbon fibres, woven into a two-dimensional preform and processed with several cycles of pitch impregnation/carbonization/grapitization to a final density of 1.88×10^3 kg m^{-3}, and named the as-received carbon/carbon (C/C) composite sample. Two more surfaces were prepared, one by polishing the as-received surface with 1500 grit and final polishing on filter paper, and the other sample was CVD pyrolytic carbon coated on the as-received surface, named polished and CVD pyro carbon-coated C/C composite, respectively. The composites were supplied by Nissan Aero Space and Kashima Oil Company.

The three kinds of C/C composite were cut into sizes 15 mm × 10 mm × 1.5 mm by a diamond wafer blade for iridium coating. The samples were cleaned in acetone for 1.2 ks and then dried in an oven for 1.8 ks to remove the acetone from the porous surface of the C/C composite.

2.2. Coating and heat treatment

Iridium coatings of varying thicknesses were deposited simultaneously on one side of the as-received, polished and CVD pyro carbon-coated C/C composites by d.c. sputtering without substrate heating; details of coating conditions are given in Table I. The coating target iridium was 99.99% pure, in the form of a disc of 50 mm diameter and 1 mm thick.

The coated samples were cut into 7 mm × 3 mm × 1.5 mm sizes for heat treatment tests; the samples were once again cleaned in acetone for 1.2 ks and dried in an oven for 1.8 ks before testing.

Heat treatment was performed in a manually controlled water-cooled vertically mounted induction furnace in an argon gas atmosphere. The samples were placed in the molybdenum baskets and held above the graphite tube, once the required temperature of the furnace had been reached, the molybdenum baskets were inserted in the tube and held at that temperature for the desired time and then slowly cooled to room temperature by turning the power off. The temperature was measured by an optical pyrometer. The weight of the sample before and after heat treatment was measured on a microbalance accurate to ± 0.000 01g.

2.3. Micro analysis of coated C/C composites

After the coating and heat-treatment processes, the samples were characterized by optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images of both surface and cross-section views were taken using a Hitachi S-530S scanning electron microscope to examined the thickness, homogeneity and structure of the iridium coating. TEM images were taken by Jeol JEM-200B, and the images were focused on the interface between the coating layer and substrate to determined the phase structure and degree of crystallinity. The TEM samples were cut perpendicular to the interface, then polished, dimple ground and thinned by the argon ion-milling process. There was difficulty in retaining all of the components of the coating due to interfacial porosity and poor adhesion.

X-ray diffraction patterns were obtained from varying thicknesses of iridium coating on three kinds of C/C composite surfaces in the as-deposited condition and after heat treatment. Data were obtained at a scanning speed of 2 deg min^{-1}, using a Jeol X-ray diffraction DX-QERP12 operated at 30 kV and 20 mA.

TABLE I Iridium coating conditions

Base pressure	4×10^{-4} Pa
Ar pressure	4 Pa
Sputtering voltage	1 kV
Target to substrate distance	50 mm
Deposition rate	0.02 nm s^{-1}

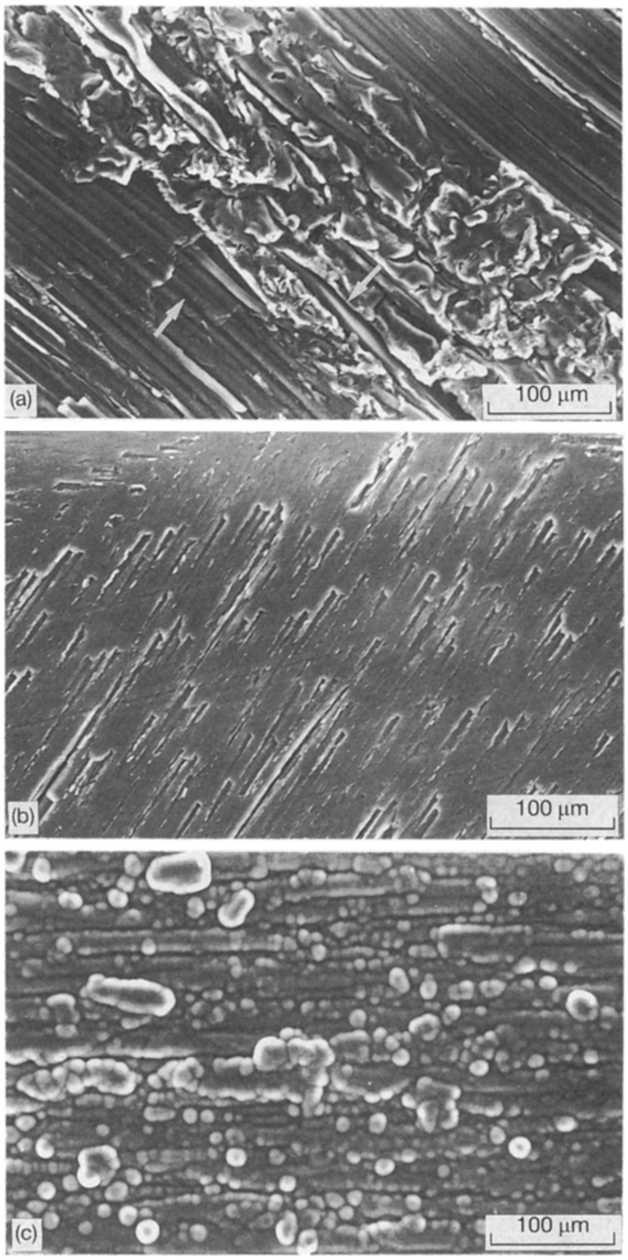

Figure 1 Scanning electron micrographs of three surfaces of C/C composite without iridium coating; (a) as-received, (b) polished, and (c) CVD pyro carbon-coated C/C composite.

3. Results and discussion

3.1. Microanalysis of the three kinds of C/C composite surfaces

Fig. 1 shows the three kinds of C/C composite surfaces without iridium coating. The as-received C/C composite surface, Fig. 1a, shows surface roughness, and voids are present between the fibre bundles and the matrix; the fibre–matrix interface is also microfissured, numerous microcracks exist both within the matrix and along the partially bonded interface indicated by arrows, due to weaving and processing of the C/C composites. To eliminate the effect of random orientation and roughness of the as-received surface of the C/C composite, it was polished; the surface irregularities were then reduced, but a few gaps between the fibre bundles or broken fibres due to polishing and the polishing scratches on the polished surface of the C/C composite were still visible, Fig. 1b.

Because problems occur on the surface of the C/C composite in producing a smooth iridium coating, the effect of applying CVD pyro carbon on the as-received surface to remove the surface roughness of the C/C composite was studied. It was found that the CVD pyro carbon-coated C/C composite surface was a replica of the as-received surface, but the use of CVD pyro carbon coating of 10 μm on the as-received surface, gave good surface coverage. This treatment eliminates the roughness of the C/C composite. Fig.1c shows globular grains of pyro carbon with pitted surfaces and no voids, but a few cavities are visible.

3.2. Microanalysis of as-deposited samples

SEM investigation showed the as-deposited iridium 4 μm thick coating to simply duplicate the morphology of the underlying substrate surface, which was quite rough on a microscale in the case of the as-received surface, with a high concentration of pits, voids and gaps, as shown in Fig. 2a. The polished surface allowed the coating to be deposited homogeneously on the surface; even a thin coating covered the

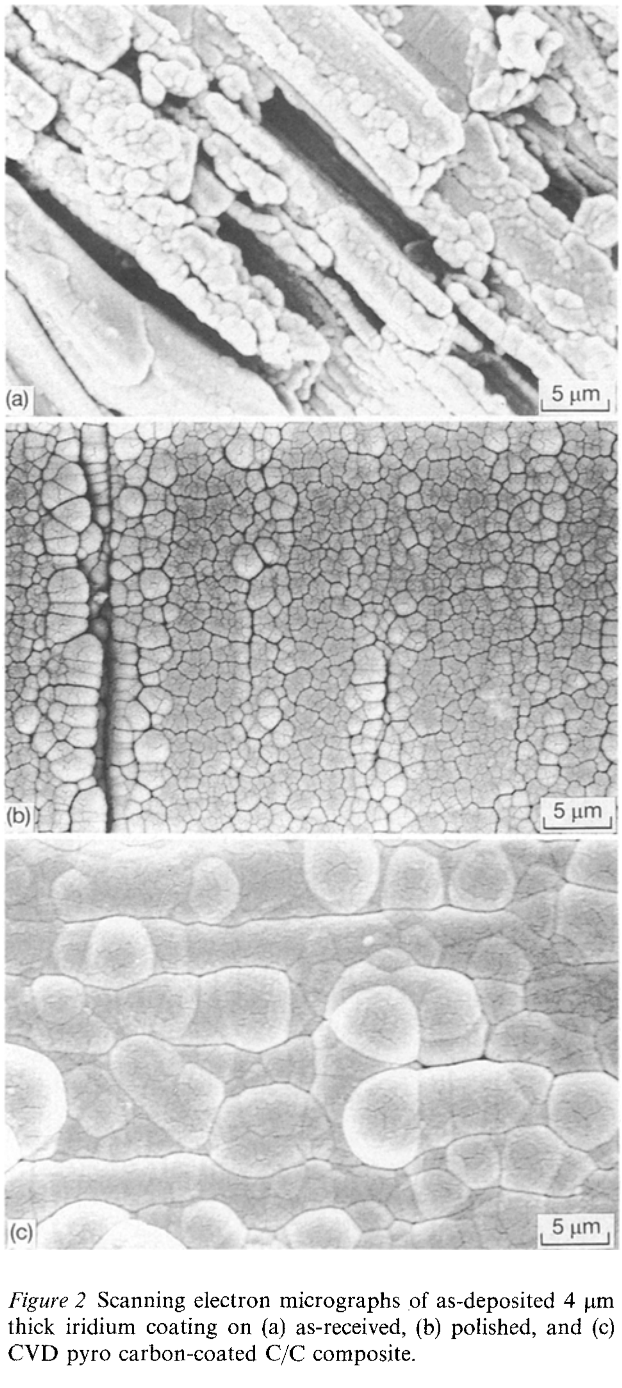

Figure 2 Scanning electron micrographs of as-deposited 4 μm thick iridium coating on (a) as-received, (b) polished, and (c) CVD pyro carbon-coated C/C composite.

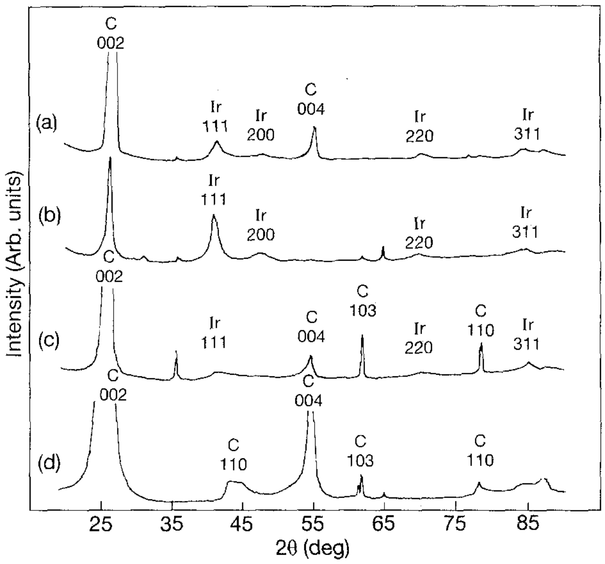

Figure 3 XRD patterns of as-deposited 4 μm thick iridium coating on (a) CVD pyro carbon-coated, (b) polished, (c) as-received surface of C/C composite, and (d) as-received non-iridium coated C/C composite.

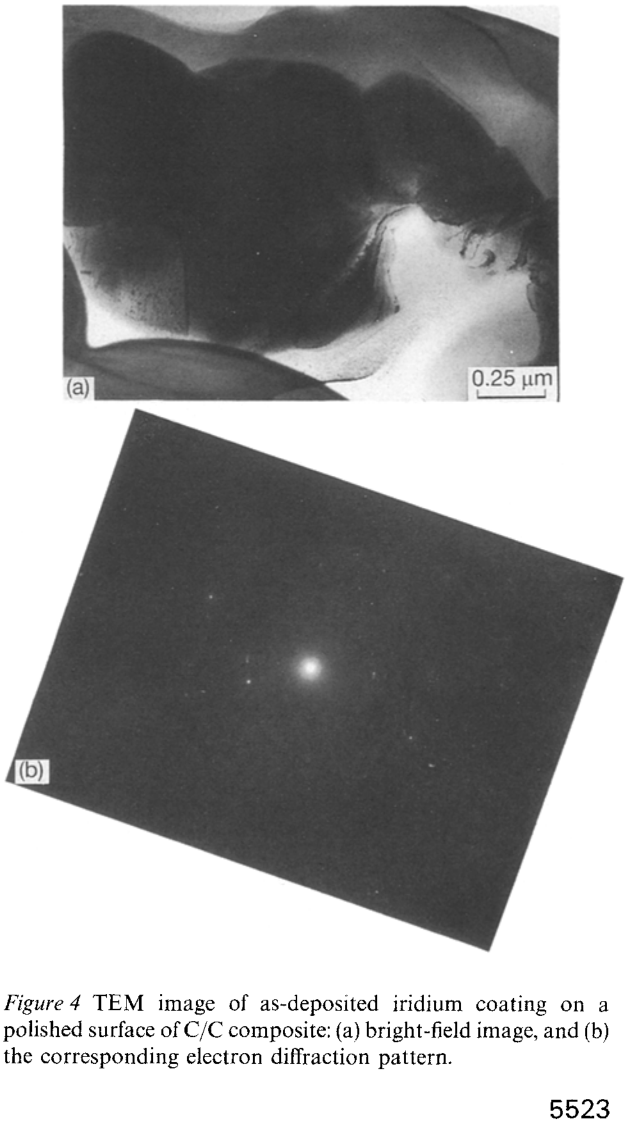

Figure 4 TEM image of as-deposited iridium coating on a polished surface of C/C composite: (a) bright-field image, and (b) the corresponding electron diffraction pattern.

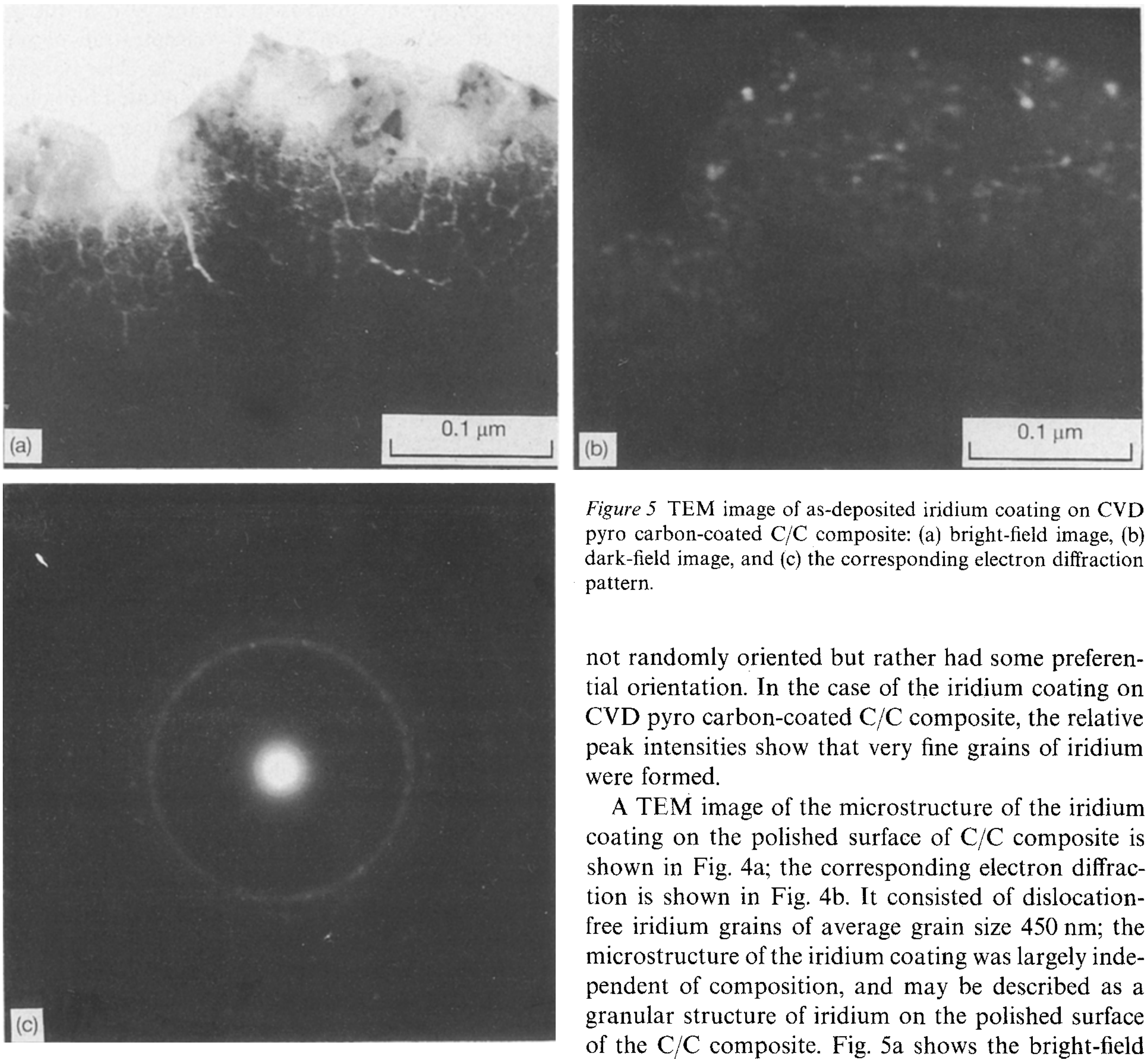

Figure 5 TEM image of as-deposited iridium coating on CVD pyro carbon-coated C/C composite: (a) bright-field image, (b) dark-field image, and (c) the corresponding electron diffraction pattern.

surface except for broken fibres on the surface of the C/C composite, as shown in Fig. 2b. On the polished surface, the agglomeration of the iridium coating was more pronounced near the voids and gaps, and numerous micrometer-sized holes were observed to appear in the coating, preferentially on the broken fibres. This was successfully done with the minimum thickness of iridium coating on CVD pyro carbon-deposited C/C composite. Fig. 2c shows that iridium forms a continuous grainy structure of 4 μm thick coating on CVD pyro carbon-deposited C/C composite and shows less agglomeration than that on the polished surface and presumably formed a continuous coating more readily than on the as-received surface.

Fig. 3 shows the XRD analysis of as-deposited and non-iridium-coated C/C composite. Iridium on the as-received surface gives a broad and very weak Ir (111) peak which shows that very fine grains are formed; this also corresponds to the bulk lattice arrangement. In the case of the polished surface, the Ir (111) peak is strong and sharp and also the C (002) peak is not very strong, as in the as-received and CVD pyro carbon-deposited C/C composite, which shows that large grains of iridium were probably formed on the polished surface of the C/C composite and the grains were not randomly oriented but rather had some preferential orientation. In the case of the iridium coating on CVD pyro carbon-coated C/C composite, the relative peak intensities show that very fine grains of iridium were formed.

A TEM image of the microstructure of the iridium coating on the polished surface of C/C composite is shown in Fig. 4a; the corresponding electron diffraction is shown in Fig. 4b. It consisted of dislocation-free iridium grains of average grain size 450 nm; the microstructure of the iridium coating was largely independent of composition, and may be described as a granular structure of iridium on the polished surface of the C/C composite. Fig. 5a shows the bright-field image of the as-deposited iridium coating on CVD pyro carbon-coated C/C composite showing iridium grains. Fig. 5b shows the dark-field image of the same area; again it shows very fine grains of iridium, less than 12 nm, on fine grains of pyro carbon-coated C/C composite. Fig. 5c, shows the diffraction ring which also indicates very fine grains of iridium on the CVD pyro carbon-coated C/C composite. Results of TEM studies are in good agreement with the XRD results.

To investigate further the behaviour of the iridium coating on the polished surface of the C/C composite with increasing argon gas pressure, the samples were iridium deposited at 10 Pa argon gas pressure; the other parameters remained constant. A comparison of Figs 2b and 6 shows that better coverage of iridium with less agglomeration effect was observed with increasing argon gas pressure; it seems that this was the result of an increase in the mass of the bombarding species, and heavily ionized molecules increase the sputtering rate with deep penetration of iridium on the C/C composite.

3.3. Microanalysis of iridium coating heat treated at 2000 K

The 4 μm thick iridium coatings deposited on three different kinds of C/C composite surfaces were heat

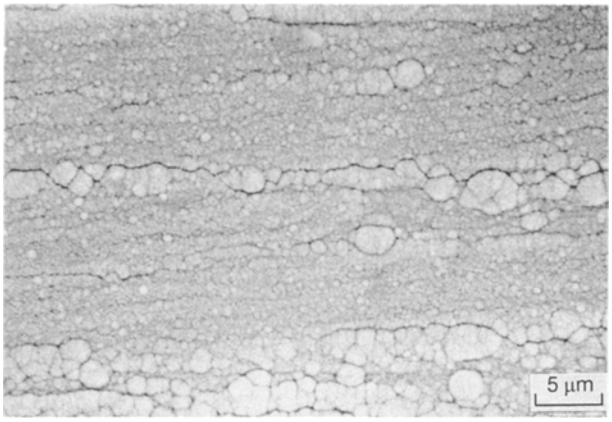

Figure 6 Scanning electron micrograph of as-deposited 4 µm thick iridium coating on a polished surface of C/C composite, iridium-deposited at 10 Pa argon gas pressure.

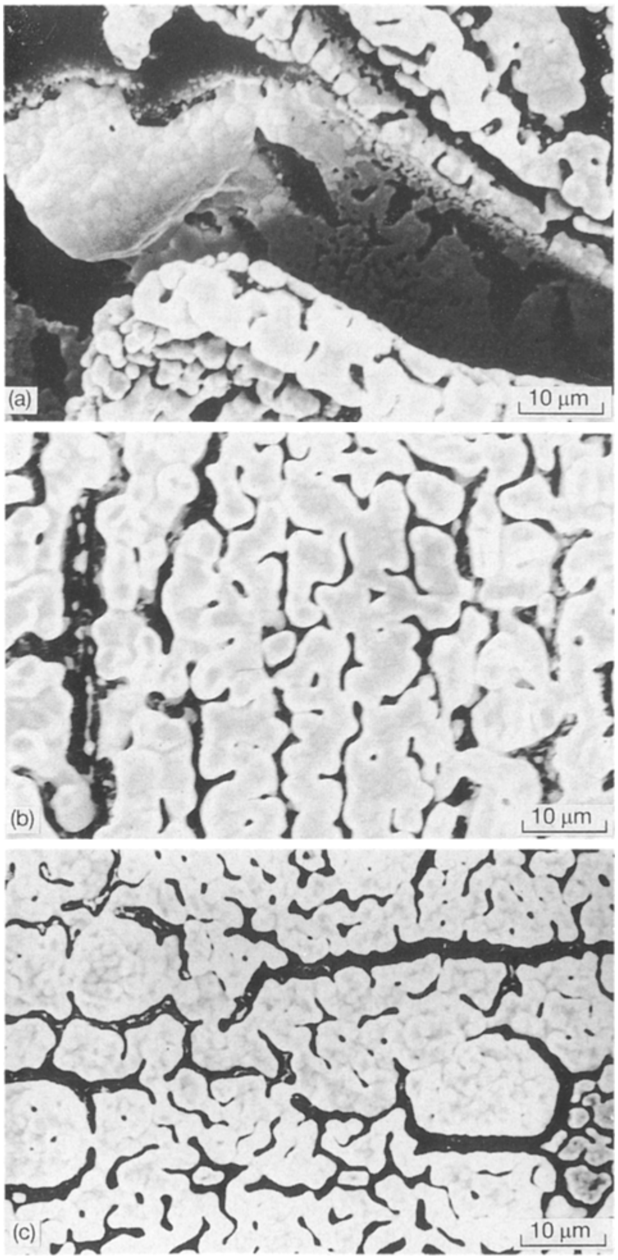

Figure 7 Scanning electron micrograph of iridium coating after 1.2 ks heat treatment at 2000 K: (a) as-received, (b) polished, and (c) CVD pyro carbon-coated C/C composite.

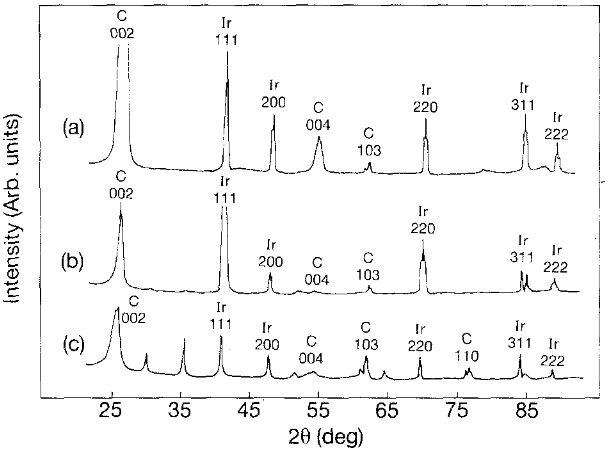

Figure 8 XRD patterns of iridium coating after 1.2 ks heat treatment at 2000 K: (a) CVD pyro carbon-coated, (b) polished, and (c) as-received surfaces of C/C composite.

Figure 9 TEM image of the iridium coating on the polished surface of C/C composite after heat treatment, showing crystalline grains with very small voids.

treated at 2000 K for 1.2 ks, to encourage grain growth. With grain growth these coatings broke into interconnected islands of iridium, of the order of several micrometres across, as shown in Fig. 7. On three surfaces iridium transport occurred by diffusion of iridium, resulting in interconnected islands with rounded rather than sharp outlines. Fig. 7a shows the as-received surface is characterized by an iridium coating which did not cover the C/C composite in some areas and large and small interconnected islands and the formation of agglomerations of iridium away from that area. Iridium deposited on polished and CVD pyro carbon-coated C/C composites was found to consist of islands, approximately 12 µm diameter, separated by an iridium-free region about 2 µm wide, Fig. 7b and c.

Fig. 8 shows XRD analysis of the iridium coating on three surfaces of C/C composites after heat treatment at 2000 K for 1.2 ks. Comparison of Figs 8 and 3 shows that the Ir (1 1 1) peak was essentially weak in the case of the as-deposited iridium coating on three surfaces; however, the X-ray diffraction on three surfaces after heat treatment shows a strong and sharp Ir

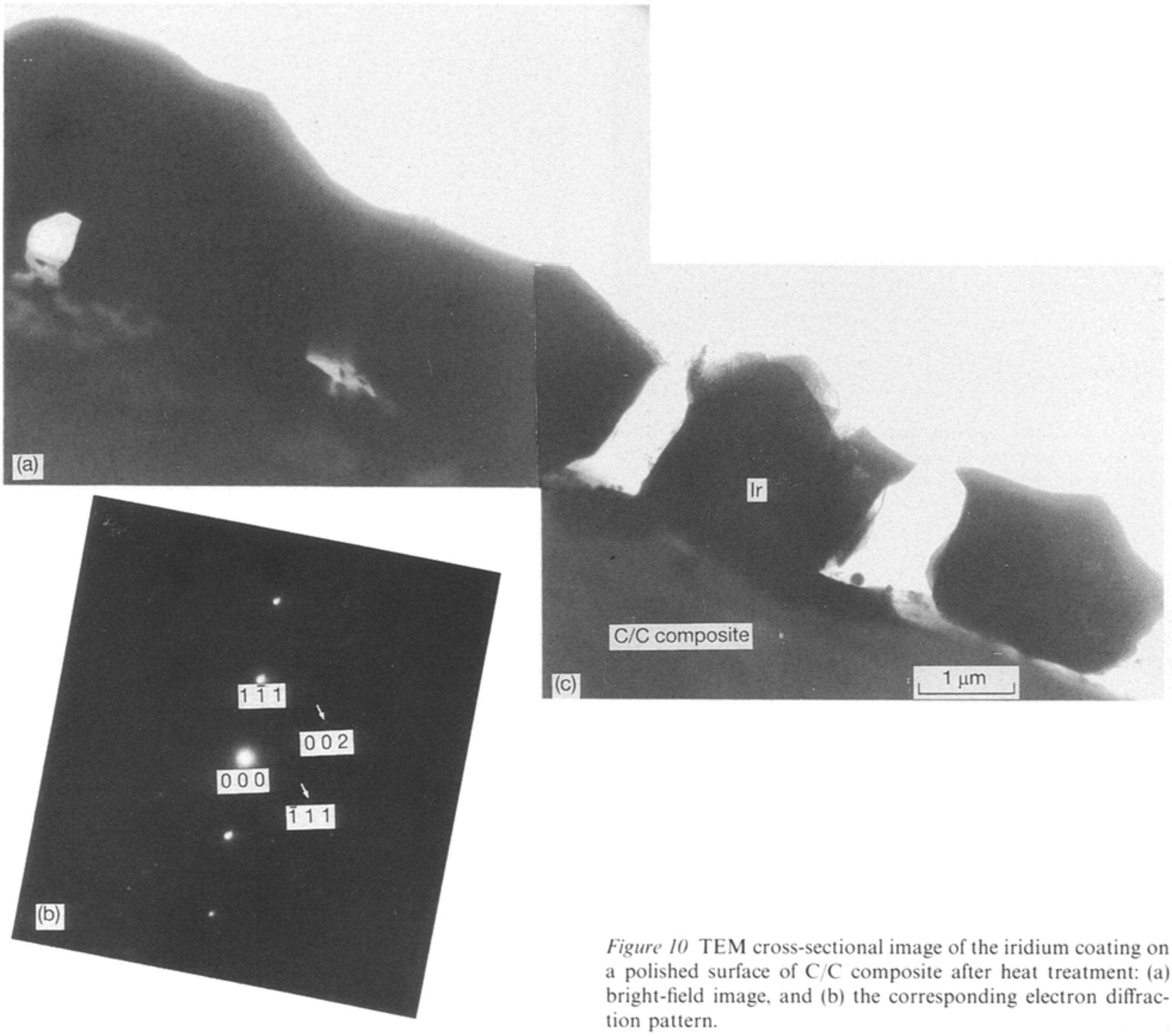

Figure 10 TEM cross-sectional image of the iridium coating on a polished surface of C/C composite after heat treatment: (a) bright-field image, and (b) the corresponding electron diffraction pattern.

(1 1 1) peak on three surfaces of the C/C composite, indicating large crystalline grains of iridium were formed on it. Furthermore, Fig. 8 also shows that the Ir (1 1 1) peak is very strong and sharp in the case of the polished surface of the C/C composite, which shows that comparatively large grains of iridium were formed on the polished surface of the C/C composite than on the as-received and CVD pyro carbon-coated C/C composite; in all three cases no iridium compound was formed.

A TEM image of iridium on a polished surface of C/C composite is shown in Fig. 9. It consisted of dislocation-free iridium grains having a mean grain size of 1.6 µm. Fig. 9 also shows that very small voids were formed on the crystalline grains of iridium, probably as the result of liberation of entraped gases from the composite during heat treatment at high temperature. Fig. 10 is a cross-sectional transmission electron micrograph of a 4 µm thick iridium coating on a polished surface of C/C composite which shows good interfacial bonding with no secondary phase at the interface. In addition to grain growth during heat treatment, a number of pores, up to 1 µm, were formed in the coating. The formation of pores or holes in the sputtered deposited iridium coating after heat treatment at high temperature occurred via a rapid surface-diffusion mechanism in order to reduce the high surface energy associated with coating configuration. Fig. 10b is a corresponding electron diffraction pattern. Fig. 11 shows islands of iridium on a polished surface of C/C composite and graphite outside the iridium layer, indicating the penetration of iridium in to the C/C composite during heat treatment at high

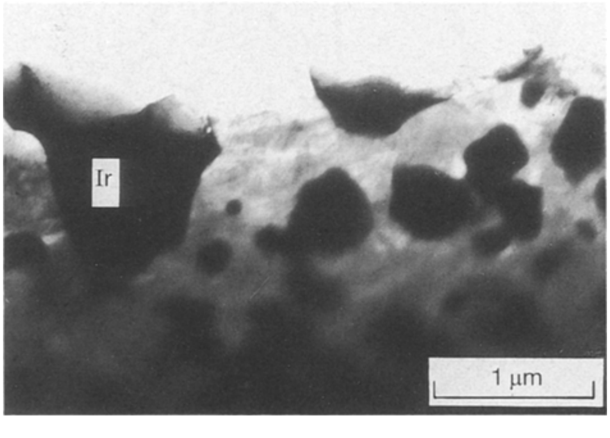

Figure 11 TEM cross-sectional image of the iridium coating on a polished surface of C/C composite, showing penetration of iridium in the C/C composite.

temperature. Wetting is difficult to achieve in molten metals owing to their relatively high surface tension values (60–2400 mJ/m^{-2}) [7]. Results shows poor wettability of the C/C composite by iridium.

4. Conclusions

The results of this initial work demonstrate the applicability of the iridium as coating material on the C/C composite.

1. Uniformly adhering iridium coatings were obtained on polished and CVD pyro carbon-deposited C/C composite by d.c. sputtering; very fine grains of iridium were formed on CVD pyro carbon-coated C/C composite.
2. With increasing argon pressure better coverage of iridium on the polished surface was obtained and the deposition rate was also increased.
3. An iridium coating, 4 μm thick, was found to remain intact on the three kinds of C/C composite surfaces after heat treatment at high temperature, and interconnected islands of iridium were formed on the three surfaces of C/C composite.
4. Some penetration effect and no interfacial reaction of iridium with the C/C composite were observed.

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