Diamond-like carbon / epoxy low-friction coatings to replace electroplated chromium

S. Podgoric[1,2,*], B.J. Jones[3,†], R. Bulpett[3], G. Troisi[2] and J. Franks[2]

1. Hawker Pacific Aerospace, Hayes, UB3 1HP, UK

2. School of Engineering and Design, Brunel University, Uxbridge, UB8 3PH UK

3. Experimental Techniques Centre, Brunel University, Uxbridge, UB8 3PH UK

Abstract

A series of layered structures based on epoxy-resins coated with diamond-like carbon (DLC) are examined as potential replacements for electroplated chromium in aerospace applications. Diamond-like carbon coatings can offer superior mechanical properties and tribological performance; however, in some applications high internal stresses and poor adhesion limit their practical use. A DLC / epoxy system is developed and studied utilising pin-on-disk testing, analysis with scanning electron microscopy and atomic force microscopy, resulting in an optimum system with characteristics superior to those of chromium plated steel. This new coating system has a great potential in restoring worn or damaged aircraft components, without the health and environmental issues associated with chromium plating. The components can be rebuilt and improved over the original condition thus allowing an extension of service life and eliminating the need for costly replacements.

Keywords: Chromium; Friction; Surface structure, morphology, roughness, and topography; Diamond-like carbon; Epoxy resin

1 Introduction

It is increasingly important that damaged or worn aircraft components are repaired using cost effective and environmentally friendly coating systems. Conventional electroplating processes, such as hard chromium plating, are extensively used on aircraft components to improve their functionality and reduce wear. While hard chrome plating offers certain benefits, it also has some categorical disadvantages. Being a known carcinogen and respiratory toxicant, chromium exposure poses a significant occupational health hazard. The plating process disperses a fine mist of chromic acid into the air where exposure to hexavalent chromium (hex-Cr or Cr(VI)) occurs as a result of inhalation; exposure can also occur via dermal contact from spray and accidental spillage of chrome plating solutions. Hexavalent chromium has been linked to cancer in humans following prolonged inhalation, and mortality studies carried out on chromium electroplaters found an increase in broncho-pulmonary cancer deaths [1,2]

---

[*] Tel: +44 (0)208 5891958 Fax: +44 (0)208 5891900 *e-mail*: sander.podgoric@hawker.com

[†] Tel: +44(0)1895 265409 Fax: +44 (0)1895 812544 *e-mail*: b.j.jones@physics.org

Chromium can also be released to the environment via accidental spillage, spray and disposal of waste plating solution. On entering the environment it is biomagnified in terrestrial and aquatic food chains resulting in bio-accumulated levels of chromium in fish and other wildlife, for which the chemical can be highly toxic. Chromium plating solutions typically use lead anodes which decompose over time. The lead chromates formed from this decomposition are classed as hazardous waste and their treatment and disposal is very costly. The plating process is also time-consuming as it requires several pre and post plating treatments to ensure adequate adhesion and coating integrity. In many cases the coating has to be removed at every overhaul interval, the components reworked to remove defects and new coating applied in order to recover assembly design dimensions.

Clearly, the availability of non-toxic, high-performance coatings, employing sustainable coating technologies, would benefit aircraft manufacturing and maintenance companies by enabling the reduction of electroplating emissions and the implementation of best environmental practices. Several manufacturers have trialled alternative coatings [3,4]. Thermal spray coatings such as Tungsten Carbide Cobalt-Chrome do not cause hydrogen embrittlement and produce a better wear resistance and finish than chrome. Resin based composite processes have been shown to combine efficient corrosion prevention with a self lubricating behaviour. Unfortunately with these coating techniques, there are limitations to the applied coating thickness and suitability for all applications [3,4].

Previous research has established that diamond-like carbon (DLC) coatings have the potential to minimise the friction and wear of various moveable devices, for example in the automotive, medical and manufacturing sectors [5-11]. Diamond-like carbon (DLC) is an amorphous form of carbon containing both diamond-like (sp^3) and graphitic (sp^2) bonds, and coatings possess many attractive properties such as high hardness, low friction and high chemical stability and have been successfully used in many different applications. Plasma enhanced chemical vapour deposition (PECVD) is a well-established laboratory and industrial technique to produce uniform, thin-film coatings of DLC over a wide area or an irregularly shaped device, minimising the need to manipulate the sample during coating, and without the application of external heating, enabling the straightforward coating of temperature sensitive materials.

High internal stresses in plasma-deposited DLC can limit coating thickness to less than $10\mu m$ [12,13] thus limiting practical applications, particularly in maintenance and overhaul of aircraft components. These drawbacks can be mitigated to a degree by tuning the coating deposition and hence film structure. PECVD is a flexible process allowing control over the composition of the DLC film, including the graphitic / diamond-like ratio, as well as the incorporation of hydrogen and other species. This can have a considerable effect on the levels of residual stress, as well as affecting the film properties such as hardness, elasticity, the final surface structure and chemistry, as well as the concentration of defects, and the ability of the film to bond to different materials [11,12]. Inevitably, there is a trade off, film flexibility and reduced stresses can be achieved, but often at the expense of coating hardness. In order to produce a thick coating with optimum wear properties,

which can be applied to restore and rebuild aircraft components to factory specifications, a different approach is required.

This paper demonstrates a new coating system, based on a layered structure of epoxy interlayer with DLC applied for the surface finish, which has great potential for restoring worn or damaged aircraft components in a more efficient manner, without the health and environmental concerns associated with chromium plating.

2 Experimental

Two airworthiness approved epoxy coating materials, EP3 and EP4, composed of a stable epoxy resin and dry lubricant filler, were obtained from the sole-rights holder, Lufthansa Technik Intercoat GmbH. These epoxy resins are the BPA A glydicylether resins produced from bisphenol A and epichlorhydrin; EP3 differs from EP4 by the addition of a glass-fibre filler. The coatings were applied to 4340M steel substrates, and machined to the required dimensions, to give a coating approximately 1.5mm thick, with a surface roughness, R_a, of approximately 84.1nm (EP4) and 94.8nm (EP3), and hydrophobicity characterised by a water contact angle of $101\,^{\circ}\pm 4\,^{\circ}$.

A graded DLC thin film was deposited on the machined epoxy coatings, using a PECVD method to provide a final layered coating. The precursor gas was a mixture of acetylene, tetramethylsilane (TMS) and argon; the ratio was adjusted by controlling the flow rate of these gases individually. Prior to deposition, the chamber was evacuated to a background pressure below 8×10^{-5} torr. Substrates were sputter-cleaned in argon plasma with flow rate of 30 sccm, pressure of 8×10^{-2} torr and a bias voltage of 300 V. This reduces impurities on the substrates, through energetic argon ion bombardment. Interfacial layers are deposited with gradually reducing levels of TMS to enhance the adhesion of the film to the substrate [11], for deposition of the final DLC film the argon flow rate was adjusted to 20 sccm, acetylene to 60 sccm and the bias voltage adjusted to 450V; producing a layer ~4μm in thickness, with similar structure and properties to the optimum film developed for dry drilling processes [11]. Control of both the epoxy and DLC components, as well as the interfacial structure, enables the development of the optimum wear resistance properties.

Surface structure of substrates and trial coatings were examined utilising a Zeiss Supra 35VP field emission scanning electron microscope (FE-SEM), operating in variable pressure mode. Though this does not necessarily provide the best quality images, the samples can be examined without the addition of a conducting layer, an advantage that ensures no artefacts are introduced due to the coating process, and that samples can be subsequently tested with other methods, and re-examined to study changes in the surface structure. Surface topography of the DLC / Epoxy composites was studied utilising a Digital Instruments Dimension 3100 scanning probe microscope (SPM), operating in intermittent (tapping) mode with a Veeco silicon cantilever resonant at ~260kHz.

Wear testing was conducted utilising a Teer Coatings POD-2 computer-controlled pin on disc tester, used for measuring wear and friction properties of thin coatings. The tester uses a fixed ball counterpart against a

p3

coated test piece to measure the tribological properties of the coatings. The following test conditions were used: 4N load, 10mm track diameter, 5mm diameter WC-6%Co ball**,** 40rpm, 0.02m/s, sliding distance 36m.

3 Results and Discussion

3.1 Surface Structure and Optimization

Figure 1 shows the surface morphology of epoxy-and-DLC coated specimens examined by scanning electron microscopy (SEM). Parallel grooves and ridges, as well as spheroidal protuberances, are related to the corresponding features on the ground epoxy surface. Figure 1a shows the DLC layer, growing homogeneously on the EP4 surface. Random surface speckles are also evident in the coating, possibly related to levels of residual compressive stresses, otherwise the carbon film deposited at the final stage of the coating process is compact and dense.

The SEM micrograph in figure 1b depicts of the DLC - EP3 combination coating. Initial analysis of EP3 coated with DLC revealed the presence of pin-hole defects in the surface coating. Further examination using SEM suggested that the holes were produced by stress cracking around the glass fibres present in the epoxy resin and exposed at the substrate surface. This spallation is thought to be closely related to the thermal deformation of the EP3 substrate during the DLC coating process. Thermal stress can be a particularly difficult problem for DLC because of the small coefficient of thermal expansion. The heating effect inherent in the deposition process may cause the substrate to expand by a greater amount than the DLC overlayer. The coating/substrate interface area will change either resulting in the development of stress in the DLC film, or causing partial delamination of the carbon layer [14]; substrates of composite materials of differing thermal expansivity may cause additional problems.
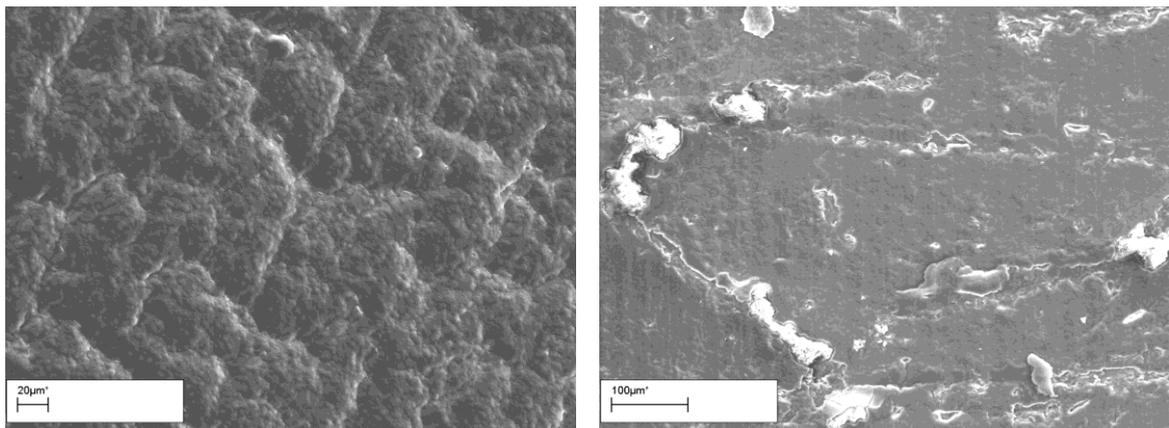

Fig. 1.   SEM Micrographs of epoxies coated with DLC, (a) EP4-DLC and (b) EP3-DLC combination coatings

Typical atomic force microscopy (AFM) images of substrates and coatings are shown in figure 2. AFM images show the topography of the DLC coated EP4 is similar to the epoxy substrate topography on a macro level; however, on the micro- and sub-micron scale the intrinsic DLC structure [15] dominates the surface,

demonstrating the importance of optimising the chemical and structural configuration of the carbon layer. However, it is also particularly important to place emphasis on the mechanical properties of the epoxy layer, the surface finish and the preparation of the material prior to coating with DLC [16,17]. Salvadori *et al* [17] found that in the early stages of the deposition process on a rough surface, the tops of the peaks grow faster than the troughs are filled. Thus in the beginning of the deposition, the DLC film roughness tends to increase, becoming larger than the original roughness of the substrate surface. With PECVD deposited on epoxy, we may see some increase in the roughness on a lateral scale over 50µm, with the coating enhancing the morphological features of the ground epoxy (figure 2, top); on a sub-micron level the DLC acts to reduce the surface roughness.
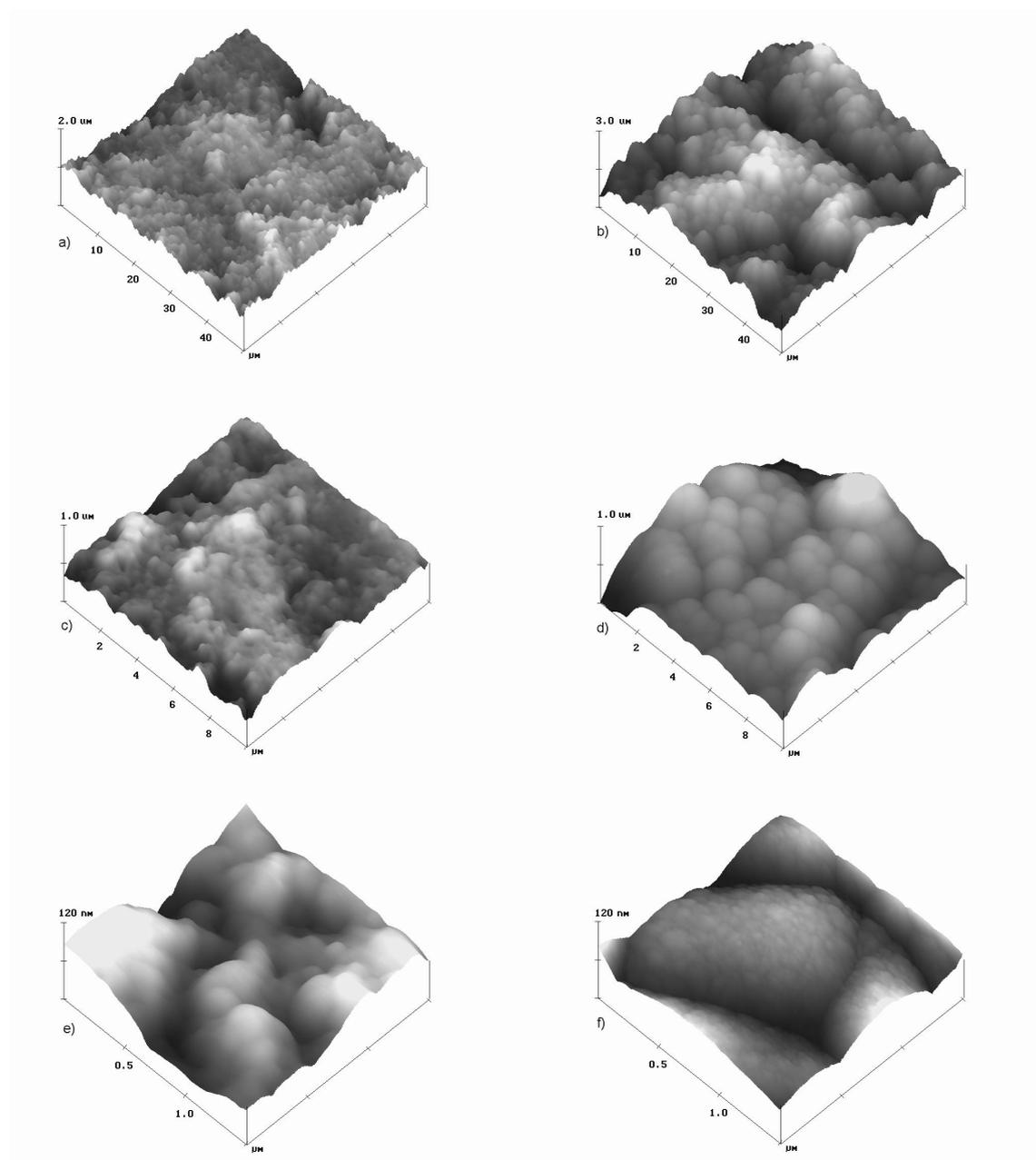

Fig. 2.   AFM Micrographs of EP4 epoxy (left) and EP4 epoxy+DLC coating (right), over areas of 50 µm (top), 10µm (centre) and 1.5 µm-square (bottom).

p5

When coating the samples with DLC we also place emphasis on the cleaning of the substrate prior to the application of the coating. It was noted that when Ar cleaning time was less than 10 minutes, a considerable amount of spallation occurred of DLC on bare steel substrates. This was overcome by increasing the Ar cleaning time in excess of 20 minutes. Choi *et al* [18] demonstrated the importance of cleaning steel prior to the application of DLC and showed the spallation behaviour of DLC for various Ar sputter cleaning time. Statistical analysis showed that the fraction of the spallated area reduced from 41.7% to 4.0% as the cleaning time increased from 15 to 30 min. Further increasing the cleaning time to 60 min reduced the spallated area to 0.3%. Our results are consistent with Choi *et al* and show that increasing the Ar cleaning time can be very effective to enhance the adhesion of DLC coatings.

3.2 Coating Performance

Prior experience in the aircraft landing gear industry has shown that the wear performance of chrome plated components was found to be inadequate, figure 3 shows a landing gear trunnion pin where chrome plating has worn and delaminated. Wear and corrosion of the substrate are also evident.

Comparative wear analysis of DLC, DLC and epoxy and hard chrome plated specimens was completed and statistically analysed, as shown in figure 4. Evaluation tests were made for sliding motion, which though not exactly duplicating in-service wear conditions, has the broadest application on aircraft landing gear components. Figure 4 (a-f) shows the quantitative results from the tribological tests of hard chrome plating, DLC, EP3 and EP4 coatings and epoxy-DLC combination coatings, together with results from a new sample set produced and tested in the same manner.

Figure 3. Typical landing gear component exhibiting chrome plate damage

During testing of chrome plated samples, the value of the friction coefficient increased due to the abrasive wear mechanism, i.e. the production of third body particles in the wear track. Some of the particles were lost from the system whilst some were entrapped between the ball and the coating surfaces. These entrapped

fragments produced further degradation on both surfaces as a third body abrasive wear mechanism. Vibration during tests, due to high ball and sample wear, produced a very high friction coefficient, the testing conditions produced a wear track of depth exceeding 15 microns.
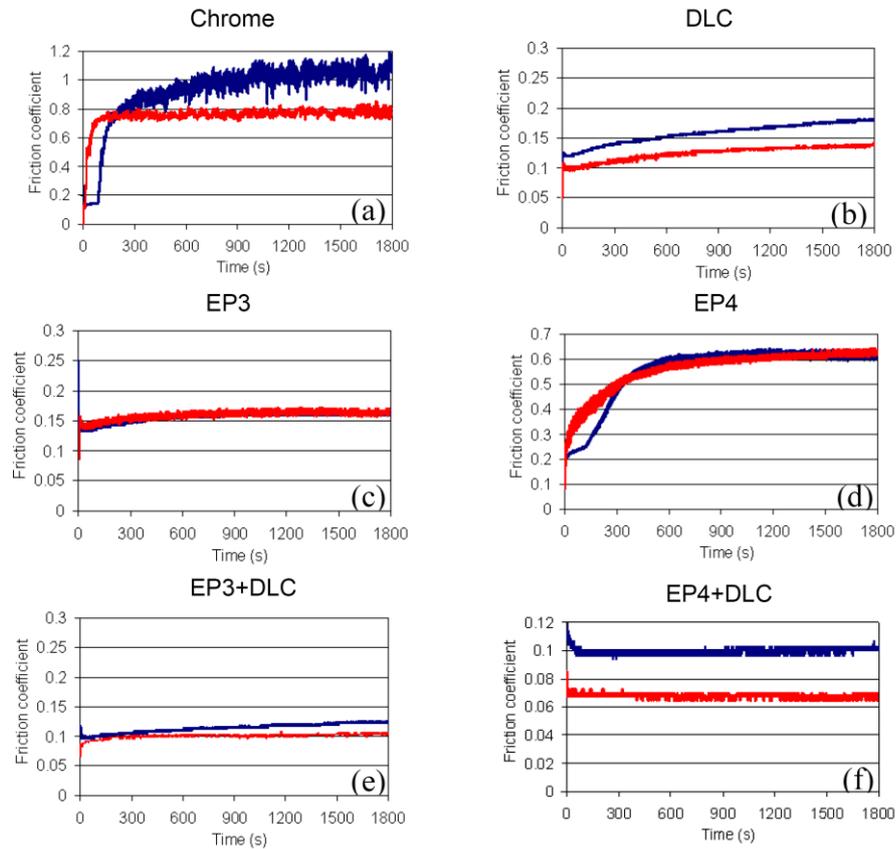

Fig. 4. (left) Comparison of friction coefficients vs. time, displaying results of two tests per condition for (a) chrome plating (b) DLC deposited directly on high strength steel substrate (c) EP3 epoxy, (d) EP4 epoxy, (e) EP3-DLC combination coating and (f) EP4-DLC combination coating.

The wear test results of DLC deposited directly on steel substrate show that the friction coefficient increases during the test and eventually reaches a steady state value of 0.14. Figure 5 illustrates the wear track of the DLC coating after the wear test. The wear surface of the coating reveals a multi-layer film structure. The wear track exhibits some local damage, which initially appears as slight smoothing of the outermost peaks of the DLC coating followed by spallation of the top layer. In some locations the coating has worn through to the substrate steel. This is possibly due to poor adhesion of the coating or formation of the transfer layer. Previous studies [17,19] have shown that at the beginning of the wear test, wear material is deposited on the sliding ball causing the transfer layer to form. Further wear is observed as the DLC slides against its transfer layer.
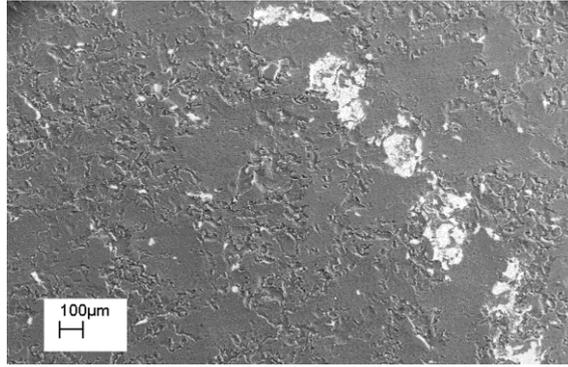
Fig. 5. SEM Micrographs of wear track of DLC deposited directly on steel substrate

As shown in figure 4 (d), the EP4 coating shows some improvement over chromium plate, and this is further enhanced by the glass fibre reinforcement in EP3. However, there is a significant advantage in using a DLC-epoxy combination, as shown in figure 4 (f); After 30 minutes sliding testing under dry conditions, DLC - EP4 epoxy combination coating portrays some deformation but the material continues to maintain its integrity, figure 6 (a). The friction coefficient reaches a best steady state level of 0.07 within the first few seconds and there is no degradation of sample properties. From the coatings studied, the combination of DLC deposited on EP4 epoxy produces the best wear resistance properties. It would appear that the EP4 epoxy provides enough local deformation without damage to the DLC coating, and reducing the loosening of wear particles from the surface. These initial results demonstrate the potential of using DLC and epoxy coatings in applications where chrome plating is currently used to protect the substrate from excessive wear.
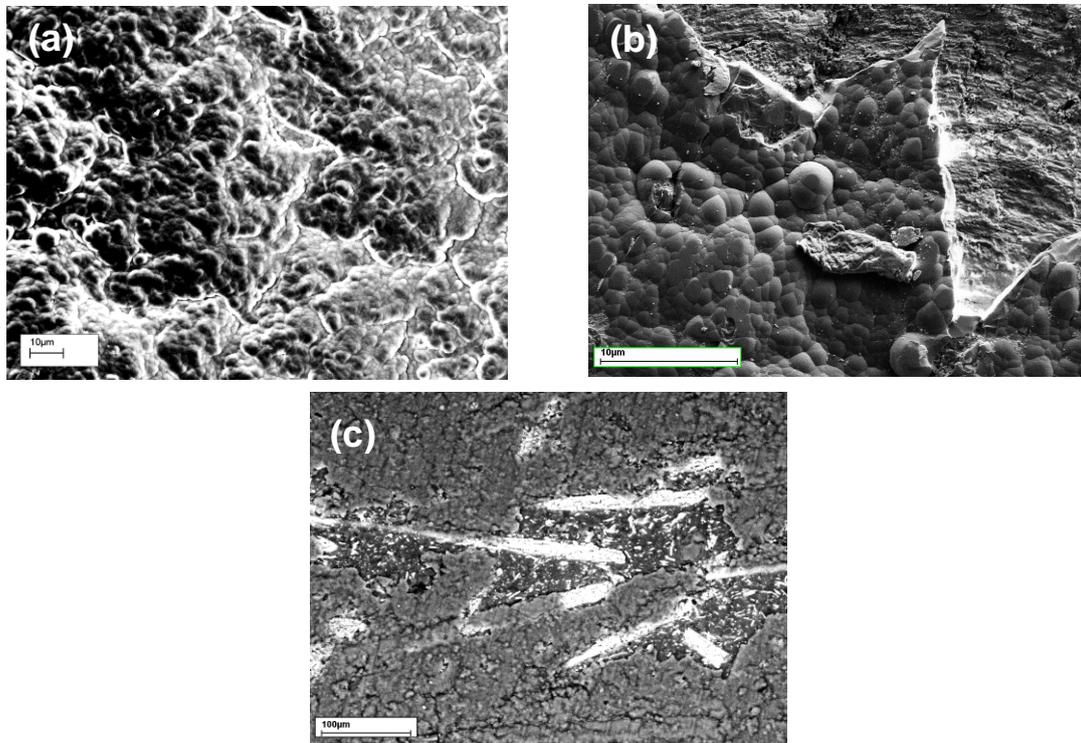

Fig. 6.   SEM Micrographs of wear tracks of epoxy and DLC coatings: (a) EP4 epoxy coated with DLC, (b) EP3 epoxy coated with DLC and (c) Wear track on EP3 + DLC, a lower magnification back-scattered electron image showing atomic number contrast, highlighting fibres in epoxy

The combination of EP3 epoxy and DLC did not perform as well as EP4 epoxy and DLC. We relate this to the glass fibres in the epoxy, which while providing reinforcement and enhancement of material properties when the epoxy is applied as the sole coating, affects the adhesion and integrity of the DLC coating, thus worsening the performance of the DLC-epoxy combination. The spatial variation in the material properties of the epoxy substrate may also increase stresses in DLC and thus add to cracking and coating delamination. Typical evolution of DLC film cracking, full and partial delamination is shown in figure 6(b and c).

4 Conclusion

This study demonstrates that DLC can be successfully deposited on high strength steel and epoxy resin substrates by PECVD technique, to improve tribological properties. AFM images show the DLC coating conforms to the epoxy substrate topography on a macro level; however, at a sub-micron scale the intrinsic DLC structure dominates the surface.

The tribological testing has shown that DLC-EP4 optimised coating exhibits extremely low friction coefficient, superior to that of chrome plating or stand alone epoxies used in current aircraft refurbishment processes. In contrast, DLC deposited on glass-fibre filled epoxy resin, EP3, is readily removed during testing due to delamination related to the glass fibres, and does not significantly improve the tribological performance of this material.

The optimised DLC-EP4 epoxy coating tested offers excellent protective properties that have a great potential of replacing chrome plating in aircraft landing gear applications. Some of the coating limitations caused by the build up of internal stresses in single-layer DLC can be overcome by the use of an epoxy resin interlayer. The new DLC/epoxy coating system has potential to enable restoration of mechanical components in a more efficient and sustainable manner than chromium plating techniques.

Acknowledgements

References

[1] T. Birk, K. A. Mundt, L. D. Dell, R. S. Luippold, L. Miksche, W. Steinmann-Steiner-Haldenstaett and D. J. Mundt, J. Occup. Environ. Med., **48**, 426 (2006)

[2] M. Goldoni, A. Caglieri, D. Poli, M.V. Vettori, M. Corradi, P. Apostoli and A. Mutti, Anal. Chim. Acta **562**, 229 (2006)

[3]   K.O. Legg, M. Graham, P. Chang, F. Rastagar, A. Gonzales and B. Sartwell, Surf. Coat. Technol. **81,** 99 (1996)

[4]   US – Canadian Hard Chrome Alternatives Team (HCAT). *Validation of WC/Co HVOF Thermal Spray Coatings as a Replacement for Hard Chrome Plating On Aircraft Landing Gear.* Part 1 – Materials Testing, 21 Nov 2002

[5]   A. Matthews and S.S. Eskildsen, Diamond Relat. Mater. **3**, 902 (1994)

[6]   V. S. Sundaram, Surf. Coat. Technol. **201**, 2707 (2006)

[7]   B. Jones, Mater. World **16**:8, 24 (2008)

[8]   C.P.O. Treutler, Surf. Coat. Technol. **200**, 1969 (2005)

[9]   R. Hauert, Tribol. Int. **37,** 991 (2004)

[10] M. Kano, J. Jpn. Soc. Tribologis., **47**, 815 (2002)

[11] M. Zolgharni, B.J. Jones, R. Bulpett, A.W. Anson and J. Franks, Diamond Relat. Mater. **17**, 1733 (2008)

[12] P. Bohac, K. Rusnal, O. Blahova, V. Kulikovsky and M. Sosnova. *International Symposium on Superhard Coatings*, Ein-Gedi, Israel, 27 Feb-1 March, (2006)

[13] C.H. Su, C.R. Lin, C.Y. Chang, H.C. Hung and T.Y. Lin, Thin Solid Films **498**, 220 (2006)

[14] Z.H. Xie, R. Singh, A. Bendavid, P.J. Martin, P.R. Munroe and M. Hoffman, Thin Solid Films **515**, 3196 (2007)

[15] B.J. Jones, S. Wright, R.C. Barklie, J. Tyas, J. Franks and A.J. Reynolds, Diamond. Relat. Mater. **17**, 1629 (2008)

[16] A. Dorner, C. Schürer, G. Reisel, D.G. Irmer, O. Seidel and E. Müller, Wear **249**, 489 (2001)

[17] M.C. Salvadori, D.R. Martins and M. Cattani, Surf. Coat. Technol. **200**, 5119 (2006)

[18] H.W. Choi, K.R. Lee, R. Wang and K.H. Oh, Diamond Relat. Mater. **15**, 38 (2006)

[19] K. Wazumi, K. Fuchigami, K. Uematsu, Y. Koga and A. Tanaka, IHI Engineering Review, **38**, 32 (2005)