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Cross sectional TEM analysis of duplex HIPIMS and DC magnetron sputtered Mo and W doped carbon coatings

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Abstract. A FIB lift-out sample was made from a wear-resistant carbon coating deposited by high power impulse magnetron sputtering (HIPIMS) with Mo and W. TEM analysis found columnar grains extending the whole ~1800 nm thick film. Within the grains, the carbon was found to be organised into clusters showing some onion-like structure, with amorphous material between them; energy dispersive X-ray spectroscopy (EDS) found these clusters to be Mo- and W-rich in a later, thinner sample of the same material. Electron energy-loss spectroscopy (EELS) showed no difference in C-K edge, implying the bonding type to be the same in cluster and matrix. These clusters were arranged into stripes parallel to the film plane, of spacing 7-8 nm; there was a modulation in spacing between clusters within these stripes that produced a second, coarser set of striations of spacing ~37 nm.

1. Introduction

Carbon based coatings provide excellent resistance to mechanical wear for their substrate, and are therefore of great interest for use on components that are required to resist a harsh working environment in critical applications. These coatings are deposited by various techniques such as pulsed closed-field unbalanced magnetron sputtering (CFUBMS), cathodic arc evaporation, magnetron sputtering and plasma assisted chemical vapour deposition (1). Recently a new technique, High Power Impulse Magnetron Sputtering, has been introduced, providing highly ionised metal plasma for deposition of highly dense and adherent coatings (2). The paper discusses the fine microstructure of Me-doped Carbon coatings deposited by a combined HIPIMS-DC Magnetron sputtering process, where in this case Me = (Mo, W). The advantages of this combined process are high rate deposition and precise control over the coating structure, texture and residual stress (3).

2. Methods

Mo and W doped carbon coatings were deposited onto steel by non- reactive mixed process of DC magnetron sputtering and HIPIMS (2) using an industrial size HAUZER 1000- 4 coating system. The substrates were rotated inside a sputtering chamber with four magnetron sources furnished by sputtering targets of pure graphite and Me. Prior to the coating deposition the substrate was bombarded by accelerated Me ions generated by the HIPIMS discharge, which provides for high coating adhesion (scratch adhesion critical load values, Lc=70 N). This procedure was followed by the deposition of 120 nm MeN transition layer followed by 1.8 μm Me-doped carbon layer.

Cross-sectional TEM samples were prepared from the coatings using the FEI Nova dual beam FIB-SEM at Loughborough University. TEM characterisation was initially carried out in a JEOL 2010F TEM (200 kV) at Sheffield University, and further analysis carried out in the JEOL double aberration corrected R005 (300kV), both with energy dispersive X-ray spectroscopy (EDS), electron energy-loss spectroscopy (EELS) and scanning TEM (STEM) capability.

3. Results and discussion

Low magnification STEM and CTEM images (Figure 1) show the ~1800 nm thick film to have multiple levels of striated structure: a set of finer stripes of spacing 7-8 nm wide, and a coarser set of spacing ~37 nm wide. Contrast from these regimes of stripes was complimentary between HAADF and BF STEM images.

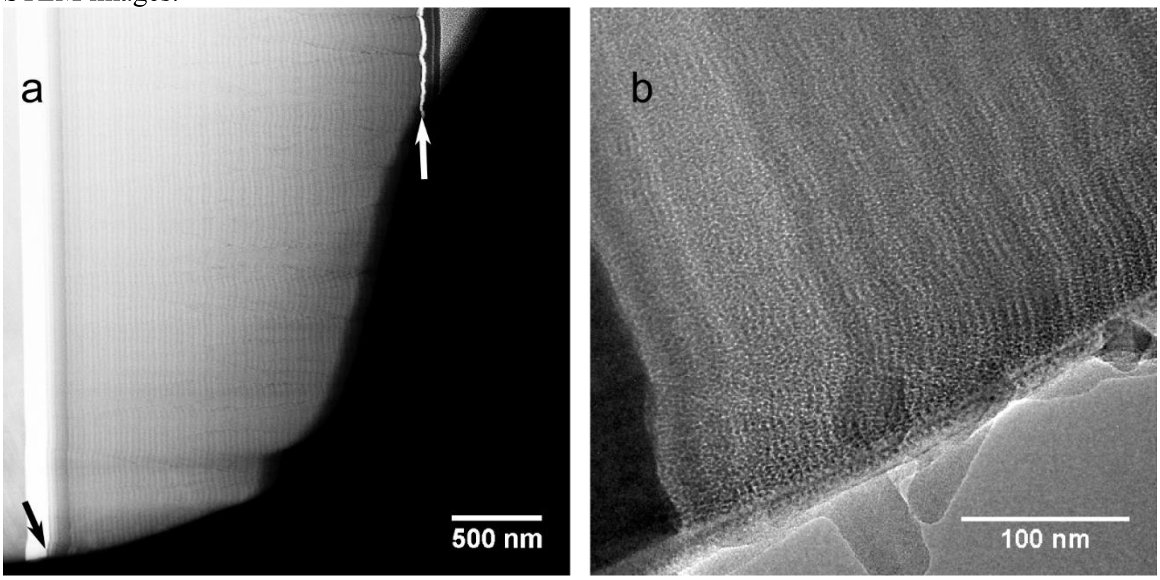

Figure 1 (a) HAADF-STEM image of whole film. Black arrow (left) marks top of nitride layer and bottom of coating. White arrow (right) marks top of film and gold protective coating deposited before FIB. (b) CTEM image of bottom of film showing two regimes of striations on different scales.

The finest set of striations are seen at higher resolution to be made of onion-like clusters, shown in Figure 2. EDS spot microanalysis showed very small concentrations of Mo and W in both clusters and matrix, with little discernible difference between cluster and matrix. EDS spot analysis of a thinner sample (0.05 inelastic mean free paths) from a wear test prepared later showed more Mo and W in the clusters than the matrix, in areas far from the wear surface which should be comparable to this unworn sample. STEM contrast supported this, with the clusters appearing brighter in HAADF and darker in BF. EELS showed no difference in the C-K edge between cluster and matrix, implying the bonding type to be the same in both. Unfortunately, though high-resolution HAADF-STEM was possible at the very edge of the specimen, the disordered nature of the surrounding material did not allow for good enough contrast to determine the positions of the metal atoms inside the clusters as yet.

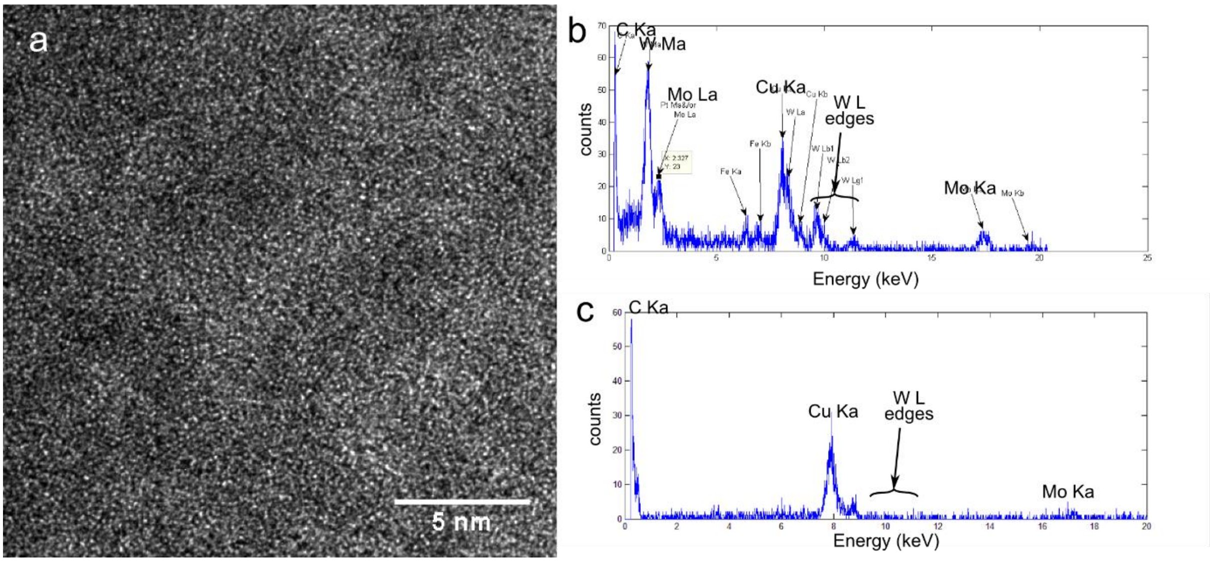

Figure 2 (a) HRTEM image showing onion-like parts in clusters. (b) EDS spectrum from cluster in thinner sample made later (not this sample, but deposited by the same procedure). (c) EDS from the matrix in this sample.

The finer stripes are made of these clusters arranged in lines. The coarser stripes appear to be a modulation in the spacing of the fine stripes and in the intensity from the matrix material between them (Figure 3); EDS from wide areas in lighter and darker stripes show the HAADF-STEM-brighter stripes to contain more Mo and W.

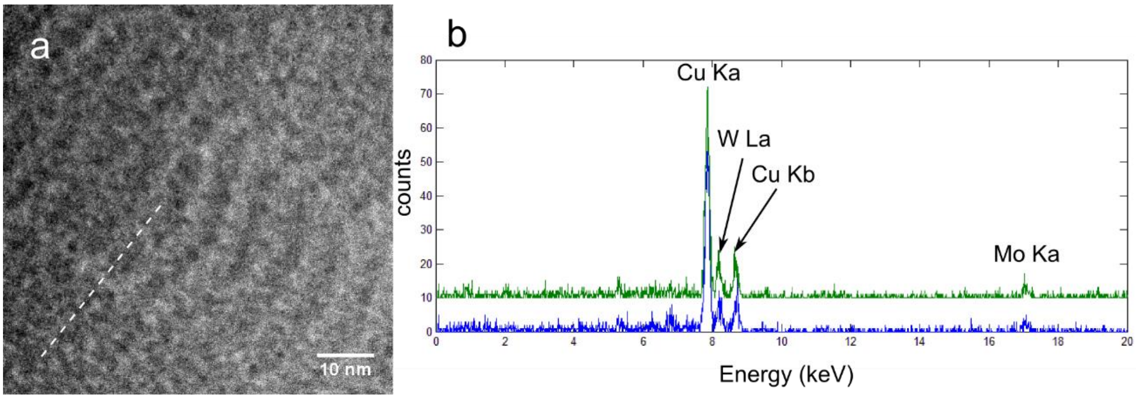

Figure 3 (a) CTEM image showing finer stripes to be clusters arranged in lines, and coarser stripes to be a modulation in the inter-cluster spacing within these lines. The top-left of the image is in a darker stripe; the bottom-right is in a lighter stripe, with the dotted line marking the angle of the stripe. (b) EDS spectra from wide areas within a HAADF-lighter coarse stripe (green top line) and within a HAADF-darker coarse stripe (blue bottom line). The HAADF-light stripe has a little more Mo and W.

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The striated microstructure exists within columnar grains that persist up through the coating as it grows. The grain boundaries are denuded of clusters so are seen as dark in HAADF STEM (Figure 4) and bright in CTEM and BF STEM. The stripes in the microstructure are domed across the grain, indicating the boundaries have an effect on the process of clusters organising into stripes.

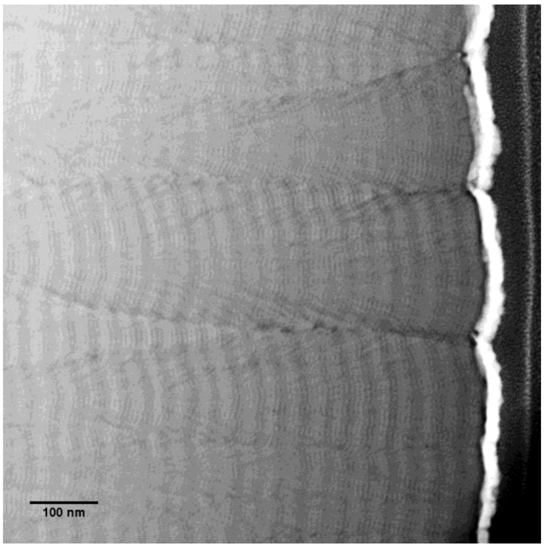

Figure 4 HAADF STEM image of the top of the coating showing columnar grains with domed tops (white line is gold protective coating applied before starting FIB).

The coating has been found to be extremely wear-resistant in the wear test work which is ongoing as the next phase of this project; the changes in microstructure which achieve this high wear resistance are complex and not yet fully characterised.

4. Conclusions

This HIPIMS carbon film co-deposited with Mo and W has a columnar microstructure that persists through the thickness of the film. Within these columnar grains, the material is organised into clusters with an onion-like structure observable in some places; EDS microanalysis shows these clusters to contain more of the Mo and W, while EELS analysis shows no change in the C-K edge between cluster and matrix. The clusters are organised into lines, giving fine stripes parallel to the film plane, 7-8 nm thick, proceeding up the grains. Within the stripes, there is a further modulation in the spacing between the clusters, giving a wider set of stripes of spacing ~37 nm.
Further work will characterize the microstructures developed under different deposition conditions (in particular the incident energy imparted to the atoms during deposition), and the microstructural changes that occur at the surface during wear.

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