Tracing C changes in a C/CrC PVD coating using Raman spectroscopy and EELS

Z Zhou*a, IM Rossa, WM Rainfortha, and P Eh Hovsepianb
aDepartment of Engineering Materials, University of Sheffield, Sheffield, S1 3JD, UK
bMaterials Engineering Research Institute, Sheffield Hallam University, Sheffield, S1 1WB, UK
E-mail: z.zhou@sheffield.ac.uk

Abstract. A C/CrC coating was deposited by unbalanced magnetron sputtering of graphite and Cr metal targets in argon atmosphere for low friction tribological applications. The coating possessed a nanocomposite structure with amorphous carbon embedded in a metastable fcc CrC matrix. The nanocomposite structure was annealed at 750°C in Ar+5%H2 atmosphere for 30 minutes to evaluate its thermal stability. Microstructures of the as-deposited and annealed coating were characterised using Raman spectroscopy and cross sectional transmission electron microscopy coupled with electron energy loss spectroscopy (TEM/EELS). Raman spectroscopy suggested the presence of graphitic carbon in the coating after annealing. EELS (ELNES of C K) combined with HRTEM investigation of the cross sections revealed graphitic C at the very top (~200nm) of the coating and amorphous C at the remaining part of the coating after annealing at 750°C. The advantages and limitations of Raman spectroscopy and TEM techniques in studying C/CrC coating are also discussed.

1 Introduction
Nanoscale hydrogen free C/Cr coatings have been produced by unbalanced magnetron sputtering of graphite and Cr metal targets with microstructures and properties strongly dependent on the substrate bias voltage [1]. The coatings evolve from an amorphous (-65V to -95V substrate bias voltage) through an ‘onion-like’ carbon structure (-120V) to nanoscale multilayer structure (-350V and -450V) and finally a uniform fine grain structure (-550V). The multilayer coating deposited at a bias voltage of -350V has attracted considerable attention. The coating possesses a nanocomposite structure with amorphous carbon embedded in a CrC matrix. The nanoscale amorphous carbon clusters self-assemble into layers alternated by CrC, giving a multilayer appearance. The fcc CrC is a thermodynamically non-equilibrium phase which can be stabilized by high ion energy magnetron sputtering. The thermal stability of the coating is therefore of great concern.

Raman spectroscopy is a popular non-destructive technique for characterization of carbon in C based coatings especially diamond like carbon coatings with minimum sample preparation. The main features in the Raman spectra of carbons are the D (disorder) and G (graphite) peaks, which lie at ~1360 and ~1560cm⁻¹ for visible excitation. Both D and G peaks are due to sp2 vibrations only. The G peak is due to the band stretching of all pairs of sp2 atoms in both rings and chains. The D peak is due to the breathing modes of sp2 atoms in rings. For diamond or samples containing a significant fraction of diamond, the sp3 peak is seen at 1332cm⁻¹ [2].

In the current work, the thermal stability of the multilayer structure (-350V substrate bias) was investigated by annealing heat treatment at 750°C in an Ar+H2 atmosphere for 30 minutes. Detailed Raman spectroscopy and cross sectional TEM study was conducted to understand the microstructure changes of the coating.
2 Experimental procedures

C/Cr coatings were deposited by the combined steered cathodic arc/UBM sputtering (ABSTM: Arc-Bond sputtering) technique using a Hauzer HTC 1000-4 PVD coater. The coating chamber had three graphite and one chromium metal targets, with AISI304 stainless steel substrates. The coating process comprises three steps: (i) Cr⁺ etching in cathodic arc mode by applying substrate bias of -1200V; (ii) CrN base layer deposition using reactive sputtering of Cr in Ar+N₂ atmosphere with substrate bias -75V; (iii) C/Cr multilayer formation using UBM sputtering in a non-reactive Ar atmosphere with substrate bias at -350V. More details of the coating process have been reported elsewhere [1].

The Raman spectroscopy analysis was conducted at room temperature by using a Renishaw inVia Raman microscope with 20mW 514 nm laser. The spectra were acquired with 10% power filter, which was used to avoid heating of the samples. The objective lenses (x50) produced a ~1μm laser spot. Cross sections for TEM were prepared by conventional methods with ion milling to electron transparency by a Gatan precision ion polishing system (PIPS). Bright field TEM micrographs and selected area diffraction patterns were recorded using a Phillips EM 420 TEM and a JEOL 2010 field emission gun (FEG) TEM. Electron energy loss spectra were acquired on the JEOL 2010 FEGTEM equipped with a Gatan GIF2000 energy filter.

3 Results and discussion

Figure 1 compares the Raman spectra of the plan-view surfaces of the as-deposited coating and the coating after annealing at 750°C (intensity normalized to maximum). The as-deposited coating shows a featureless spectrum, whereas the annealed coating has Raman bands at 1356, 1591, 2950cm⁻¹ assigned to carbon D, G and D'' [2,3]. The additional band at 2710cm⁻¹, was historically named G', since it is the second most prominent band always observed in graphite samples (the first is G), now designated as 2D as it is actually 2nd order of D peak [2]. Thus, the spectrum of the annealed surface is believed to contain polycrystalline graphitic carbon. Raman studies of similar C/Cr coatings suggested a transformation from graphitic (sp² C-C) bond to metal carbide (Cr-C) bond owing to increased ion energy bombardment from -65V to -350V bias voltage [4]. The as-deposited coating at -350V was then believed to be essentially carbide with minimum sp² bonded carbon. After annealing at 750°C, more ordered carbon was present in the coating. Discovering where the ordered carbon is located is the first step to understand the stability of the carbide coating. Cross section TEM coupled with EELS was then conducted to trace the change of C changes after annealing.

Figure 1. Raman spectra of the plan-view surface of as-deposited coating and coating annealed at 750°C.

Figure 2 gives the TEM cross sections of the as-deposited coating (1.29 μm thick) and 750°C annealed coating. The as-deposited coating is composed of a CrN base layer (~250nm) and the C/CrC coating (~1040nm). The C/CrC coating is composed of C clusters (bright contrast) and CrC matrix (dark contrast), as shown in Figure 2a. The C clusters segregated into non-continuous layers, giving the coating multilayer appearance. Three major zones are shown in Figure 2b after annealing at 750°C. (1) 1/6 from the very top of the coating lost its multilayer and became nanocrystalline. (2) ½ of the coating in the middle zone was still multilayer C/CrC, as
identified by electron diffraction (inset). (3) 1/3 from the bottom of the coating had lost its multilayer structure, but the columnar grain structure could be clearly seen. C clusters were still visible with larger size than the as-deposited condition. Carbon cluster coalescence occurred at the very bottom of the coating. Selected area electron diffraction revealed that the columnar grains at the bottom of the coating were probably Cr$_3$C$_2$ and the top nanocrystallites contained Cr$_2$O$_3$.

Figure 2. TEM cross sections of (a) as-deposited coating and (b) coating annealed at 750°C.

Figure 3 shows EEL spectra from all these three zones compared to the multilayer as-deposited coating. Reference spectra of CrC[5], Cr$_3$C$_2$[6] and natural graphite[7] were also included. Note (1) no significant difference in the carbon core loss between CrC and Cr$_3$C$_2$ reference spectra, (2) CrC and Cr$_3$C$_2$ both have no C sp$^2$ bond but show sharp peaks at 285.0eV, the same energy as π peak in graphite. All the spectra are aligned and normalised to the peak at 285.0eV (i.e. the shift of C K edge is not considered here). The EEL spectra were acquired using a 200nm selected area aperture with microscope in diffraction mode (i.e. image-coupling to spectrometer). The microscope condition yielded a 1.1eV energy resolution. With a 0.5ev/channel dispersion, both C-K and Cr L$_{2,3}$ edges were observed in all these three parts of the coating. The spectrum of the as-deposited coating resembles the CrC reference with a higher σ peak than the reference, probably due to large contribution of amorphous C clusters included in the selected area. The C K ELNES of the columnar grains at the bottom of the annealed coating (zone 3) is consistent with Cr$_3$C$_2$. The mid zone 2 had reduced σ intensity compared to the as-deposited condition, suggesting it may have less amorphous C than the as-deposited condition. It is evident that the size of the C clusters became larger in the 750°C annealed sample than the as-deposited coating. The spectrum of the top nanocrystalline zone 1 resembles the features of typical hydrogenated diamond like carbon coatings [8], having a sharp π peak followed by a pronounced σ peak. However, the graphite σ peak at 292.5eV followed by a plateau was not observed, even with a 0.1eV/channel dispersion. Since the spectra intensity was normalized to π peak, it allows comparison of the Cr concentration, suggesting a depletion of Cr towards the coating surface.

Figure 4 compares the morphology of the C clusters in the as-deposited condition to those at zones 2 and 1 of the annealed coating. It is evident that the C retained its amorphous nature in the C/CrC nanocomposite region (zone 2), as shown in Figures 4a and b, although the population of C clusters reduced after annealing. In contrast to the EELS data, there was clear evidence of graphitic C at zone 1 (Figure 4c). The EEL spectrum from the top zone 1 was more likely to be collected from an area of random orientated graphite crystallites. The lateral spatial resolution of the laser Raman microscopy is ~1μm, which is similar to the thickness of the entire C/CrC coating and therefore Raman was not performed on cross sectional samples. The penetration depth of a 632nm laser Raman beam was estimated to be in the range of 50-100nm with x100 objective [9], so the Raman spectra acquired from the plan-view surfaces should have only included the top zone featuring graphitic carbon detected by HREM. Thus, the cross section TEM coupled with selected area EELS and HREM suggested that the only at the top zone 1 was graphitic carbon found, C remained amorphous in the middle C/CrC and bottom C/Cr$_3$C$_2$ zones.
Figure 3. EEL spectra from the three zones in the coating annealed at 750°C compared to the as-deposited coating and references.

4 Conclusions

The C/CrC nanocomposite has partially changed its multilayer structure after annealing at 750°C into three zones: top nano-crystallites, middle C/CrC composite (with larger size of C clusters than as-deposited condition) and bottom columnar Cr$_3$C$_2$ with significant C clusters coalescence. Raman spectroscopy on the plan-view surfaces detected graphitic carbon. EELS and HREM study revealed graphitic carbon at the top 200nm layer whereas C clusters remains largely unchanged amorphous at the middle C/CrC and bottom Cr$_3$C$_2$ zones.

References:
[1] Hovsepian P Eh, Kok Y N, Ehiasarian A P, Haasch R, Wen J G, Petrov I 2005 Surf. Coat. Technol. 200 1572
[2] Ferrari A C 2007 Solid State Commun. 143 47
[3] Vidano R P, Fishbach D B, Willis L J, Loehr T M 1981 Solid State Commun. 39 341
[4] Kok Y N, Hovsepian P Eh, Haasch R, Petrov I 2005 Surf. Coat. Tech. 200 1117.
[5] Gassner G, Patscheider J, Mayrhofer P H, Hegedus E, Toth L, Kovaics I, Pecz B, Srot V, Scheu Ch, Mitterer C 2006 J. Vac. Sci. Technol. 24B 1837
[6] Hug G, Leapman R, and Jaouen M. Microbeam Analysis-1995, Breckenridge: VCH Publishers, Inc. p303-304.
[7] Abidate O. http://www.cemes.fr/~eelsdb/
[8] Fan X, Dickey E C, Pennycook S J, Sunkara M K. 1999 Appl. Phys. Lett 75 2740.
[9] Vallerot J-M, Bourrat X, Mouchon A, Chollon G 2006 Carbon 44 1833.