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Tribological response and characterization of Mo–W doped DLC coating

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ABSTRACT

DLC coatings and nanostructured carbon coating have been successfully used to prevent against wear and corrosion. Their thermal stability and internal stress have been improved by the addition of transition metals. This work characterizes the surface morphology against two different materials and growth mechanisms of an hydrogen-free carbon coating doped with a W–Mo. The wear resistance is evaluated under dry and room temperature by a set of pin on disc tests at different load and against two different counterfaces, Al_2O_3 and stainless steel 440 C. The as-deposited and worn surfaces were characterized by electron microscopy techniques, interferometry, nanoindentation and Raman spectroscopy. The as-deposited coating presented a hardness of 14 GPa and an elastic modulus of 179 GPa with a dense surface finished and a columnar structure. The average friction coefficient was between 0.15 and 0.25, with almost no wear on the counterfaces. The W–Mo doped DLC coating showed high resistance against wear with wear rates between 3.79×10^{-8} $mm^3\ N^{-1}\ m^{-1}$ and 2.65×10^{-7} $mm^3\ N^{-1}\ m^{-1}$ due to its Mo–W carbide content in the amorphous matrix. A major presence of carbides prevent from adhesion to the counterface by reducing the number of dangling bonds.

1. Introduction

It is well known that molybdenum, tungsten and nanostructured carbon coatings have self-lubricating properties, hence they are efficient in the reduction of friction and wear. There is no evidence of the three of them working in the same tribosystem, so this work intends to elucidate how they interact between them including the benefits of an unbalanced magnetron sputtering and HIPIMS technology. This technology has been used in recent studies of CrAlγN/CrN nanoscale multilayer coatings deposited on γ-TiAl [1] and now it is used for this Mo–W DLC coating. DLC coatings have shown good mechanical properties with typical values of hardness of 7–30 GPa and of elastic modulus of 60–210 GPa for hydrogenated films, whereas for non-hydrogenated films the values are hardness between 12 and 18 GPa and elastic modulus between 160 and 190 GPa [2]. The phases of DLC are a mixture of sp^3, sp^2 and minor quantities of sp^1 within an amorphous carbon matrix. The sp^3 content mainly controls the elastic constant due to its high directional σ bond sum to the short range ordering of sp^2 clusters, for example hydrogenated films with the same sp^3 but different sp^2 clustering have presented different optical, electronic, and mechanical properties [3]. The hybridised bond, sp^2, normally forms clusters inside the matrix and the arrangement of these clusters is an important characteristic since it changes their properties. The sp^2 clusters are joined as chains or rings with delocalized π bonds and their analysis is frequently performed by Raman spectroscopy [4] or EELS.

The short-range order of these films compel more than one characterisation technique to fully describe these structures.

The use of transition metals and silver in nano-structured coatings is becoming more popular due to their thermal stability because they can resist temperature or pressure cycles without great changes in their microstructure [5], also called by Veovodin et al. chameleon coatings. The three adaptive mechanism in the most recent *chameleon coatings* are: structural transitions with hexagonal (i.e. DLC), diffusion of soft metals to contact surface (i.e. TiN) and lubricious oxide formation at contact surface (i.e. Magnéli phases) [6]. In the case of carbon based coatings, the addition of Mo delays graphitization up to 40 °C in air and at 500 °C in low pressure atmospheres, the addition of Mo_2 S increases the thermal stability by decreasing the graphitization rate. Molybdenum oxides act as abrasive particles providing hardness and stability at high temperatures but at the same time they damage the formed tribolayer which promotes lubrication. MoO_3 above 500 °C becomes volatile so at higher temperatures the COF may suffer

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changes due to the formation of a new tribolayer, which will help to decrease the friction. With the addition of tungsten graphitization starts at a temperature around 300 °C and at higher temperatures a low COF is obtained since some tungsten oxides are formed and promote the formation of a protective tribolayer. WO_3 is a predominant oxide in some systems and it increases lubrication within the surfaces hence above 500 °C the COF decreases, after a previous increase between 200 °C and 400 °C [7]. The addition of metallic elements, particularly transition metals, change the bondings within the material, due to the new C–Me and C–C bonds, affecting its mechanical properties.

Around 100 million tools and automotive parts are coated just with DLC coatings to increase their properties per year, according to the 2014 review from Klaus Bewilogua [8], with a market volume of several 100 million EUR. Due to the increasing demand for wear and corrosion resistant coatings different methods and combination of deposition methods have been studied in recent year. HIPIMS technology has helped to bring interesting structures particularly with transition metals carbides by increasing the density of bombarded molecules in thin films, although it hinders the kinetics of the process [9].

2. Methods

2.1. Materials

DLC coatings were deposited on 30 mm discs of an M2 high speed steel (HSS) polished to a mirror finish with 6 μm and 1 μm diamond pastes. The polished samples and the Si wafers were cleaned in an industrial sized automated ultrasonic cleaning line to remove surface impurities and then dried in a vacuum drier before loading into the coating chamber. An industrial sized Hauzer HTC 1000-4 PVD coating machine which combines UBM (unbalanced magnetron) and HIPIMS (high power impulse magnetron sputtering) at Sheffield Hallam University (Sheffield, UK) was used for the deposition of the doped Mo–W DLC. Three graphite targets were operated in UBM mode and a compound target containing both Mo and W was operated with HIPIMS mode during coating deposition. All the samples were subjected to three-fold rotation in order to achieve homogeneity in the direction of coating growth. Prior to the coating deposition, the targets were sputter-cleaned and the sample surfaces were further pretreated by HIPIMS ion etching (using both Mo and W) [10]. A base layer was deposited in reactive $Ar+N_2$ atmosphere in order to enhance its adhesion to the substrate, which was followed by the deposition of the Mo–W–C coating in argon atmosphere. Stainless steel 440 C balls 4 mm in diameter were used as counterface with 1 N and 2 N of loads. A second set tests were undertaken against Al_2O_3 balls as counterface with the same dimensions as the SS balls with loads of 0.2 N, 1 N and 2 N. Balls and discs were ultrasonically cleaned in methanol and dried prior to wear testing.

Coating hardness and Young's modulus were obtained by a nanoindenter, Hysitron Triboscope Nanomechanical Test Instrument set with an AFM microscope Veeco Dimension. A pre-set value was 10 mN was used to avoid substrate influence during hardness measurement for 20 repetitions. Oliver and Pharr method was used assuming a Poisson's ratio of 0.3 [2].The surface morphology, thickness and quality of the as deposited film was analysed by scanning electron microscopy (FEI, Inspect F), equipped with an energy dispersive X-ray spectroscopy (EDS) system. Atomic force microscopy (AFM)was undertaken using a Dimension 3100 operated in tapping mode. X-ray diffraction was undertaken using a Siemens D5000 (Cu) diffractometer under a continuous scan from 10° to 120° of 2θ with a step size of 0.02° with Bragg–Brentano geometry.

2.2. Wear test

Dry sliding pin-on-disc tests were undertaken using a UMT Bruker tribometer. Each test was run at a rotational speed of 0.1 ms^{-1} for a total sliding distance of 1 km. All tests were carried out at room temperature ≈26 °C. Al_2O_3 balls were used for loads of 2 N, 1 N and 0.2 N tests. Then a second set of test was undertaken with stainless steel 440 C balls for the loads of 1 N and 2 N. The coated disc had a diameter of 3 cm and a thickness of 0.6 cm, whereas all the counterfaces were 4 mm in diameter.

Bruker Contour GT interferometry and SEM (FEI Inspect F) with an operating voltage of 10 kV was used to examine the wear tracks morphology and transfer layer formed on pin counterfaces.

Raman spectroscopy (Renishaw inVia Raman spectrometer) with an exciting laser wavelength of 514 nm at a power of 20 mW were carried out on the wear tracks after wear tests. Raman spectra with a focused spot diameter of approximately 1 μm were performed from 50 to 3000 cm^{-1}. TEM specimens from the wear scars were made using focused ion beam (FIB) using an FEI Quanta dual-beam which allowed site specific area analysis of the worn surfaces. To protect the wear scar surfaces from the incident ion beam bombardment, an approximately 2 μm carbon film was deposited on the top of the surface using a gas injection system (GIS). Initial sectioning of the surface was undertaken using a 30 kV Ga+ ion beam. In-situ lift out of the TEM sample was undertaken using an Omniprob™ micro-manipulator. Transmission electron microscopy (TEM) was undertaken on a JEOL 2010F operating at 200 kV. High-resolution microstructures were observed using a HAADF scanning transmission electron microscope (STEM) images. In addition, high spatial resolution electron energy loss spectroscopy (EELS) was used to determine the chemical composition and distribution within the worn surface.

3. Results and discussion

3.1. As deposited coating

The as deposited coating produced under the present deposition technique, Fig. 1, exhibited a dense, columnar structure with uniform surface coverage and a mean roughness of 34 nm measured by atomic force microscopy. Cross sectional TEM examination indicated a coating thickness of 2.1 μm on top of a 123 nm nitride base layer. Microstructural observations using TEM showed an amorphous matrix in the columnar structure of ≈200 nm in width with areas of crystalline onion-like clusters, which probably correspond to localised W and Mo carbides Fig. 1c. TEM images revealed a multilayered structure, commonly found in Me-DLC [11–13]. It is possible to classify the structure of coatings into four characteristic zones that will depend primarily on the substrate temperature and other important variables [14]. Thornton suggested that for sputtered coatings the gas could modify the model and identified more regions between zone 1 and zone 2, consisting of poorly defined fibrous grains. This columnar equiaxed structure exhibited in the coating under study refers to a zone 2 structure which makes films less susceptible to delamination, less prone to crack formations and provides a complete surface coverage even with low thickness [15]. W-DLC film typically presents a columnar structure [16,17], whereas Mo-DLC tend to form a granular (onion-like) structure [18,19]. Mo-DLC coatings form a granular pattern whose density is reduced as the carbon content increases in the matrix [20] while reducing hardness.

The coating did not exhibit any sign of rupture during the nanoindentation testing, demonstrating the coatings mechanical integrity. The hardness exhibited was 14 GPa and the elastic modulus was 179 GPa, which gives an H/E ratio of 0.078. The