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Microstructural, mechanical and tribological properties of tungsten-gradually doped diamond-like carbon films with functionally graded interlayers

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ABSTRACT

A series of tungsten-gradually doped diamond-like carbon (DLC) films with functionally graded interlayer were prepared using a hybrid technique of vacuum cathodic arc/magnetron sputtering/ion beam deposition. With 'compositionally graded coating' concept, the deposition of wear-resistant carbon-based films with excellent adhesion to metallic substrate was realized. In the films, a functionally graded interlayer with layer sequence of Cr/CrN/CrNC/CrC/WC was first deposited onto the substrate, and then, a DLC layer doped with gradually decreasing content of W was coated on. The W concentration gradient along depth of the film was tailored by adjusting the W target current and deposition time. The characterized results indicate that the microstructural, mechanical and tribological properties of these films show a significant dependence on the W concentration gradient. A high fraction of W atom in carbon matrix can promote the formation of sp^2 sites and WC_{1-x} nanoparticles. Applying this coating concept, strongly adherent carbon films with critical load exceeding 100 N in scratch test were obtained, and no fractures or delaminations were observed at the end of the scratched trace. The hardness was found to vary from 13.28 to 32.13 GPa with increasing W concentration. These films also presented excellent tribological properties, especially significantly low wear rate under dry sliding condition against Si_3N_4 ball. The optimum wear performance with friction coefficient of 0.19 and wear rate of 8.36×10^{-7} mm^3/Nm was achieved for the tungsten-gradually doped DLC film with a graded W concentration ranging from 52.5% to 17.8%. This compositionally graded coating system might be a potentially promising candidate for wear-resistant carbon-based films in the demanding tribological applications.

1. Introduction

Diamond-like carbon (DLC) films have great potential for applications as surface protective materials in tribological fields, due to their high hardness, low friction coefficient and chemical inertness [1–3]. In the past decades, various deposition techniques have been developed to synthesize these films. However, the major drawback of DLC film is its high intrinsic residual stress ranging from a few GPa to 10 GPa [4] acquired during deposition process, which limits the enhancement of film thickness and adhesion strength with metallic and ceramic substrates. For instance, Stüber et al. [5] reported that pure DLC films deposited by d.c. magnetron sputtering showed a high compressive stress in the order of 4 GPa as well as low adhesion, for which the critical loads of failure in scratch test were below 10 N. Hydrogen-free DLC films deposited by filtered cathodic vacuum arc [6] delaminated from substrates as the coating thickness exceeds 180 nm. To combat this problem, optimization of deposition parameters [7–9], diamond-like nanocomposite [10,11], functionally graded interlayer [12–14], thermal annealing [15], multilayer preparation [16,17], and elemental doping (metal or nonmetal) [18–20] have been investigated.

Functionally graded interlayer is a design of tailored structure in the form of compositionally graded variation between the substrate and carbon film. As, traditionally, single-layer carbon coatings generally exhibit much higher hardness and elastic modulus, and lower thermal expansion than metal substrates, the produced high residual and thermal stresses concentrate inside the coating and along the coating/substrate interface [21], which may consequently lead to cracking and debonding [22]. On the contrary, the functionally graded interlayer is a special combination of composite materials, the composition and microstructure of which are not spatially homogeneous but vary with respect to a predetermined profile (typically graded structure transition from a metal-bonding layer to a metal carbide layer), designed in order to improve certain characteristics (usually mechanical) over monolithic materials [23]. From this point of view, Choy et al. [12] reported a functionally graded interlayer with an optimized layer in sequence of Ti/TiN/TiNC to reduce the residual stress and increase the critical load to 47 N in the scratch test of DLC films. Deng and Braun [13] presented similar results with a graded layer in sequence of Ti/TiN/TiNC/TiC. Yu et al. [14] proposed another chemically graded Cr/CrN/CrC interlayer for the deposition of thick DLC films with improved adhesion up to 52 N in scratch test.

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The incorporation of metal into carbon matrix to form metal-doped DLC (Me-DLC) [24] has been proved as another effective method to reduce residual stress and improve the adhesion of DLC films. With regard to Me-DLC films, metal or metal carbide nanoclusters were observed to form and disperse homogeneously in amorphous carbon matrix [18,25]. These films can be defined as metal-homogenously doped DLC films. However, few references reported on Me-DLC films doped in the form of graded metal concentration. In a compositionally graded system, no abrupt change in composition might ensure the possibility of limiting stress at critical locations and thus suppressing the onset of plastic deformation, damage, or cracking [26]. From this point of view, a metal-gradually doped DLC film can be developed. On one hand, a metal-rich carbon structure doped with high metal concentration forming at the interface with an attendant reduction of residual stress [27,28] would certainly enhance the adhesion between the film and substrate. On the other hand, a purer diamond-like carbon structure doped with low metal concentration forming at the top surface can perform with a lower friction coefficient and greater resistance to wear [29].

In this work, we investigated the use of the two basic concepts discussed above to improve both the adhesion and wear resistance of DLC films. A series of tungsten-gradually doped DLC films with functionally graded interlayers were synthesized by using a hybrid technique of vacuum cathodic arc/magnetron sputtering/ion beam deposition. The functionally graded interlayer was optimized in the layer sequence of Cr/CrN/CrNC/CrC/WC. The subsequent tungsten-gradually doped DLC layer was deposited by gradually changing the sputtering target current and deposition time. The effect of W concentration gradient on the microstructure, mechanical properties and wear resistance of these films were discussed.

2. Experimental details

2.1. Film deposition

The investigated films were prepared by a multifunctional ASM600DMTG coater [30]. In this work, arc evaporators equipped with chromium target were used as metal source for depositing the functionally graded interlayer. One rectangular magnetron equipped with tungsten target was sputtered as cathode material. Pure argon (99.99 vol.%), methane (99.99 vol.%) and nitrogen (99.99 vol.%) gases were fed through an anode layer ion source into the chamber to act as process and reactive gases, respectively. Mirror-polished high speed steel (W18Cr4V) plates and n-type Si (100) wafers were selected as substrates. Before deposition, the vacuum chamber was pumped to a base pressure of 1.0×10^{-2} Pa, and the total pressure during deposition of the films was about 0.3 Pa. The ambient temperature during deposition was 100 °C.

The coating process included two distinct steps: functionally graded interlayer deposition and tungsten-gradually doped DLC deposition. For the deposition of functionally graded interlayer Cr/CrN/CrNC/CrC/WC, details regarding Cr/CrN/CrNC/CrC have been described elsewhere [30]. After the deposition of CrC layer, the arc evaporators were closed. Then a WC layer was deposited by sputtering from W target in an argon and methane mixture. In this stage, the current of W target gradually decreased from 10 to 7 A at a rate of 0.5 A for every 5 min, and the gas flow rate of methane was 120 sccm. The total thickness of the functionally graded interlayer Cr/CrN/CrNC/CrC/WC was designed to be 1.2 μm. The following step was the deposition of tungsten-gradually doped DLC films by direct current magnetron sputtering and ion beam deposition. And now the initial W target current was 7 A. The graded variation of W concentration in carbon matrix was tailored by gradually decreasing the target current from 7 A to a specific end current (0, 1, 2, 3.5, and 5 A, respectively, in this work) in due time. Afterwards, the target current was maintained constant at the end current for the deposition of a more diamond-like carbon layer doped with low concentration of metal at the top surface. Thus, five groups of tungsten-gradually doped DLC films with different W concentration gradients were prepared for the investigation on the effect of target current. The total thickness of all the films was controlled at about 2.4 μm. In addition, a pure DLC thin film was deposited for comparison.

2.2. Characterization

FEI Quanta 200 FEG field emission scanning electron microscope (SEM, USA) was used to examine the surface and fracture microstructures. A three dimensional (3D) white-light interfering surface profiler (Micro XAM-3D, USA) was applied to measure the surface roughness (R_a) of the films, and observe the scratched and worn surfaces. The in-depth elemental composition of the samples was measured using a PHI700 scanning Auger (AES, Japan) nanoprobe. The Raman measurement was performed using a Renishaw 2000 Raman system (England). The excitation wavelength used was 514.5 nm from an Ar^+ laser. The crystallization of the as-prepared films was identified through analyzing X-ray diffraction (XRD) patterns recorded by a Philips PW 1710 automated diffractometer using a glancing incidence angle of 2°. The chemical bonding state of atoms in the films was analyzed using PHI Quantera SXM X-ray photoelectron spectroscope (XPS, Japan), and an Ar^+ ion beam was used to etch the top surface to a depth of about 3 nm so as to remove the contaminants before the XPS measurement. A nanoindenter (MTS XP, USA) was used to evaluate the hardness (H) of the films in a continuous stiffness measurement (CSM) mode. A suitable load applied was selected on the basis of the indentation depth, which should be equal to 1/10 of the film thickness.

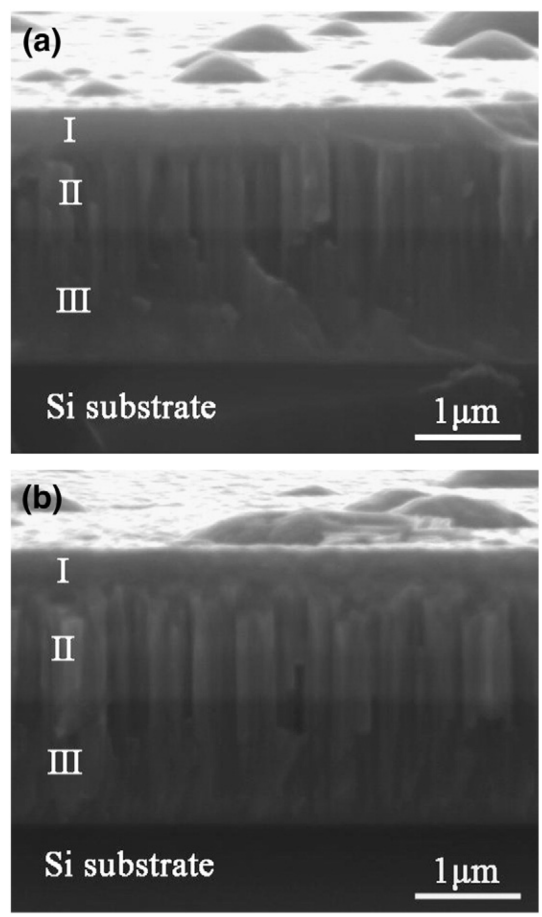

Fig. 1. Typical SEM fracture morphologies of the W-gradually doped DLC film samples prepared at W target end current: (a) 1 A, and (b) 3.5 A. The digital symbols correspond to W-DLC top layer (I), W-gradually doped DLC sublayer (II), and functionally graded interlayer (III), respectively.