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Effect of substrate bias voltage on structural and mechanical properties of pulsed DC magnetron sputtered TiN–MoS_x composite coatings

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ABSTRACT

TiN–MoS_x composite coatings were deposited by pulsed DC closed-field unbalanced magnetron sputtering (CFUBMS) using separate Ti and MoS_2 targets in an Ar and N_2 gas environment. The effect of substrate bias voltage on the structure and mechanical properties of TiN–MoS_x composite coating has been studied. The structure and composition of the coating were evaluated using field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) by X-ray and grazing incidence X-ray diffraction (GIXRD). Scratch adhesion tests, Vickers microhardness tests and ball-on-disc tests with a cemented carbide (WC-6%Co) ball were carried out to investigate mechanical properties of the coating. Application of substrate bias was found to transform the structure of TiN–MoS_x composite coating from open columnar to a dense columnar structure. The changes in grain size and texture coefficient appear to be associated with variation in substrate bias voltage. The mechanical properties of the coating such as adhesion and composite microhardness were also observed to be related to the change in bias voltage. A maximum hardness of 22 GPa was obtained for a coating deposited at substrate bias voltage of −40 V. The improved structural and mechanical properties of the coating deposited at −40 V were also reflected in its excellent wear resistance property.

1. Introduction

Though solid lubricant coatings (MoS_2, WS_2 etc.) have shown potential in tribological performance under vacuum or dry air, it has been observed they fail to perform satisfactorily under humid atmospheric condition owing to their poor abrasion resistance [1]. Since it is practically improbable to obtain super low friction, hard, oxidation and wear resistance properties from a single coating system, recent research has been directed towards incorporation of a lubricious phase like MoS_2 into a harder matrix (TiN, TiB_2, CrN, CrB_2 etc) in order to maintain a reservoir of solid lubricant through out the coating thickness [2–9]. Such hard solid lubricant film was effective in maintaining a coefficient of friction less than 0.3 through a long, stable lifetime without showing significant deterioration in hardness [2–7]. In a recent study, the effect of MoS_x content in TiN–MoS_x composite coatings was investigated on structure, mechanical and tribological properties of the coating. It was shown that very low friction characteristics (with friction coefficient, μ less than 0.05) under normal atmospheric conditions could be achieved with acceptable mechanical properties [6].

Medium frequency (20–350 kHz) pulsed magnetron sputtering (PMS) was found to be effective in improving the coating property. While operating in reactive sputtering mode, the application of PMS was beneficial in reducing the formation of arcs particularly for films of materials of low electrical conductivity and consequently the number of defects in the growing film is also reduced [10–12]. Application of pulsed DC in biasing the substrate enhances the ion current drawn towards the substrate [12]. The PMS process can, therefore, have a significant influence on PVD coating structure and properties [10–14] and even on the tribological property as observed for TiN and TiO_2 coatings [13,14]. It is reasonable to assume that the application of PMS can certainly provide a beneficial impact on TiN–MoS_x composite coating, if deposition parameters are properly chosen.

Among deposition parameters, negative bias voltage applied to the substrates could significantly change film properties due to enhancement of adatom mobility and the effects of ion bombardment. The ion bombardment during coating deposition would play an important role in affecting the morphology, structure, composition and mechanical properties of the coatings [15,16]. For pure MoS_2 or even MoS_2–Ti composite film, the increase in bias caused preferential re-sputtering of S resulting in a reduced S/Mo ratio [17,18], which can affect different properties of the film. A recent study on pure MoS_x films deposited by

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bipolar pulsed DC showed that even an S/Mo ratio of 0.8 was able to provide good lubricious property due to the strong basal plane orientation and application of a bias voltage was found to reduce the coefficient of friction [19]. Therefore, an understanding of substrate bias effects is necessary to improve the physical and mechanical properties of MoS_2-based coatings. However, there is no information on the effect of substrate bias voltage on the properties of pulsed magnetron sputtered TiN–MoS_x composite coatings. Therefore, the objective of the present work is to study the effect of bias voltage on structure and mechanical properties of TiN–MoS_x composite coating.

In the present work, TiN–MoS_x composite coating was deposited using separate Ti and MoS_2 targets under Ar and N_2 atmosphere in a closed-field unbalanced magnetron sputtering (CFUBMS) system. Pulsed DC was employed for the power supply of targets as well as substrate bias. Five different substrate bias voltages were employed and the structural modification in the coating system was studied by grazing incidence X-ray diffraction (GIXRD), field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS). Scratch tests and Vickers microhardness tests were performed to assess the effect of bias on adhesion and hardness of the coating, respectively. Finally, a ball-on-disc test was employed to study the effect of structural modification on tribological properties of TiN–MoS_x composite film.

2. Experimental methods and condition

All the coatings were deposited on M2 grade HSS and AISI 1040 steel substrates using dual cathode closed-field unbalanced magnetron sputtering with simultaneous activation of Ti and MoS_2 targets under N_2 gas environment. The detailed description of the system and the process were presented elsewhere [5,6]. Both the targets as well as the substrates were powered with three pulsed DC power supplies, each of 10 kW with variable voltage and current controllers. The power supplies were operated using a pulse frequency (f) of 35 kHz and pulse on time (T_{on}) of 25 μs (duty cycle = 90%) both for the cathodes as well for the substrate bias for all coated specimens. Cathode power density for Ti was 2.17 W/cm^2 and that for MoS_2 was kept at 0.55 W/cm^2. Ar and N_2 flow rates during co-deposition of TiN and MoS_2 were maintained at 15 and 7 sccm, respectively using mass flow controllers. All coatings were deposited at a working pressure of 0.3 Pa and substrate temperature of 200 °C.

Surface morphology of the coatings was studied by a high resolution (Carl Zeiss, Supra 40) FESEM. The composition of the as-deposited films was determined by EDS at 20 keV coupled with the FESEM. Film thickness was also determined by observing the coating fractographs under FESEM. GIXRD was used for the verification of the crystal phases of the coatings. Diffraction measurements were performed with a high resolution Philips, PANalytical PW 3040/60 X'Pert PRO instrument using Cu Kα radiation of wavelength 1.5418 Å at an incident angle of 2°. A 2θ scan range from 10° to 80° was selected. The voltage and current settings were 45 kV and 40 mA, respectively. The samples were continuously scanned with a step size of 0.05° (2θ) and a count time of 2 s per step. The data were later analysed with X'pert High score software (Philips Analytical B.V., Netherlands) and peaks were identified by comparing with standard JCPDS data files. The crystallite size of the coating was analysed using Williamson–Hall plot method [6,20,21]. The integral breadth of a single diffraction peak (β_r) was determined from the fitted peak of the XRD pattern using Pseudo-Voigt function after appropriate background correction.

The adhesion of the coating was studied by a TR-101M5, DUCOM scratch tester. The scratch tests were performed with a Rockwell C diamond stylus (0.2 mm radius) drawn across the surface of the coating at a constant linear speed of 12 mm/min. The normal load was varied linearly from 5 to 70 N. Adhesion performance is usually quantified as the normal load required to delaminate the coating completely and is referred to as critical load L_c. Five tests were done on each sample to confirm the critical load. However, further analysis by FESEM (Carl Zeiss, Supra 40) and EDS was also carried out to show the exact location of coating failure in order to confirm the critical load for each test. Vickers microhardness tests were carried out in order to determine composite film hardness using a LM-700 Digital Indentation Tester, LECO. At least five indentations were considered under 0.05 N load (dwell time = 15 s) for each sample followed by observation under FESEM for better accuracy of measurement. Wear test was carried out using a ball-on-disc tribometer (TR-201-M3, DUCOM) at 10 N loads at track diameter of 12 mm. The test was continued for 90 min with a linear speed of 200 mm/s (1080 m of track length) or until coating failure. A 5 mm cemented carbide (WC-6% Co) ball was used as the counter part. The test was carried out at room temperature (25–27 °C) and 50 ± 5% relative humidity. The wear track and the ball counter face were later studied with scanning electron microscope (JEOL 5800, Japan) and EDS. The depth of the wear track was measured atleast at 10 different locations of wear track using Taylor-Hobson, Surtronic 3 + surface profilometer.

3. Results and discussion

3.1. Composition analysis

Due to peak overlaps between both the Mo Lα (2.29 keV) and S Kα (2.31 keV) peaks, compositional analysis by EDS is complicated and hence the films were quantified in terms of the overall percent of both Mo and S, as done in earlier literature [2–7]. The compositions of different films are given in Table 1. However, recent work suggested that despite the partial overlap, it is possible to get the actual S and Mo content by EDS and results found from EDS matches with Rutherford backscattering [19] and Elastic Recoil Detection [3] analysis, which makes possible the calculation of S/Mo atomic ratio from EDS.

The S/Mo atomic ratio was calculated and plotted in Fig. 1 which clearly illustrates the re-sputtering of S due to increased bias. The enhanced ion flux due to increase of bias, preferentially re-sputters the S atom, causing S depletion. The S/Mo ratio was found to be in the range of 0.15–1, which is in fairly good agreement with past literature pertaining to TiN–MoS_x composite film where S/Mo ratio of 0.3–0.7 was reported [3]. Table 1 also reveals reduction in total (Mo + S) content in the deposited film with increase in bias voltage. Even pure MoS_x coating deposited using bipolar pulsed DC showed an S/Mo ratio of 0.8 [18]. It is also of interest, that the pure MoS_x film

Table 1
EDS analysis result of different coated specimens.

Specimen code	Substrate bias (U_s)	Mo + S content	
		Wt %	Atomic %
C1	0 V	40.23	29.50
C2	−30 V	30.43	13.75
C3	−40 V	28.38	12.49
C4	−60 V	26.61	10.61
C5	−90 V	21.88	7.26