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Structure, mechanical and tribological properties of self-lubricant W–S–N coatings

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ABSTRACT

W–S–N self-lubricant coatings were deposited by d.c. reactive magnetron sputtering at two total discharge pressures of 0.6 and 1.2 Pa. The nitrogen content and S/W ratio varied from 0 to 30 at.%, and 0.6 to 1.6, respectively. The effect of deposition conditions on chemical composition, structure and mechanical properties was studied; coatings with the most promising properties have been selected for tribological testing. Coatings were nanostructured with nanograins of tungsten disulfide; the size of which decreased with increasing nitrogen content. Hardness increased with N content up to 7 GPa for coating deposited with a discharge pressure of 1.2 Pa; coatings deposited at lower pressure exhibited hardness around 9 GPa. Friction and wear behavior in humid air and dry nitrogen was evaluated using a pin-on-disk tribometer. The wear tracks and the ball wear scars were analyzed by Raman spectroscopy and scanning electron microscopy. Although the friction coefficient in dry nitrogen was significantly lower than in humid air, the wear rate was similar for both environments. Detailed wear track surface analysis showed that the tribolayer formed on the surface contained mostly tungsten disulfide and tungsten oxide.

1. Introduction

The use of Transition Metal Dichalcogenides (TMD) as low friction materials is historically very well established. TMDs have been successfully applied in various areas as solid lubricants, oil additives or burnished coatings. Together with the development of vacuum deposition techniques, TMDs are readily fabricated as thin films. Their layered structure consists of consecutive sheets of transition metal atoms (typically Mo, W) sandwiched between two hexagonally packed chalcogenide layers (S, Se); these layers are bonded together by weak van der Waals forces, allowing easy slip.

Excellent tribological performance of TMD coatings generally relies on i) formation of the sliding-induced transfer layer on the counterpart and ii) a progressive reorientation of the outermost layer of the coating [1,2]. Under typical conditions (sliding in vacuum or pure gases) the shear stress at the sliding interface is at a minimum, giving rise to extremely low friction, sometimes even below the sensitivity of the measuring instrument [3]. On the contrary, sliding in humid air inevitably leads to the reaction of the TMD coating with water vapor. This results in the incorporation of contaminants within the hexagonal structure and oxidation. As a consequence, the friction is high and the wear resistance decreases, diminishing the coating lifetime.

In order to overcome such drawbacks, the alloying of TMDs with other elements is a common solution. Among TMDs, MoS_2 and WS_2 have been the most studied, and the addition of several elements has been tried. In the case of MoS_2, Ti has been the preferred element [4–6] although other ones have also been tested, such as Al [7], Au [8], Cr, Ni [9], Ta [10], Pb [11], and Zr [12]. Far fewer studies exist for metallic alloys of WS_2, with results reported for Ti [13,14] and Cr [15]. On the other hand, WS_2 coatings alloyed with non-metallic elements such as carbon [16] or nitrogen [17] have been extensively studied. Recently, an amorphous W–S–N coating deposited by r.f. magnetron sputtering exhibited progressive crystallization and favorable re-orientation of the TMD crystals during the sliding; the friction coefficient in dry nitrogen was as low as 0.003 (contact pressures over 1 GPa) and the coating withstood more than 2 million cycles [18]. Both the wear track and ball wear scar were covered by a thin tribofilm of well-oriented WS_2 (i.e. with basal plane parallel to surface). Encouraged by these promising results, we decided to deposit a new set of nitrogen-doped W–S–N coatings. By varying the nitrogen content of the coating, this allows us to investigate the effect of coating structure on the tribological behavior in humid air and dry nitrogen.

2. Experimental details

W–S–N coatings were deposited by d.c. reactive magnetron sputtering in an Ar/N_2 atmosphere from a WS_2 target. Two total discharge pressures were studied, 0.6 and 1.2 Pa, for which the partial

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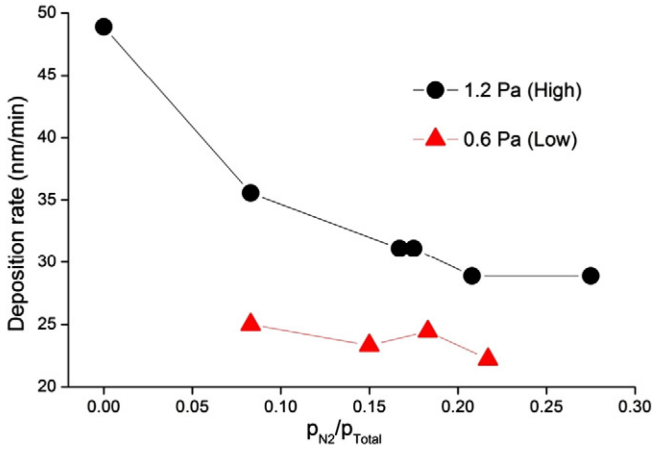

Fig. 1. Deposition rate as a function of nitrogen content in the discharge gas (guide lines are just displayed for clarity).

pressure of N_2 increased from 0 up to 0.13 and 0.33 Pa, respectively. The same Ar flow rate was used in all depositions. Prior to the depositions the chamber was pumped down to 10^{-5} Pa. The substrates were sputter-cleaned in an argon atmosphere for 20 min using an ion gun. In this study the coatings are denominated as WSNxyL or WSNxyH, where 'xy' is the atomic % of nitrogen and 'L' and 'H' signify low and high discharge pressures, respectively (e.g. WSN10H is a coating with 10 at.% of nitrogen deposited with 1.2 Pa discharge pressure). In light of the results obtained during coating development, it was deemed suitable to deposit the W–S–N coatings without an adhesion-improving interlayer. The substrates were silicon wafers (for analytical purposes) and M2 steel (for mechanical testing).

The chemical composition of the coating was determined with Electron Probe Microanalysis (EPMA), using a Cameca SX-50 system. X-ray photoelectron spectroscopy (XPS—Thermo Scientific) was used to investigate the chemical bonding. Results were obtained using monochromated, micro-focused Al K-Alpha X-ray source, with a spot size of 400 μm for coating analysis, and 100 μm for chemical analysis of the wear track. A flood gun was used for charge neutralization. Sample surfaces were sputtered with Ar ions at energies of 3 keV, and an ion current of 1 μA, covering an area of 2 × 2 mm.

The crystal structure was analyzed with X-ray diffraction (XRD) in a Philips X-Pert system using Cu Kα radiation ($\lambda = 0.179$ nm) in grazing mode (2°). Surface and cross section morphologies of the coatings were observed by atomic force microscopy (AFM) and scanning electron microscopy (SEM) equipped with energy-dispersive X-Ray spectroscopy (EDX) with an acceleration voltage of 15 kV. The chemical bonding was analyzed by Raman spectroscopy (Horiba Jobin Yvon, 532 nm, laser spot ~1 μm, 20–25 mW) using the lowest laser intensity available to avoid damaging the coatings. The Raman spectra of the wear track and the ball wear scar were acquired from the center and border (wear track) or the front and wear debris (ball scar).

Tribological behavior was evaluated using a pin-on-disc tribometer (CSM Instruments) in two environments, i.e. humid air (relative humidity ~45%) and dry nitrogen. Testing in dry nitrogen was performed by employing an enclosure attached to the tribometer and continuous flow of nitrogen. Nevertheless, the final atmosphere contained residual oxygen and water vapor. The sliding partner was 100Cr6 steel ball. The linear speed, normal load and number of cycles were always kept constant at 10 cm s^{-1}, 1 N and 3000, respectively. The friction coefficient is a mean value, with the 'running-in' phase dismissed if not stated otherwise. The wear rates were calculated as the worn volume per sliding distance per normal load. The worn volumes were measured by a white light interferometer (Zygo NewView 7200).

The hardness (H) and Young's modulus (E) of the coatings were determined by depth-sensing indentation (Nanotest, Micromaterials) with a Berkovich tip. The measurements were carried out on the wear track as well as the free surface to observe variations in hardness. A penetration depth of 30–40 nm was set as a compromise with respect to i) a thickness of the tribofilm with prominent orientation (typically less than 10 nm), ii) surface roughness and iii) error of measurement. The adhesion/cohesion of the coatings to the M2 steel substrate was evaluated by scratch testing. The load was increased linearly from 0 N to 50 N, using a Rockwell C indenter with a 200 μm tip radius.

3. Results and discussion

3.1. Deposition rate and chemical composition

The evolution of the deposition rate as a function of increasing N_2 partial pressure/total pressure ratio is shown in Fig. 1. The total pressure has a high influence on the deposition rate, behavior attributed to the bombardment of the growing coatings by the neutrals reflected by the target. The decrease in pressure gives rise to higher values of the target potential and, consequently, to more energetic neutrals, as well as fewer collisions in the interelectrode region. Therefore, higher bombardment rates can be expected to result either in higher re-sputtering from the growing coating surface or in more compact deposited coatings; both effects lower final thickness and decrease the deposition rate. The increase of nitrogen partial pressure influenced the deposition rate, particularly in the case of high total pressure. Three main factors determine the deposition rate in the present study: (i) as it will be shown later, a strong improvement in the density of the coatings can be achieved when reactive sputtering is used; the increase in density is significant when nitrogen is introduced, (ii) in relative values, the number of Ar atoms available in the discharge atmosphere is reduced when N_2 partial pressure increases (total pressure is kept constant), and (iii) the lower pressure leads to increased re-sputtering from the coating surface. The

Table 1
Summary of chemical composition, thickness and adhesion of the coatings.

Sample	Total pressure (Pa)	N_2 partial pressure (Pa)	Chemical composition (at.%)				S/W ratio (–)	Thickness (μm)	Critical load L_{C2} (N)
			W	S	N	O			
WSN0H	1.2	0	36	58	0	6	1.6	2.2	–
WSN10H	1.2	0.1	40	48	10	2	1.2	1.6	12
WSN16H	1.2	0.2	37	44	16	3	1.2	1.4	12
WSN20H	1.2	0.21	36	42	20	2	1.2	1.4	9
WSN25H	1.2	0.25	35	38	25	2	1.1	1.3	11
WSN30H	1.2	0.33	32	34	30	4	1.1	1.3	14
WSN14L	0.6	0.05	52	32	14	2	0.6	0.8	10
WSN21L	0.6	0.09	44	32	21	3	0.7	0.7	9
WSN24L	0.6	0.11	40	32	24	4	0.8	1.1	14
WSN28L	0.6	0.13	38	32	27	3	0.8	1	12