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The effect of bilayer period and degree of unbalancing on magnetron sputtered Cr/CrN nano-multilayer wear and corrosion

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ABSTRACT

Cr/CrN nano-multilayers were grown on H13 steel and silicon (100), having different periods (Λ), at room temperature using the unbalanced magnetron sputtering technique by varying the degree of unbalancing (K_G) to investigate the effect on multilayer properties. The multilayers' total thickness was ~1 μm and the total number of layers varied from 10 (Λ = 200 nm), 20 (Λ = 100 nm) to 100 (Λ = 20 nm) layers. Film microstructure, hardness, wear and corrosion resistance were measured regarding bilayer period and degree of unbalancing. The results showed that wear resistance was lower for low K_G values and that corrosion resistance was higher and hardness was improved. Nano-hardness was found to be higher for multilayers grown with Λ = 20 nm for all K_G values, reaching a maximum 25 GPa value for K_G = 0.87.

1. Introduction

Transition metal nitride (TMN) coatings are of technological interest because their properties such as wear and corrosion resistance [1,2], low friction coefficient, good adhesion, extreme hardness [3,4] and good electrical conductivity [5] lead them to having ready applications in different fields, for instance as protective coatings for cutting tools, machine parts, molds for automotive piece production [6,7], diffusion barriers in electronic applications [8,9] and as decorative coatings for surface finishing due to their attractive colors [10]. CrN coatings have attracted special attention amongst TMN coatings due to their improved mechanical properties, oxidation resistance to high temperatures and better deposition rates [11,12]. CrN coatings have been proposed as replacements for electrolytic hard chromium due to their hardness and better corrosion resistance, such coating being deposited by electroplating involving carcinogenic hexavalent chromium vapors being released; they also represent a good alternative to the concomitant environmental contamination being produced by electrolytic hard chromium production [11,12].

Despite CrN coatings having such properties, some applications require improved properties which monolayers cannot fulfill, such as greater hardness or corrosion resistance. This is why structures combining several layers (multilayers) have been studied during the last decade to improve monolayer properties as they can combine different materials for producing a structure having improved properties. For instance, mechanical properties can be enhanced for reaching hardness values as high as 50 GPa [13]. Metal/ceramic multilayers (particularly chromium/chromium nitride ones) have aroused special attention as they have a number of advantages compared to their monolayer counterparts, such as greater hardness and resistance to wear and corrosion [14–18]. The period (the thickness where the multilayer composition is repeated) has also been shown to have an effect on multilayer properties [18]; this is usually attributed to the presence of a higher number of interfaces preventing the movement of dislocations as these produce plastic deformation in materials and the propagation of micro-cracks responsible for fractures in ceramics [19,20]. The re-nucleation process present in multilayer structures reduces the amount of pores, thereby resulting in better corrosion resistance [21–23].

A number of techniques have been used for producing Cr/CrN multilayers, such as cathodic arc [14,17,24–28], pulsed laser [18,29–31], DC magnetron sputtering [32–36], R.F. magnetron sputtering [16,37] and unbalanced magnetron sputtering [38–40]. The unbalanced magnetron (UBM) sputtering technique has gained importance amongst magnetron sputtering configurations for producing high quality coatings [11,41–44], due to its superior performance when

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compared to conventional balanced magnetron sputtering [12]. The outer ring of magnets in a UBM configuration is strengthened in relation to the central pole causing the field lines to not become confined to the target region but also directed towards the substrate, thereby resulting in a high flux of coating atoms [41], contrary to a conventional configuration. Some secondary electrons (and therefore ions) are able to follow these field lines and high ion currents can be extracted from the plasma without the need for externally biasing the substrate [41] although applying a substrate bias voltage also increases ion current and therefore modifies coating structure and properties [45,46]. The ion current increases ion bombardment on the substrate surface, thereby improving adatom mobility [11]. It also allows to increase the relationship from the ion's flux to the flux of condensing atoms, thereby changing the film's structure [47]. The ion to atom flux arrival ratio depends on the degree of magnetic field unbalancing (for a fixed substrate-target distance, pressure and power) [48].

Although the UBM technique has been widely used for producing different monolayer [49–53] and multilayer coatings [45,54–57], the influence of this degree of unbalancing on magnetron sputtered coating properties has been poorly studied. Olaya et al. [44,51,58] studied the influence of magnetic field configuration (balanced and unbalanced) and the degree of magnetron unbalancing on CrN, TiN, ZrN, TaN and NbN monolayer properties while Flores et al. [59] studied the magnetic field's effect on TiN/Ti multilayer plasma characteristics and corrosion properties by varying the degree of unbalancing through a concentric electromagnet coil around the magnetron. The present work has studied the effect of the degree of unbalancing and bilayer period on the hardness, wear and corrosion resistance of Cr/CrN nano-multilayer coatings produced by the UBM technique which, as far the authors know, has not been done before.

The degree of magnetron unbalancing was estimated by using the coefficient of geometrical unbalance K_G, according to [60]:

$$K_G = \frac{Z(B_{Z=0})}{2R} \quad (1)$$

where R was average erosion zone radius and $Z(B_{z=0})$ the distance from the target surface to the point on the axis of the magnetron where the magnetic field changed its direction, i.e. where the B_z component had zero value. A high K_G value implied a low level of magnetron unbalance and vice versa. Different K_G values were obtained by varying the relative vertical position between the central magnet assembly and the target; a map of the magnetic field flux was derived for the different magnet arrangements as a function of both radial and axial distances.

2. Experimental details

2.1. Deposition system

Cr/CrN nano-multilayers were deposited in non-commercial equipment by the UBM technique; this consisted of a stainless-steel cylindrical chamber (1 m in diameter, 80 cm length) provided with a pumping system which consisted of a rotary vane mechanical pump and a turbo molecular pump having nominal 10 m^3/h and 1800 m^3/h pumping velocity, respectively. The system had an unbalanced magnetron Gencoa sputter VT 100 which allowed varying the magnetic field through a variation in the number of turns (N_V) of a millimeter screw changing the distance between the magnet assembly and the target.

2.2. Magnetic field characterization

Three groups of multilayers (Λ = 200, 100 and 20 nm) were produced at three different magnetic field configurations (K_G = 0.87, 1.16 and 1.32) that were measured by portable Phywe teslameter with a Hall effect probe. Both magnetic field components (B_r and B_z) were measured as a function of Z (axial distance), r (radial distance) and N_V (number of turns). An increase in N_V corresponded to enlarging the distance between the central magnet and the target, thereby modifying the magnetic field configuration.

2.3. Multilayer deposition

Commercial AISI H13 tool steel (composition: 0.32–0.45 C, 0.8–1.20 Si, 0.20–0.50 Mn, 4.75–5.5 Cr, 0.8–1.20 V, 1.10–1.75 Mo, Fe balance (wt.%)) and silicon (100) were used as substrates. The steel samples were polished using 100 to 1200 sandpaper, pretreated by quenching (1000 °C–1025 °C) and tempering (175 °C–15 °C) and mirror polished. The substrates were ultrasonically cleaned in acetone and alcohol in sequence and dried in flowing compressed air before being placed in the deposition chamber.

The Cr/CrN multilayers were produced with 200 nm, 100 nm and 20 nm bilayer periods and deposition time was adjusted to set total thickness at about 1 μm for all cases. A floating substrate was used which had no external bias. The chromium layers were grown in an Ar atmosphere (99.99 purity) while N_2 (99.99 purity) mixed with argon for CrN layers was blown at intervals corresponding to planned nitride layer. Ar and N_2 flow rates were set at 9 standard cubic centimeters per minute (sccm) and 3 sccm, respectively, and regulated with MKS mass flow controllers. The target was a 4 in. diameter and 0.125 in. thickness chromium disk (99.95% purity) which was sputtered using a MDX 1K DC power supply (Advanced Energy) working in 400 mA current regulation mode. A shutter was located between the target and the sample surface in each interval to stabilize deposition pressure before growing the corresponding layer. Base pressure was less than 1×10^{-3} Pa. All multilayers were grown at room temperature and the sample–target distance was set to 5 cm. Table 1 summarizes the experiments' deposition conditions.

2.4. Multilayer characterizations

Multilayer crystallographic phases and preferential orientations were identified by X-ray diffraction (XRD) using an X-PertPro Panalytical system (6° grazing incidence, 90°/s spinning velocity and monochromatized CuKα radiation). The cross-sectional morphology of the multilayers grown on Si (100) was studied using a FEI-KUANTA 200 scanning electron microscope (SEM) operating at 30 kV.

Deposited sample hardness was measured by depth-sensing CSM nano-hardness tester with a Berkovich diamond tip. The loads were chosen so that the indenters' penetration depth did not exceed 10% of film thickness; in such case, loads between 3 and 4 mN fulfilled that condition and the penetration depths were 80 to 90 nm. Hardness was calculated by using the Oliver and Pharr model [61] and all results were reported as being the mean value of ten measurements having less than 10% standard deviation.

Table 1
Deposition conditions: period (Λ), unbalance coefficient (K_G), working pressure (P_w), discharge power (P), discharge current (I)

Sample	Λ (nm)	K_G	P_w ($\times10^{-3}$ mbar)	P (W)	I (mA)
Cr/CrN-1	200	1.32	2.6/4.7	140/137	400
Cr/CrN-2	100	1.32	2.4/4.8	140/137	400
Cr/CrN-3	20	1.32	2.3/5.1	141/137	400
Cr/CrN-4	200	1.16	2.4/4.8	150/147	400
Cr/CrN-5	100	1.16	2.4/4.8	151/148	400
Cr/CrN-6	20	1.16	2.3/4.9	152/147	400
Cr/CrN-7	200	0.87	2.4/4.4	187/182	400
Cr/CrN-8	100	0.87	2.4/4.6	183/179	400
Cr/CrN-9	20	0.87	2.3/4.9	183/179	400