

**CHARACTERIZATION OF CR/CRN NANO MULTILAYERS
OBTAINED THROUGH REACTIVE SPUTTERING WITH
DIFFERENT DEGREES OF UNBALANCE IN THE MAGNETRON**
**CARACTERIZACIÓN DE NANOMULTICAPAS DE Cr/CrN
OBTENIDAS POR SPUTTERING REACTIVO CON DIFERENTES
GRADOS DE DESBALANCE EN EL MAGNETRÓN**

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ABSTRACT

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Nanoscale hard coatings of bilayers of Cr/CrN were obtained and characterized through unbalanced magnetron sputtering (UBMS) in an atmosphere of Ar and Ar + N₂ on silicon and hardened and tempered H13 steel, with a degree of unbalanced K_G between 0.87 and 1.37. The deposition parameters were as follows: a power of 160 watts, Ar and N₂ flow rates of 9 and 3 sccm, and a substrate target distance of 5 cm. A Gencoa VT 100 magnetron with varying degrees of unbalance, obtained by displacing its central magnet, was used. The electrochemical behavior of these coatings was characterized using the technique of potentiodynamic anodic polarization. The coatings' microstructure and hardness were analyzed via X-ray diffraction (XRD) and nanoindentation tests; Cr, CrN and Cr₂N phases were obtained, with a hardness that increases with the degree of unbalance between 18.90 and 24.97 GPa.

Key words: Hard coatings; Cr/CrN, Sputtering; Unbalanced magnetron.

RESUMEN

Se obtuvieron y caracterizaron recubrimientos duros a escala nanométrica, de bicapas de Cr/CrN, mediante sputtering con magnetrón desbalanceado (UBMS) en atmósferas de Ar y Ar + N₂ sobre silicio y sobre acero H13 endurecido y templado, con grados de desbalance KG entre 0.87 y 1.37. Los parámetros de la deposición fueron los siguientes: una potencia de 160 vatios, flujos de Ar y N₂ de 9 y 3 sccm y una distancia blanco-sustrato de 5 cm. Se utilizó un magnetrón Gencoa VT 100 con diversos grados de desbalance, obtenidos por el desplazamiento de su imán central. El comportamiento electroquímico de estos recubrimientos se caracterizó

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mediante la técnica de polarización anódica potenciodinámica. La microestructura y dureza de las multicapas fueron analizadas mediante difracción de rayos X (DRX) y análisis de nanoindentación; se obtuvieron fases de Cr, CrN y Cr₂N, con durezas entre 18.90 y 24.97 GPa que aumentaron con el grado de desbalance.

Palabras clave: Recubrimientos duros; Cr/CrN, Sputtering; Magnetron desbalanceado.

1. Introduction

Chromium, hard chromium, and chromium nitride are well known as coatings for protection of metallic materials [1, 2]. Titanium nitride (TiN) has been extensively researched and positioned as a prototype for hard coatings. TiN is now still being widely used in protective coatings for bearings, gears, and cutting and forming tools. However, the fracture toughness and the oxidation resistance of TiN coatings are not satisfactory for many advanced engineering applications, and it has been replaced in many advanced applications by Cr_xN. Although the hardness of CrN is slightly lower than that of TiN, its performance is superior in other ways: it has a lower friction coefficient, increased wear resistance, and a toughness that prevents crack initiation and propagation; CrN has a higher resistance to oxidation, erosion and corrosion [3, 4, 5, 6], is more stable at high temperatures, grows with lower residual stresses, and can achieve growth rates up to 3 times higher than TiN [7, 8]. New hard coatings have been obtained by the addition of further elements to produce ternary or quaternary systems [9] or nanoscale multilayers that increase the hardness and toughness as the period is reduced. Coatings with alternating configurations of pure metal and metal nitride exhibit superior mechanical and tribological properties [10,11,12].

The efficiency of the physical vapor deposition (PVD) process and the deposits' characteristics have been improved by applying magnetic fields in order to concentrate the plasma around the target, increasing the ionization processes. Unbalanced magnetron sputtering (UBMS) is one of the most effective systems for depositing high-quality coatings, as a consequence of the higher ion current densities and enhanced ion bombardment available during the deposition process. This bombardment causes a small warming in the substrate and provides the energy that facilitates the diffusion processes of adsorbed atoms, forming layers with a lower density of defects, especially vacancies, and lower residual stresses. Many of the articles on UBM provide little information on the relative intensities of the two magnetic poles or on their geometric arrangement; a systematic study of these aspects and their correlation with the coating's properties is therefore relevant. In the present paper, Cr/CrN nano-multilayers were obtained with five values of KG [13], combining the advantages of the wear resistance of nitride and the corrosion re-

sistance of Cr-based coatings, in order to study the influence of these coatings on performance.

2. Experimental Procedure

Cr/CrN nano-multilayers were deposited with non-commercial equipment using the UBM technique, which consists of a stainless-steel cylindrical chamber provided with a pumping system (a rotary vane mechanical pump and a turbo molecular pump); the system had a Gencoa sputter VT 100 unbalanced cylindrical magnetron, which allowed varying the magnetic field through a variation of the distance between the internal magnet and the target. A Cr disk with a 4" diameter that was 1/8" thick and had 99.95% purity was used as a target, and was located 50 mm from the substrates, which was sputtered using an MDX 1K DC power supply (Advanced Energy), working at 160 watts power regulation mode. A shutter was located between the target and the sample surface at each interval in order to stabilize the deposition pressure before growing the corresponding layer; base pressure was less than 1×10^{-3} Pa and all multilayers were grown at room temperature. Table 1 summarizes the experiments' deposition conditions. Multilayers were deposited onto H13 steel and Si(100) substrates; metallic substrates were machined into disks with a 15 mm diameter and a 2 mm thickness and were polished to a mirror finish with alumina paste; previously, they had been subjected to quenching and tempering processes in order to increase their surface hardness. Before introducing the substrates into the deposition chamber, all substrates were cleaned in an ultrasonic bath of ethanol and then in acetone. Twenty-five Cr/CrN bilayers were deposited with a thickness of approximately 40 nm each on a Cr layer of approximately 100 nm. The electrochemical behavior was evaluated with the potentiodynamic anodic polarization test, carried out on a three-electrode cell in which the samples were connected to a working electrode; an Ag/AgCl reference electrode and a platinum counter electrode were used. The exposed area was 0.196 cm². After 1 h of sample immersion in a 3% NaCl solution, scans were conducted in the -250 to 1000 mV range using a 3 mV/s scan rate, with a PCI/300 Gamry potentiostat. Coating surface hardness (H) and Young's modulus (E) were measured using a CSM nanohardness tester, related to ISO 14577 (CSM Instruments SA Switzerland). In this experiment, a 5 mN maximum load was selected, and the linear loading/unloading rates were kept at 10

mN/min. Young's modulus (E) was obtained from the slope of the unloading part of the load-displacement curve using

the Oliver and Pharr method [14]. The hardness and Young's modulus measurements were calibrated using a fused silica standard sample.

Table 1. Coating process variables and the results of the nanohardness H and the elastic modulus E , where I is the discharge current and P is the work pressure.

Sample	K_G	Monolayers	I (mA)	P (Pa)	H (GPa)	E (GPa)
1	1.37	CrN [Cr]	467 [447]	0.67 [0.53]	18.905±2.337	289.9±32.4
2	1.25	CrN [Cr]	467 [448]	0.67 [0.525]	22.094±1.233	293.6±34.5
3	1.12	CrN [Cr]	442 [427]	0.68 [0.53]	23.141±2.055	311.9±20.3
4	1.00	CrN [Cr]	428 [416]	0.68 [0.52]	23.014±2.380	318.0±26.0
5	0.87	CrN [Cr]	403 [384]	0.68 [0.53]	24.966±1.448	270.4±20.0
H13	-	-	-	-	11.373±2.525	226.8±7.20

3. Results and discussion

As shown in Table 1, the discharge currents decreased with the increase in the degree of unbalance of the magnetic field; because the discharge power was kept constant, this implies that the potential difference between the target and the substrates increased with the degree of unbalance of the magnetic field. Table 1 also shows the values of nanohardness and elastic modulus, showing a steady increase in their values with the increase in the unbalance of the magnetron, i.e. when K_G decreases; this could indicate that the coatings were densified with the increase of this unbalance.

The X-ray diffraction spectra obtained in the Bragg-Brentano configuration, Figure 1, showed the presence of the following phases: Cr, CrN and Cr_2N (ICDD 01-085-1336, 01-079-2159, and 01-0076-2494 cards, respectively). With the X'Pert HighScore program, a semiquantitative analysis was performed, resulting in the percentage composition data shown in Figure 2. The largest percentage content corresponded to the cubic phase CrN, with a lattice parameter of 4.1440 Å; the Cr cubic phase, with a lattice parameter of 2.8849 Å, was the lowest percentage content phase, and the hexagonal Cr_2N phase with lattice parameters of 4.7520 and 4.4290 Å had an intermediate concentration percentage, without apparent correlation with the degree of unbalance obtained.

The results of the potentiodynamic polarization test are shown in Figure 3. It can be seen from this figure that all of the corrosion potential shifted to positive values with respect to the substrate potential, whose value was - 616 mV, and all currents decreased (for the substrate, $ICORR = 4.08 \mu A$). In the anodic region, the oscillations in the current are evidence of the film's breaking, and the trends show a passive

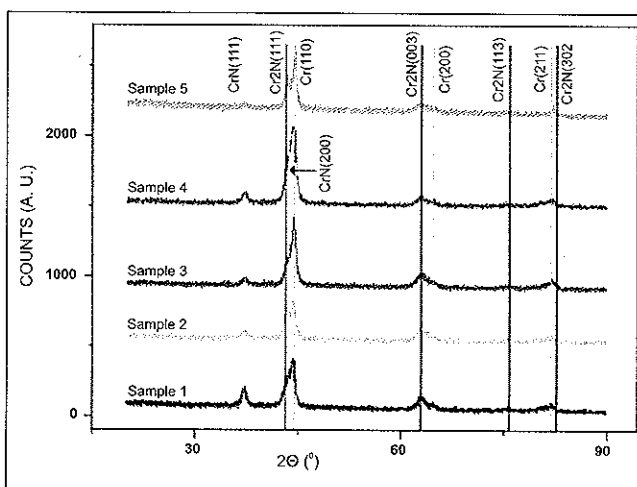


Figure 1. X-ray diffraction spectra for the Cr/ CrN coatings obtained with 5 degrees of unbalance and identifications of the phases present.

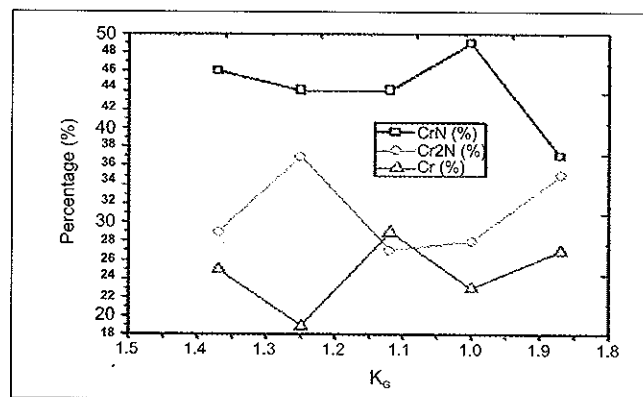


Figure 2. Percent content of the phases present in the Cr/CrN coatings obtained with different degrees of unbalance.

behavior that is especially notable for sample 5, which was obtained with the highest degree of unbalance.

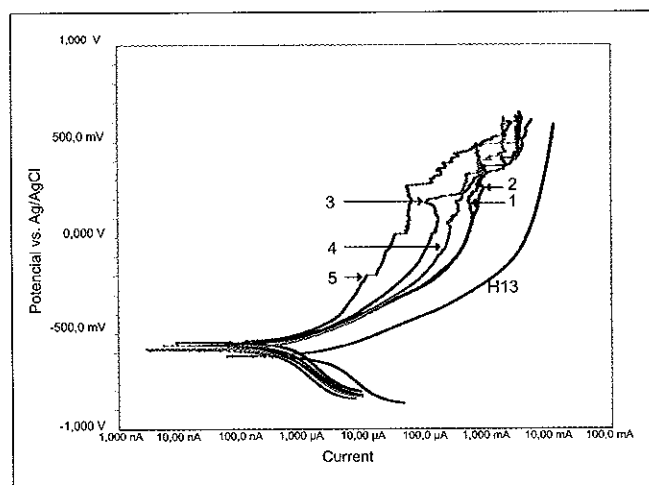


Figure 3. Potentiodynamic polarization test results of the substrate H13 and Cr/CrN coatings.

4. Conclusions

Cr/CrN coatings deposited on H13 steel with quenching and tempering treatments improved the mechanical properties of hardness and corrosion resistance. These improved properties were primarily obtained for coatings with the highest degree of unbalance in the magnetic field, but a monotonous increase was observed between the performance properties of these coatings and the degree of unbalance of the magnetic field, which could be due to an increase in the discharge voltage and therefore the energy of ions impinging on the growing film (i.e., the intensity).

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