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Novel performance in physical and corrosion resistance HfN/VN coating system

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ABSTRACT

4140 steel substrates were coated with hafnium nitride/vanadium nitride multilayered with the objective of improving their corrosion resistance. The multilayered coatings were grown via a reactive r.f. magnetron sputtering technique by systematically varying the bilayer period (Λ) and the bilayer number (n) while maintaining constant the total coating thickness (~1.2 μm). The coatings were characterized by X-ray diffraction (XRD), electron and transmission microscopy. The electrochemical properties were studied by Electrochemical Impedance Spectroscopy and Tafel curves. XRD results showed preferential growth in the face-centered cubic (111) crystal structure for $[HfN/VN]_n$ multilayered coatings. The best enhancement of the mechanical behavior was obtained when the bilayer period (Λ) 15 nm (n = 80) which yielded the highest hardness (37 GPa) and elastic modulus (351 GPa). The values for the hardness and elastic modulus are: 1.48 and 1.32 times greater than the coating with n = 1, respectively. The maximum corrosion resistance was obtained for coatings with (Λ) equal to 15 nm, corresponding to bilayer n = 80. Polarization resistance and corrosion rate was around 112.19 kΩ cm^2 and $0.094*10^{-3}$ mmy respectively, these values were 172.6 and 0.007 times better than those shown by the uncoated 4140 steel substrate (0.65 kΩ cm^2 and 0.014 mmy, respectively).

1. Introduction

The nitride materials used under physical methods on cutting or that have shown corrosive or mechanical applications exhibit favorable results. Among the different methods reactive magnetron sputtering has proven quite successful [1]. Considering this, at present it is possible to find a broad variety of hard coatings tested and used in industries, along with several substrate materials [2]. Previous studies have reported that the concept of multilayers offers a potent solution for chemical properties in hard coatings. Coatings deposited via physical vapor deposition (PVD) based on nitrides (HfN [3], VN [4] and TiCN [5]), provide high wear resistance, stability under high-service temperatures, corrosion resistance, and low thermal conductivity; recently, interstitial nitrides like vanadium nitride (VN) and hafnium nitride (HfN) are being studied because of their interesting properties such as high hardness, elastic modulus, low friction coefficient, as well as wear and corrosion resistance, [6–9]. In recent years multilayer systems based on nitride coatings such as TiN/ZrN [10], TiN/VN, Hf/HfN and W/WN [11,12] have been deposited as multilayer systems. These systems have shown good results specifically related to improved mechanical properties and oxidation resistance, as compared to the single layer, e.g., CrAlN and TiAlN coatings [13,14]. Enhancement of these properties is attributed to different mechanisms of layer formation with nanometric thickness such as the Hall–Petch effect and interface numbers acting as obstacles for the inward and outward diffusion of atomic species between layers for oxidation resistance or dissipation of crack energy in the case of toughness [15]. However, there are still very few studies in literature reporting on the electrochemical responses in nanostructured systems based on isostructural assembly of nitride coatings generated by metal transition. Considering this for the current research, Si (100) and AISI 4140 steel substrates were coated with a set of HfN/VN multilayers with a bilayer period (Λ) between 1200 and 15 nm (n = 1–80), for 1.2-μm total thickness. Therefore, the principal objective of this work is to evaluate the mechanical and corrosion resistance evolution of nanostructured multilayered HfN/VN coatings with the influence of HfN/VN deposited onto silicon (100) and industrial AISI 4140 steel substrates with different bilayer periods, Λ, and bilayer numbers, n, on their physical nature compared with uncoated industrial steel. The results are shown in this paper for possible surface applications in processes with aggressive environments such as in metals used in the mechanical industry.

2. Experimental details

Hafnium nitride/vanadium nitride multilayered system was grown on Si (100) and AISI 4140 steel substrates by using a multi-target magnetron sputtering system, with an r.f. source (13.56 MHz). The plasma cleaning procedure was used for all substrates under argon atmospheres. Two metallic targets hafnium (Hf) and vanadium (V) with

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99.9% purity were used as source materials. The deposition parameters to obtain VN and HfN films had a sputtering power of 400 W for V and 350 W for the Hf target; an unbalanced r.f. bias voltage was applied which generated a negative signal fixed at −30 V and a substrate temperature of 250 ºC under 60 rpm circular rotation substrate to facilitate the formation of the stoichiometric films. The sputtering gas was a mixture of Ar 80% and N_2 20% with a total working pressure of 0.12 Pa. The gases used were of ultra-high purity (99.999%). Film thickness was measured at approximately 1.2 ± 0.1 μm, determined by means of a (Dektak 3030) Profilometer. The crystal structure of the films was determined by using a Panalytical X'Pert PRO X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.5405$ Å). The bilayer period and multilayer assembly modulation was observed via scanning electron microscopy (SEM, 6490 LV JEOL). Microstructural analysis of films was mainly performed by TEM, using a Philips CM30 microscope operating at 300 kV.

In this work the HfN/VN multilayer on silicon (100) substrate was deposited at the same time that the HfN/VN multilayer is deposited on the steel substrate, but the HfN/VN multilayer on the silicon (100) substrate was used because this substrate facilitates the experimental characterization via XRD, XPS, SEM and TEM techniques.

The electrochemical study was performed by using a Gamry unit; model PCI 4, utilized for DC and AC measurements. Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization curves were obtained at room temperature (25 C) under static conditions (without aeration), using a cell with a working electrode of 1-cm^2 exposed area, Ag/AgCl (3.33 M KCl) reference electrode, and a platinum wire counter-electrode under a 3.5 wt.% NaCl solution with distilled water at pH 6.2. For Nyquist plots, frequency sweeps were conducted in the range of 100 kHz to 0.001 Hz using sinusoidal signal amplitude of 10 mV applied to the working electrode (sample) and the reference electrode. Diagrams for Tafel polarization curves were obtained at a sweep speed of 0.125 mV/s in a voltage range of −1000 to 1000 $mV_{Ag/AgCl}$; this voltage range was defined with respect to the open circuit potential (OCP). Prior to beginning the polarization curve procedures, the samples were submerged in the 3.5 wt.% NaCl aqueous solution for 30 min to establish the free corrosion potential values (E_{corr}) where polarization curve measurements were initiated. In this work, the surface corrosion process was carried out, analyzing surface morphology by using a 50×-objective optical Olympus PME-3 microscope and a Scanning Electron Microscope (SEM) (Phenom FEI) equipped with a light optical magnification range: 525–24× and a height sensitivity back-scattered electron detector (multi-mode).

3. Results and discussion

3.1. X-ray analyses of HfN/VN system

XRD diffraction of hafnium nitride/vanadium nitride deposited onto a Si (100) substrate with Λ between 1200 nm and 15 nm and n between 1 and 80 is shown in Fig. 1a. VN and HfN layers within the multilayered systems were polycrystalline, exhibiting diffraction peaks with a preferential orientation (111) corresponding to the HfN phase located at 34.01°; other peaks were observed at 68.06° and 71.67°, corresponding to the (311) and (222) planes, respectively. These were attributed to the HfN structure. The diffraction peaks at 44.23° and 38.09°, corresponded to the (200) and (111) VN planes, respectively. Comparatively, in Fig. 1b the shift of diffraction patterns towards high angles is in relation to compressive residual stress characteristics for those multilayered systems (Table 1). These preferential orientations are in agreement with JCPDS 00-035-0768 (VN) and JCPDS 00-033-0592 (HfN) from ICDD cards. Moreover, it was observed that the HfN (111) peak position suffers slight deviation from the bulk value, indicating a possible stress relief of HfN/VN multilayers with a thinner bilayer period ($\Lambda = 15$ nm; $n = 80$).

3.2. XPS analysis for HfN and VN single layers

The XPS survey spectrums for HfN and VN single layers that make up the HfN/VN multilayer coatings are shown in Fig. 2. For HfN material in Fig. 2a the peaks at 523.2 eV, 397.6 eV, 224.8 eV and 18.4 eV correspond to O1s, N1s, Hf4d5, and Hf4f binding energies, respectively. The change of binding energy of the HfN verifies the formation of binary Hf(N) compounds, therefore, calculation of the peak area gives an atomic ratio of Hf:N = 1.1:0.9, which is similar to the stoichiometry of $Hf_{1.1}N_{0.9}$ [16]. Comparatively, Fig. 2b shows the peaks of VN material at 630.4 eV, 532.0 eV, 516.8 eV, and 397.6 eV corresponding to V2s, O1s, V2p3/2, and N1s binding energies, respectively. The change of binding energy of VN verifies the formation of binary V(N) compounds, therefore, calculation of the peak area gives an atomic ratio of V:N = 1.1:0.9, which is similar to the stoichiometry of $V_{1.2}N_{0.8}$ material [17].

According to the XPS literature on Hf-N and V-N materials [16,17] when peaks are fitted from experimental results it is necessary to first adjust the N energy band because it is the element that provides greater reliability for XPS, then take this initial adjustment as the base and the other peaks related to the remaining elements are

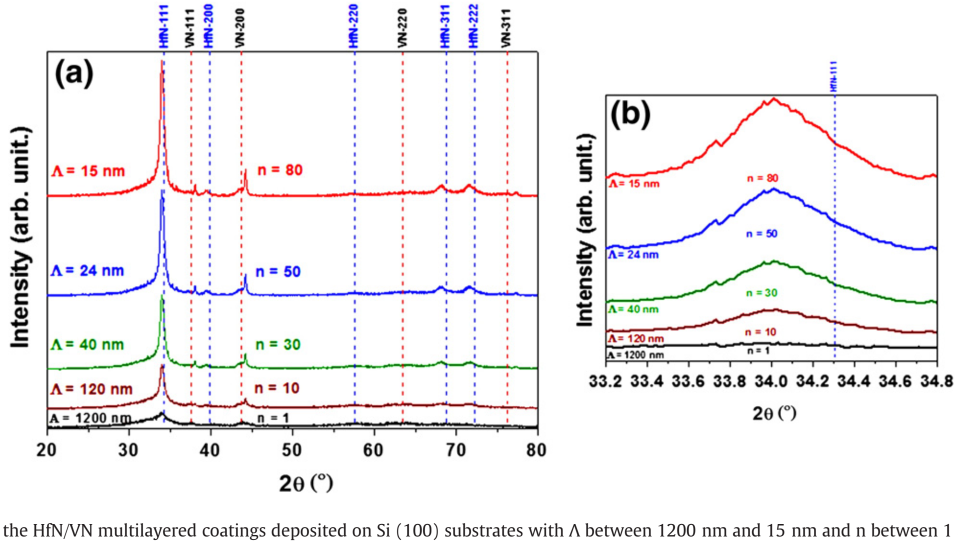

Fig. 1. The XRD patterns of the HfN/VN multilayered coatings deposited on Si (100) substrates with Λ between 1200 nm and 15 nm and n between 1 and 80: (a) dashed lines indicate the position of the peaks obtained from JCPDS 00-035-0768 (VN) and JCPDS 00-033-0592 (HfN) files from ICDD cards and (b) maximum peak with shift toward high angles in relation to increasing bilayer numbers (n).