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# Diagnostic of corrosion–erosion evolution for [Hf-Nitrides/V-Nitrides]*n* structures

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ABSTRACT

HfN/VN multilayered systems were grown on 4140 steel substrates with the aim to improve their electrochemical behavior. The multilayered coatings were grown via reactive r.f. magnetron sputtering technique by systematically varying the bilayer period ($\Lambda$) and the bilayer number ($n$) while maintaining constant the total coating thickness (~1.2 μm). The coatings were characterized by X-ray diffraction (XRD), and electron 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 maximum corrosion resistance was obtained for coatings with ($\Lambda$) 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; moreover, these multilayered system showed a decrease of 80% on mass loss due to the corrosive–erosive process, in relation to multilayered systems with $n = 1$ and $\Lambda = 1200$. HfN/VN multilayers have been designed and deposited on Si (100) and AISI 4140 steel substrates with bilayer periods ($\Lambda$) in a broad range, from nanometers to hundreds of nanometers to study the microstructural evolution and electrochemical progress with decreasing bilayer thickness.



## 1. Introduction

Thin films deposited by physical vapor deposition (PVD) methods on cutting or metal forming tools have been widely used since 1980 in tribological, corrosive, or mechanical applications showing favorable results. Among the different methods, reactive magnetron sputtering has proven quite successful [1]. In this regard, it is currently possible to find a broad variety of hard coatings tested and used in industry, 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 PVD based on nitrides (HfN [3], VN[4] and TiCN [5], provide high wear resistance, stability under high-service temperature, 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 like high hardness, elastic modulus, low friction coefficient, wear and corrosion resistance, [6–9]. In recent years, multilayer systems based on nitride coatings like 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 the 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 the literature reporting about the electrochemical responses in nanostructured systems based on isostructural assembly from nitride coatings generated by metals transition. The principal aim of this work is to evaluate the corrosion and corrosion–erosion resistance evolution of nanostructured HfN/VN multilayered coatings deposited onto silicon (100) and industrial AISI 4140 steel substrates; with different bilayer periods, $\Lambda$, and bilayer numbers, $n$, on their physical nature compared with uncoated industrial steel. Our results could be applied to modify and improve the surface properties of metals used in demanding contact conditions or aggressive environments such as the mechanical industry. For this purpose, Si (100) and AISI 4140 steel substrates were coated

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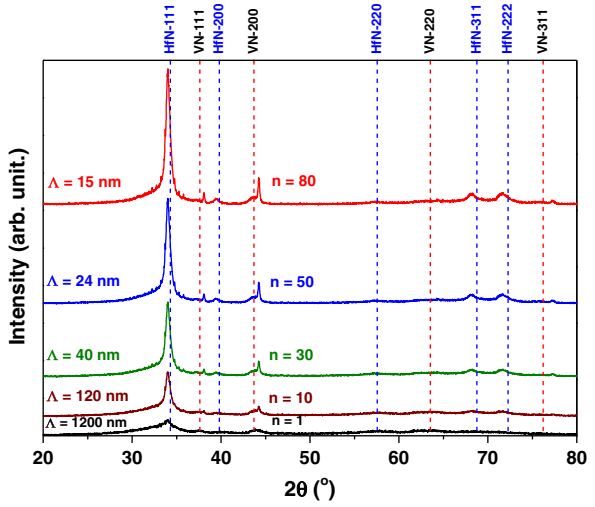


**Fig. 1.** The XRD patterns of the HfN/VN multilayered coatings deposited on Si *(100)* substrates with $\Lambda$ between 1200 nm and 15 nm and $n$ between 1 and 80. Dashed lines indicate the position of the peaks obtained from JCPDS 00-035-0768 (VN) and JCPDS 00-033-0592 (HfN) files from ICDD cards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

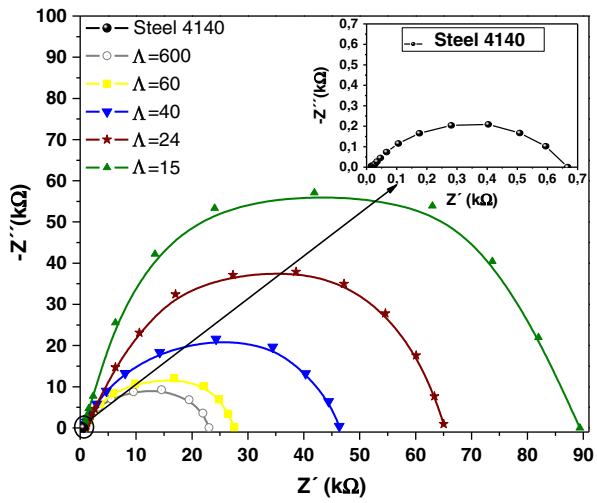


**Fig. 3.** Impedance diagrams of $[HfN/VN]_n$ multilayers grown at different bilayer periods ($\Lambda$) on AISI 4140 steel.

with a set of HfN/VN multilayered with bilayer period ($\Lambda$) between 1200 nm and 15 nm ($n$ = 1–80), for 1.2-μm total thickness.

## 2. Experimental details

[Hf-Nitrides/V-Nitrides]*n* multilayered structures were 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 atmosphere. Two metallic targets hafnium (Hf) and vanadium (V) with 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 generates a negative signal fixed at −30 V, and a substrate temperature of 250 °C 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 used gases are of ultra-high purity (99.999%). Film thickness was measured at about 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 (λ = 1.5405 Å). The bilayer period and multilayer assembly modulation were observed via scanning electron microscopy (SEM, 6490 LV JEOL). 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 from −1000 to 1000 $mV_{Ag/AgCl}$; this voltage range was defined with respect to the open circuit potential (OCP). Prior to beginning the polarization curves 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. The erosive–corrosive testing system consists of a tribometer with a glass container for erosive–corrosive storage,

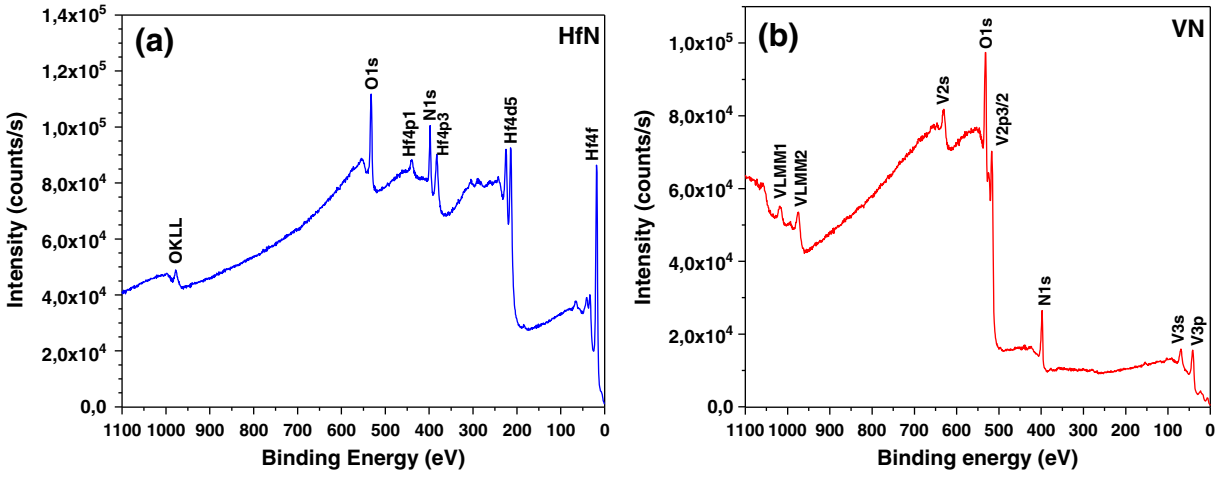


**Fig. 2.** XPS survey spectrums (a) HfN coatings and (b) VN coatings deposited on Si with an r.f. negative bias voltage of −30 V.