

Electrochemical and wear behavior of niobium-vanadium carbide coatings produced on AISI H13 tool steel through thermo-reactive deposition/diffusion

Comportamiento electroquímico y al desgaste de recubrimientos de carburo de niobio-vanadio producidos sobre acero para herramientas AISI H13 por medio de la deposición/difusión termorreactiva

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ABSTRACT

We deposited of niobium-vanadium carbide coatings on tool steel AISI H13 using the thermo-reactive substrates deposition/diffusion (TRD) technique. The carbides were obtained using salt baths composed of molten borax, ferroniobium, vanadium and aluminum, by heating this mixture at 1020° C for 4 hours. The coatings were characterized morphologically via electron microscopy scanning (SEM), the chemical surface composition was determined through X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX); the crystal structure was analyzed using x-ray diffraction (XRD), the mechanical properties of the coatings were evaluated using nano-indentation, The tribological properties of the coatings obtained were determined using a Pin-on-disk tribometer and the electrochemical behavior was studied through potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS). The results showed that the hardness of the coated steel increased four times with respect to uncoated steel, and the electrochemical test established that the corrosion current is lower by one order of magnitude for coated steel.

Keywords: Coatings, thermo reactive, niobium-vanadium carbide, spectroscopy, impedance.

RESUMEN

En este trabajo se depositaron recubrimientos de carburo de niobio-vanadio sobre aceros para herramientas AISI H13 utilizando la técnica de depósito por difusión termorreactiva (TRD). Los carburos se obtuvieron utilizando baños de sales compuestas de bórax fundido, ferroniobio, vanadio y aluminio, calentando la mezcla a 1020 °C durante 4 horas. Los recubrimientos fueron caracterizados morfológicamente mediante microscopia electrónica de barrido (SEM), la composición química de la superficie se determinó mediante espectroscopia de fotoelectrones de rayos X (XPS) y la espectroscopia de rayos X de energía dispersiva (EDX); la estructura cristalina se analizó utilizando difracción de rayos X (XRD), las propiedades mecánicas de los recubrimientos fueron evaluados utilizando nanoindentación. Las propiedades tribológicas de los recubrimientos obtenidos fueron determinadas usando un tribómetro Pin on Disk CETR-UMC-2 y el comportamiento electroquímico se estudió por medio de curvas de polarización potenciodinámica y espectroscopia de impedancia electroquímica (EIS). Los resultados mostraron que la dureza del acero revestido aumentó cuatro veces respecto del acero no recubierto, y la prueba electroquímica estableció que la corriente de corrosión es inferior en un orden de magnitud para el acero recubierto.

Palabras clave: Recubrimientos, termorreactiva, carburo de niobio-vanadio, espectroscopia, impedancia.

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INTRODUCTION

Surface treatments such as cementation and nitration have been used to produce coatings based on carbides or nitrides of transition metals to improve the tribological performance of materials meant to be subjected to high wear conditions, such as cutting tools and die formation. These coatings are commonly obtained using physical deposition processes in the vapor phase (PVD) and chemical deposition in the vapor phase (CVD) [1-2].

The main limiting factor for these procedures is the use of complex equipment and high vacuum conditions, which makes them very expensive to implement. An economical alternative has been the application of hard coatings with good wear resistance using the thermo-reactive diffusion deposition process (TRD) [3] on substrates containing a carbon percentage higher than 0.3% by weight [4]. The coatings that have been grown using this process exhibit good adhesion to the substrate, a low friction coefficient, and excellent thickness uniformity [5].

In the TRD coating process, a salt bath consisting of molten borax, aluminum as the reducing element, and carbide forming elements (CFE's) such as vanadium, chromium, titanium, and niobium can be used [4]. In studies published to date, binary metal carbides have deposited through TRD process and their wear resistance, microstructure, and mechanical behavior have been characterized. For example, several studies focused on the production of coatings of vanadium carbide and niobium carbide on steel AISI H13, AISI, AISI D2, and M2 substrates, which have been reported as producing up to 2300 HV hardness [3, 5].

Other investigations have studied the growth kinetics of niobium carbides on AISI 1040 [6], iron borides on AISI 4140 [7], and chromium carbides on AISI D2 steel [8]. These papers reported the growth kinetics of binary systems such as NbC or VC, in which the layer thickness is studied as a function of time and temperature of treatment. In the electrochemical field, there are studies of iron boride on AISI S1, S2, and S3, varying the manganese content [9].

However, to the authors' knowledge, a micro-structural and electrochemical study of the possible

ternary system (NbVC₂) has not been reported, as proposed in the present paper. The objective of this study is to produce niobium-vanadium carbide coatings on H13 steel using the thermo-reactive deposition technique.

MATERIALS AND METHODS

Niobium and vanadium carbide coatings were deposited on substrates of AISI H13 tool steel, using samples of 12 mm diameter and 4 mm thickness. This steel essentially contained 0.39 wt% C; 5.2 wt% Cr, 0.4 wt% Mn, 1.1 wt% Si, 1.4 wt% Mo, 0.95 wt% V, and the rest Fe. The coatings were produced using three compositions in the salt bath:

- 1) 81 wt.% Na₂B₄O₇, 13 wt.% Fe-Nb, 3 wt.% Fe-V and 3 wt.% Al.
- 2) 81 wt. % Na₂B₄O₇, 8 wt.% Fe-Nb, 8 wt.% Fe-V and 3 wt.% Al.
- 3) 81 wt.% Na₂B₄O₇, 3 wt.% Fe-Nb, 13 wt.% Fe-V and 3 wt. % Al TRD.

The surface treatment was conducted at a temperature of 1020° C for 4 hours, conducting a pre heating of the samples 600° C. The crystallographic phases of the coatings were determined through x-ray diffraction with X-PertPro Panalytical, working at θ -2 θ configuration in a range of 10° to 100°, operating at 45 kV, 40 mA, and using CuK alpha monochromatic radiation (1.594 Å) with a step of 0.02°. The chemical surface composition was determined using X-ray photoelectron spectroscopy (XPS), recorded with a SPECS spectrometer in the constant energy pass mode at 50 eV, using Mg K α radiation as the excitation source.

Sample cleaning was performed using ion bombardment with Ar⁺ of 3.5 keV for 5 min in a preparation chamber (base pressure 2×10^{-7} mbar) connected through a gate valve to the main chamber. The calibration of the binding energy (BE) scale was checked using the C 1s signal (284.1 eV). X-ray spectroscopy (EDS) was done at a voltage of 20 kV and collection time of 120 s in a FEI Quanta 200 scanning electron microscope.

The thickness of the coatings was determined using a Philips brand scanning electron microscope working at a potential difference of 40 kV after being attacked with Vilella 3%. 10 measurements were

performed in order to obtain an average thickness value. The hardness of the coatings was evaluated using a CSM instruments nano-indentation with a Berkovich indenter with an approach speed to sample of 2000 nm / min, a rate of application of load of 10 mN/min, and a load up to 30 mN pausing for 15 s in the load.

The tribological properties of the coatings obtained were determined using a Pin-on-disk tribometer CETR-UMC-2 using steel balls 6 mm diameter coated with a layer of Al_2O_3 . The test was performed at a temperature of 20 °C applying a load of 4 N and a speed of 50mm / s during 10 min.

The electrochemical properties of the coatings were studied using potentiodynamic polarization curves and electrochemical impedance curves (EIS). The tests were performed on a Gamry brand potentiostat 600 instrument using an electrochemical cell with a volume of 100 mL of a solution of 3% NaCl at room temperature. The work area was 0.196 cm², using a bar of platinum and a calomel electrode as the auxiliary and reference electrode, respectively. Polarization assays were performed with a scan rate of 0.5 mV/s applying bias voltages from -0.3 to 0.4 V with respect to the resting potential. EIS tests were performed by varying the frequency from 100 kHz to 0.01 MHz, applying a voltage of 10 mV.

RESULTS AND DISCUSSION

Microstructure of the carbide layers

Figure 1 shows the cross-section SEM micrograph of the ternary carbide coating obtained for Nb-V treated steel AISI H13 in the second salt bath. It can be seen that the coatings have a uniform thickness with a value of 8.8 ± 0.5 microns.

The thickness of the carbides produced with different salt bath is shown in the Table 1.

Table 1. Thickness of the carbide produce on AISI H13 Steel.

Bath	Composition	Thickness(μm)	Error
1	13 Nb-13 V	8.7	0.3
2	8 Nb-8V	8.8	0.5
3	3 Nb-3 V	8.5	0.4

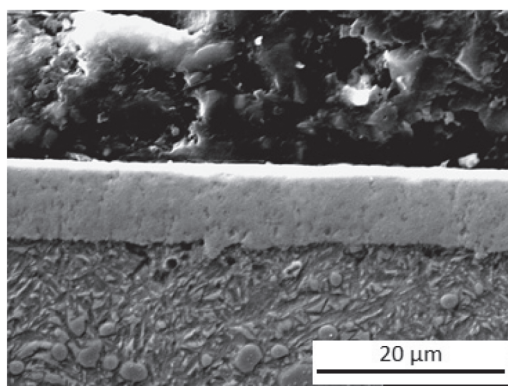


Figure 1. Cross section SEM micrograph of NbVC₂ coating produced using the TRD technique on AISI H13 tool steel in the second salt bath.

Figure 2a shows X-ray diffraction patterns of V_8C_7 and NbC coatings obtained and studied in a previous paper [10], together with X-ray patterns obtained for ternary carbides niobium-vanadium in the three salt baths used in the present study.

The XRD patterns exhibit planes associated with cubic phases of NbC (PDF 3813642) and V_8C_7 (PDF 350786). Carrying out the deconvolution of the planes (220) and (311) of the NbC phase, it was identified as the cubic phase of niobium carbide vanadium (NbVC₂) [11]. By comparing the diffraction patterns of the carbides obtained in this investigation with binary carbides previously deposited, we can observe a shift and broadening of the diffraction peaks of the NbVC₂ ternary carbide.

The simulated X-ray diffraction patterns using Powdercell 2.4 software were constructed with the purpose of obtaining the theoretical position of each of the diffraction peaks of this ternary carbide. The simulation was done taking into account the number of group and Wyckoff parameters of this compound [11]. The results obtained for the lattice parameters established that in ternary material the plane is shifted to the right when the amount of niobium in the salt bath decreases.

For all cases, upon performing deconvolution as is detailed in Figure 2b for the sample with 8%Nb and 8% V, there are two peaks, one corresponding to the niobium carbide and the other to ternary carbide (NbVC₂). In the XRD, vanadium carbide

does not appear. This can be explained since the free energy of the formation of NbC (-33.6 kcal) [12] is less than the free energy of the formation of carbide vanadium (-24 KJ/mol) [12].

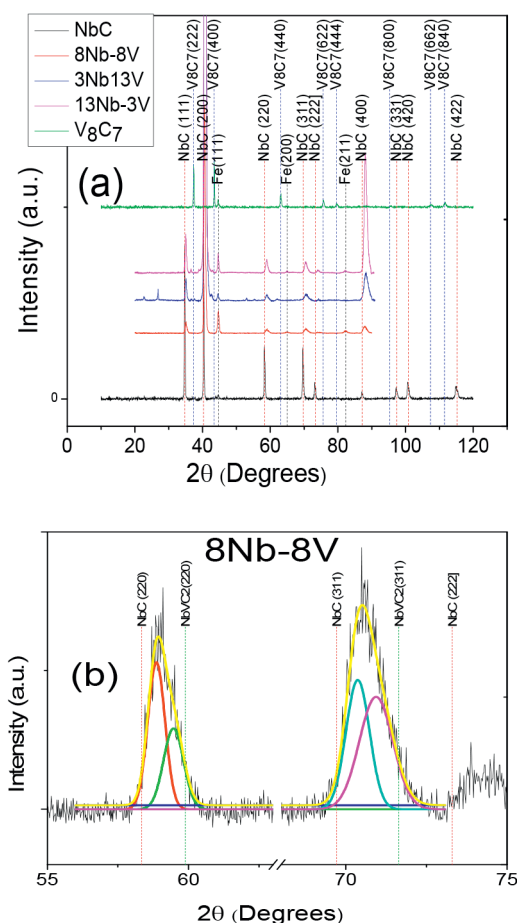


Figure 2. X-Ray diffraction patterns of vanadium niobium carbides deposited on steel AISI H13. a) Full spectrum b) sample with 8%Nb and 8%V.

The studies of the surface chemical composition of the coatings are presented in Figure 3a that show the XPS overview spectra, for carbide coating (NbC₂) obtained on AISI H13. The spectrum shows the binding energies associated with niobium, vanadium, iron and carbon. The Fe signal is probably due to the chemical composition of the bath salts with which the coatings were prepared.

Figures 3b to 3d show of high-resolution spectra obtained from the C 1s, V 2p, O 1s and Nb 3d

spectra recorded from the coatings. The C 1s spectra has three contributions; the first is centered at 284.7 eV, and corresponds to aliphatic carbon [13-14], the second contribution centered at 283.7 eV is the energy corresponding to C-V bond [15] and the third is centered at 282.6 eV, and corresponds to Nb-C bond [16]. V 2p spectrum has peaks centered at 513.1 eV that correspond to the V-C bond; a second peak is centered at 516.1 eV which belongs to vanadium pentoxide (VO₅) [13-14].

The O 1s spectrum shows three contributions; The first one, located at 529.8 eV, corresponds to niobium pentoxide, the second one at 532.3 eV, is the binding energy of oxygen in (OH) groups, and the third at 531.4 eV, corresponds to niobium oxide. Finally, the Nb 3d spectra has two peaks centered at 203.4 eV and 207.1 eV, that belong to Nb-C bonds and niobium pentoxide (Nb₂O₅), respectively [17-18].

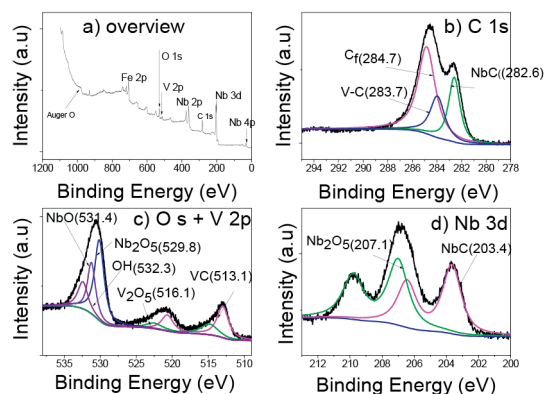


Figure 3. XPS spectra for the carbides of NbVC₂ produced on AISI H13 steel. a- overview spectra, b- S 1s spectra, c- O 1s and V 2p spectra and d- Nb 3d spectra.

Electrochemical performance

To determine the corrosion rate of the materials, potentiodynamic polarization curves were calculated. Figure 4 shows the curves obtained for coated and uncoated AISI H13. Table 2 summarizes the most important parameters obtained from this measurement. It can be seen that coated steels have an increased resistance to corrosion clearly manifested in the decrease of the corrosion current and the increase of the corrosion potential with respect to the uncoated AISI H13 steel.

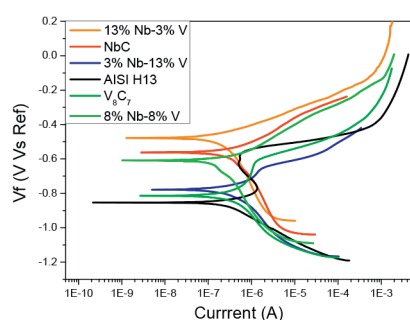


Figure 4. Potentiodynamic polarization curves for H13 steel uncoated and coated with Nb-V carbides TRD, produced using different combinations of Nb and V in the salt bath.

Table 2. Parameters obtained from potentiodynamic polarization curves. (I_{cor} corrosion current, corrosion potential E_{cor} and anodic Tafel slope β_a).

System	I_{cor} (A)	Stand. deviation	E_{cor} (mV)	β_a
13Nb-3V	5.74×10^{-7}	2.68×10^{-8}	-479.4	0.32
8 Nb-8 V	4.71×10^{-7}	1.73×10^{-8}	-612.7	0.39
3Nb-13 V	5.65×10^{-7}	2.22×10^{-8}	-778.9	0.17
NbC	3.07×10^{-7}	2.59×10^{-8}	-554.5	0.29
V8C7	6.66×10^{-7}	9.50×10^{-8}	-815.7	0.23
AISI H13	1.19×10^{-7}	1.07×10^{-7}	-807	0.39

EIS spectra obtained for exposure times in a solution of 3% NaCl for one hour and 1, 2, and 7 days, for the coated steel with NbC, V_8C_7 and mixed systems with NbVC₂ are shown in Figure 5.

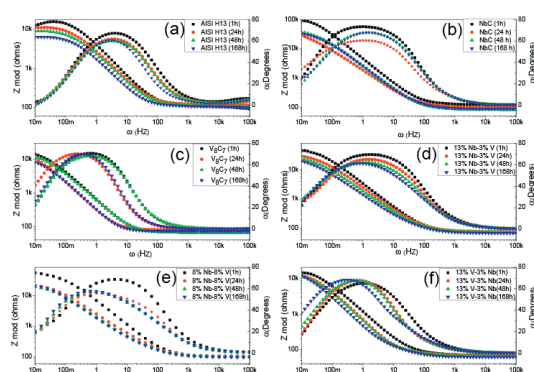


Figure 5. Bode plots of EIS spectra. For a) AISI H13(uncoated) b) NbC carbide c) V_8C_7 carbide d, e and f) Carbides of Nb and V.

Bode analysis confirmed a better electrochemical behavior in the samples with coating, which is reflected in a higher value of the impedance module. At a frequency of 0.01 Hz, impedance values are observed between 5000 and 8000 Ω for the substrate, while for the coatings, impedance values were 10 times higher for the NbC and between 3 and 5 times higher for the ternary systems at the same frequency.

Additionally we can see two distinct relaxation times at 100 mHz and approximately at 50 Hz for the coatings, which is more evident in the coating immersed for 7 days. It also can be observed that the impedance decreases with increasing exposure time, indicating the porous character of the coating. In this case, the electrolyte has penetrated through the pores of the coating [19].

Moreover, in the Bode diagram it can be seen that the carbides showed a decrease in the value of the impedance from 100 to 20 k Ω at 0.01 Hz, as a function of the time of immersion in the electrolyte. This probably occurs because increasing the immersion time increases the area of the pores, and thus there is greater penetration into the corrosive solution, which produces steel pitting corrosion; however, these results indicated that the time required for the electrolyte to penetrate the finer defects such as micro-cracks is of the order of 24 h [9, 20-21].

NbC niobium carbides (Figure 5b) exhibit the best electrochemical performance, in part because they constitute the system that has a lower degree of porosity, and also because the metal oxide Nb_2O_5 has excellent chemical stability and corrosion resistance in acidic and basic media [22].

Meanwhile, vanadium carbides V_8C_7 (Figure 5c) showed the poorest performance, reflected in impedance values of 0.01 Hz, and slightly higher than those obtained for the substrate. This could be explained by the poor structural stability of the vanadium oxide V_2O_5 [23], which make it more porous than niobium oxide and therefore more susceptible to degradation by a corrosive medium. The ternary carbides (Figure 5d, 5e and 5f) show polarization resistance of 80 k Ω , and the ternary with the highest amount of Fe-V in the salt bath exhibited the worst performance. Table 3 summarizes the values of the impedance obtained in the different test times.

Table 3. Electrochemical impedance parameters for the coated H13 steel.

System	Exposure time	Rsol (Ω)	Rcor (Ω)	Rpor (Ω)	(CPE) Ccor	n	(CPE) Cc	m	Goodness of the fit
NbC	1h	122.6	137600	118300	1.58E-06	0.65	4.53E-05	0.85	0.00053
	1d	97.29	13660	37790	4.70E-06	0.78	1.43E-06	0.73	0.000227
	2d	83.1	24260	19310	5.40E-10	0.57	8.93E-05	0.8	0.000182
	7d	86.48	19030	20310	8.02E-10	0.78	9.03E-05	0.8	0.000503
V_8C_7	1h	66.76	8136	8120	6.55E-09	0.2	3.21E-04	0.87	0.000111
	1d	79.4	8938	6937	9.49E-09	0.19	7.03E-04	0.87	0.000184
	2d	64.59	5703	8448	1.01E-08	0.25	3.64E-04	0.84	0.000091
	7d	71.69	3964	5524	1.43E-08	0.24	6.54E-04	0.89	0.000235
13 Nb - 3 V	1h	73.74	31460	26760	5.61E-07	1	6.65E-05	0.81	0.000811
	1d	76.87	15230	21870	6.64E-10	0.28	9.93E-05	0.76	0.000724
	2d	74.3	19990	14270	9.85E-10	0.31	1.40E-04	0.73	0.000372
	7d	68.1	13120	16370	1.44E-09	0.35	1.86E-04	0.72	0.000755
8 Nb - 8 V	1h	103.2	22410	38060	1.68E-09	0.34	3.29E-05	0.8	0.002006
	1d	104.9	16490	13050	1.20E-08	0.74	1.07E-04	0.68	0.000599
	2d	103.1	14840	13280	1.58E-08	0.79	1.39E-04	0.68	0.002391
	7d	99.04	16410	15360	2.18E-08	0.81	1.41E-04	0.69	0.002163
3 Nb - 13 V	1h	70.58	12180	6440	1.07E-07	0.33	1.97E-04	0.79	0.000338
	1d	71.13	9538	4354	1.38E-07	0.36	3.08E-04	0.83	0.001086
	2d	69.2	9751	5104	2.21E-07	0.39	3.51E-04	0.81	0.001875
	7d	63.63	16470	7648	2.91E-07	0.41	4.86E-04	0.78	0.005155

Hardness and wear properties

Niobium carbide recorded a hardness of 24.42 GPa, vanadium carbide (V_8C_7) 25.76 GPa, and ternary carbide obtained with 8% of Fe-Nb and 8%Fe-V has a hardness of 35.42 GPa. This increase in hardness for the ternary system is likely due to micro-strains in the coating that can be verified by the increase in the FWHM of the XRD peaks and macro-deformation evidenced by the shift of the peaks with regard to their position in a powder sample. All these factors help to decrease the crystallite size, according to Hall and Petch [24-25], which will result in an increase in the dislocation density that is reflected in the increased hardness.

Figure 6 allows us to observe the friction coefficient curve for carbides systems, deposited on steel AISI H13. It can be seen that the coefficient of friction (COF) of the carbides achieved is between 0.3 and 0.4, while that in the substrate is above 0.6; this value agrees with results obtained in other studies [26-28].

These results can be explained from of XPS analysis where we found a shoulder in 1s C in all coatings.

This shoulder is associated to graphite which has bonds type Van der Waals between the layers that reduce the resistance to slipping between them. This facility of the moving between layers is related with the decreased of the friction coefficient.

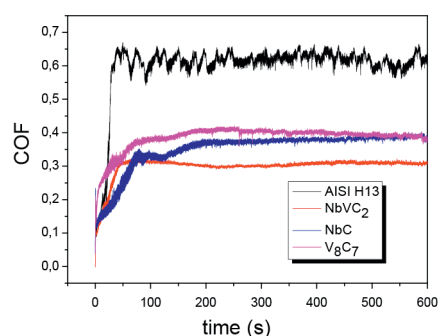


Figure 6. Friction coefficient measurement of the carbides produced on AISI H13 steel.

Figure 7 show SEM micrographs, EDX analyzes and confocal images of the coatings of NbC and V_8C_7 and NbVC₂ respectively. In the micrographs one can observe the plastic deformation of the coating; Figure 7b, 7e and 7h confirm the presence

of C, Nb and V, in the coatings. The presence of Fe is from the substrate, and the Al probably from the salt bath. Confocal microscopy (Figures 7c, 7f and 7i) allowed determining the average roughness of these coatings in $R_a = 0.724$.

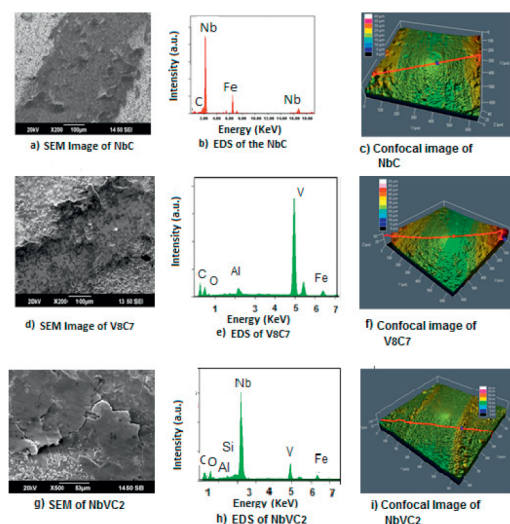


Figure 7. SEM micrographs, EDX analyzes and confocal images of the coatings of carbides produce on AISI H13 steel.

Figure 8 shows two images made by confocal laser microscopy for niobium carbide (a) and a vanadium carbide (b), deposited on steel AISI H13. Some fissures and parallel channels characteristic of abrasive wear are observed, this morphology is known as gouging or abrasion wear of two body [29]. These slots arise due to the cutting action of abrasive micro particles which are essentially embedded in the ball during the wear test.

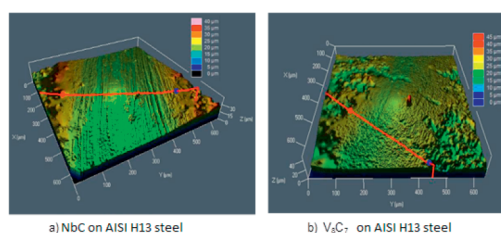


Figure 8. Confocal images for the coatings produce on AISI H13 steel a) NbC and b) V_8C_7 .

Figure 9a shows the friction coefficient curve for three different compositions of $NbVC_2$ ternary system, deposited on steel. The coefficient of friction for the three coatings ranges between 0.3 and 0.35,

lower value than obtained for the uncoated substrate. These friction coefficient values are equal to those in the binary coatings, suggesting that the carbon content and porosity of the surface of the binary and ternary coatings have close values. The SEM image (Figure 9b) reveals that the morphology of the coatings is produced by abrasion to two bodies.

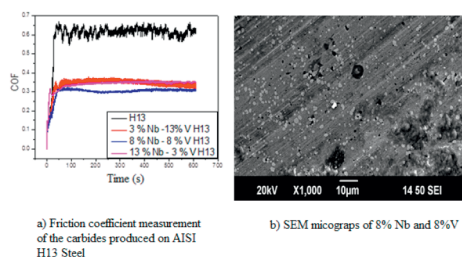


Figure 9. a- Friction coefficient measurement of the carbides produce on AISI H13 steel and b- detail of the wear mechanism.

CONCLUSIONS

Niobium-vanadium carbide $NbVC_2$ coatings were obtained using the TRD technique with a high degree of uniformity in thickness and with a hardness value of 36 Gpa. This hardness is close to values reported for super-hardness.

The coefficient friction for the carbides was in the range of 0.4, minor value than the reported for the uncoated steel (0.7). This performance can be explained for the carbon in graphite way in the carbide coatings according to the XPS results.

Potentiodynamic polarization tests showed a better performance for NbC coating deposited on steel H13 with more electropositive corrosion potentials, and EIS spectra confirmed better electrochemical performance of the coatings compared to uncoated steel. This is primarily due to the ceramic nature of carbides and their relatively low degree of porosity, which hinders the penetration of the electrolyte solution. Additionally, two time constants can be seen in the curves of phase versus frequency.

At high frequency, the coating exhibits dielectric behavior, and at low frequency it reflects the coating-substrate interface. The ternary system exhibited good electrochemical performance, being superior by a factor of approximately 5 in comparison with the uncoated steel.

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