

Production and characterization of niobium carbide coatings produced on tool steels by thermoreactive deposition/diffusion

Producción y caracterización de recubrimientos de carburo de niobio sobre aceros para herramientas producidas mediante la deposición por difusión termorreactiva

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RESUMEN

En este trabajo se depositaron recubrimientos de carburo de niobio sobre aceros AISI M2, H13 y D2, utilizando la técnica de deposición por difusión termorreactiva. Los carburos se obtuvieron usando baños de sales compuestos por bórax fundido, ferroniobio, ferrovanadio y aluminio a una temperatura de 1.020 °C durante 4 horas. La presencia de los recubrimientos fue observada por microscopía electrónica de barrido. Las fases fueron determinadas usando difracción de rayos X, y se utilizó microdureza para determinar la dureza. El comportamiento electroquímico fue estudiado mediante curvas de polarización potenciodinámica para determinar la densidad de corriente de corrosión, y espectroscopia de impedancia electroquímica para determinar la resistencia a la polarización. Los resultados fueron comparados con las propiedades del sustrato sin recubrimiento y en general se observó mayor dureza y mejor resistencia a la corrosión en los recubrimientos producidos.

Palabras clave: Difusión, carburos de niobio, impedancia, aceros para herramientas, corrosión.

ABSTRACT

In this work, niobium carbide coatings were deposited on AISI M2, H13, and D2 tool steels by thermoreactive deposition/diffusion. The carbides were obtained using salt baths composed of molten borax, aluminum, and ferroniobium at a temperature of 1020 °C for 4 hours. The coatings were observed via scanning electron microscopy. The phases were determined using X-ray diffraction, and Vickers indentation was used to determine the hardness. The electrochemical behavior was studied via potentiodynamic polarization curves to determine the rate of corrosion and electrochemical impedance spectroscopy was used to determine the resistance to polarization. The results were compared with the properties of the substrate without a coating, and in general, greater hardness and better corrosion resistance were observed with the coatings.

Keywords: Diffusion, niobium carbide, impedance, tool steels, corrosion.

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INTRODUCTION

Surface treatments are used to improve the tribological performance of many cutting tools, generally in machine elements that are subjected to high wear conditions. One of the surface treatments used is depositing layers of transition metal carbides or nitrides. These layers are commonly obtained using techniques such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) [1-2]. One of the main limitations of these procedures is the use of complex equipment and high-vacuum conditions, which make their implementation expensive. A competitive and economical alternative is the application of hard coatings with good wear resistance by a thermoreactive deposition/diffusion process (TRD) [3] on substrates containing a carbon percentage higher than 0.3% by weight [4]. The layers deposited by this process exhibit good adhesion to the substrate, low coefficients of friction and excellent uniformity in thickness [5]. For this treatment, a salt bath composed of molten borax, aluminum, or ferrosilicon can be used as a reducing agent, along with carbide forming elements (CFE's), such as vanadium, chromium, titanium, and niobium [4]. The carbide layer is formed when the metal element dissolved in the salt bath has a relatively low carbide-formation energy and oxide-formation energy greater than that of boron oxide (B_2O_3) [6-7]. Otherwise, the boron atoms are not oxidized and remain free to diffuse into the steel matrix, which combine with the iron boride layers to form iron (Fe_2B or FeB) [8-9].

Several studies have developed binary metal carbides by the TRD process and have characterized their wear resistance, microstructure, and mechanical behavior. For example, several studies have focused on the production of VC and NbC coatings on substrates of AISI H13, AISI D2, and AISI M2 steels, reporting hardnesses up to 2300 HV [3, 5]. Other investigations have studied the growth kinetics of niobium carbide on AISI 1040 steel [10], iron boride on AISI 4140 [11], and chromium carbide on AISI D2 steel [12]. These studies report that the thickness of the layers obtained for binary systems, such as NbC or VC, depends on the treatment time and process temperature. Electrochemical studies have reported on forming iron boride using borax and aluminum on AISI S1, S2, and S3 steels by changing the percentage of manganese [13].

However, to the authors' knowledge, no studies have reported on the electrochemical behavior of niobium carbide coatings or its correlation with the chemical composition of the substrate.

EXPERIMENTAL PROCEDURE

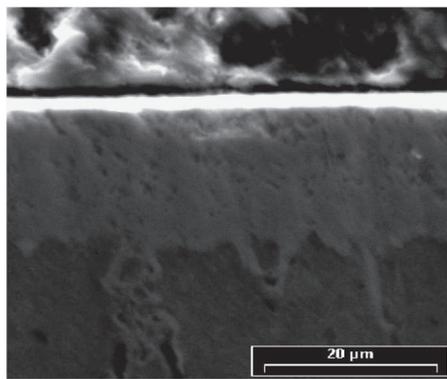
Niobium carbide (NbC) coatings were deposited on substrates of AISI D2, M2, and H13 steels using samples 15 mm in diameter and 4 mm thick. The sample preparation included polishing using abrasive grinding papers from 220 to 1200 grit and ultrasonic cleaning with acetone.

The coatings were produced in a salt bath with a composition of 81 wt.% $Na_2B_4O_7$, 16 wt.% Fe-Nb and 3 wt.% Al. The samples were heat treated at a temperature of 1020 °C for 4 hours in an electric furnace described elsewhere [14]. The phases present and the crystallographic orientation were visualized using X-ray diffraction (XRD) on an X-PertPro PANalytical instrument (configuration θ -2 θ in a range of 10° to 100°, 45 kV, 40 mA, $CuK\alpha$ monochromatic radiation, and wavelength of 1.56 Å with a step size of 0.02°). The thickness of the coatings after being etched with 3% Vilella was determined using a Philips scanning electron microscope (SEM) with a voltage of 40 kV. Ten measurements were performed to obtain an average value. The hardness of the coatings was determined from measurements using the Vickers indenter with a load of 50 g in a Leco microhardness tester by making indentations transverse to the coating, which had been previously encapsulated in bakelite.

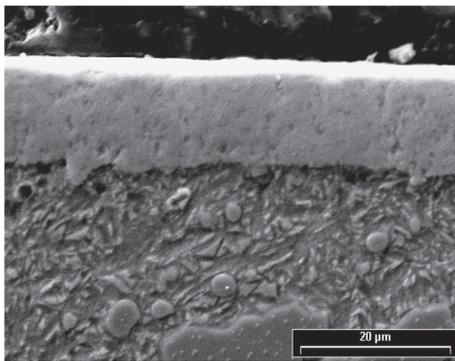
The electrochemical behavior of the coatings were studied by conducting potentiodynamic tests to obtain polarization curves and potentiostatic tests to obtain electrochemical impedance spectroscopy (EIS) using a Gamry Instruments 600 potentiostat. A three-electrode electrochemical cell was used in a volume of 100 ml of a 3% NaCl solution at room temperature. The working area was 0.196 cm² using a platinum bar and a calomel electrode as the reference and auxiliary electrodes, respectively.

RESULTS AND DISCUSION

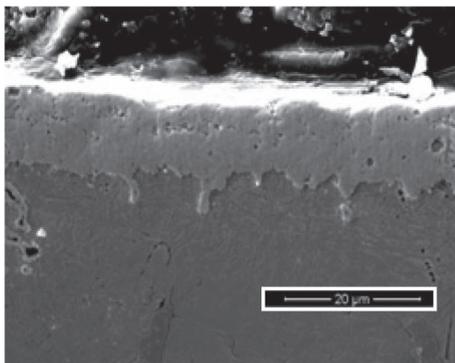
Figure 1 shows the cross section SEM in the coatings obtained on the three steels used. It can be observed that the thicknesses exhibited excellent uniformity,



(a)



(b)



(c)

Figure 1. SEM micrographs of the coated steels: a) D2 b) M2, and c) H13.

with average values of $15.8 \pm 0.5 \mu\text{m}$, $12.6 \pm 0.2 \mu\text{m}$, and $10.5 \pm 0.3 \mu\text{m}$, for the AISI D2, M2 and H13 steel respectively.

Figure 2 shows the X-ray diffraction patterns for each of the treated steels. The NbC phase was confirmed for the three steels used as substrates, exhibiting in all cases high-intensity peaks for the (111), (200),

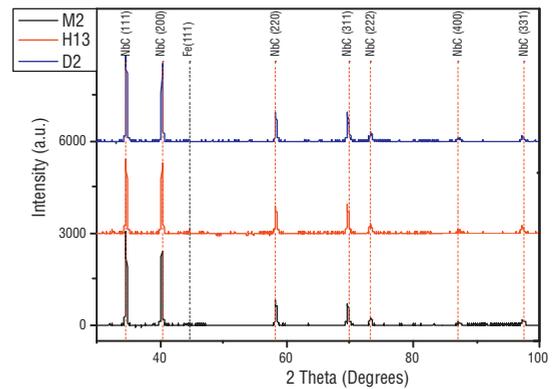


Figure 2. X-ray diffraction patterns of the coatings obtained.

and (311) crystallographic planes and low-intensity peaks for the (220), (222), (400), (331), (400), and (422) planes.

The type of layer formed can be explained by the free energies of carbide and oxide formation of the elements present in the salt bath. Niobium has a relatively low carbide formation energy of $-33.6 \pm 0.8 \text{ kcal}$ [15], whereas its free energy for the formation of NbO (-144 kcal) is greater than the free energy for the formation of B_2O_3 (-154 kcal) [16]. The layers are formed as a consequence of the direct combination of carbon in the steel with niobium dissolved in the bath. The composition of the coatings and their hardnesses are almost independent of the type of substrate and are not affected by the presence of the alloying elements of the steel.

The hardnesses obtained were $2266 \pm 83 \text{ HV}$ for AISI D2, $2241 \pm 74 \text{ HV}$ for AISI M2, and $2255 \pm 72 \text{ HV}$ for AISI H13. These hardness levels are in agreement with values reported for this type of carbide using the TRD technique [3, 5].

The corrosion rate of a coating-substrate system can be measured using current vs. potential curves, referred to as potentiodynamic polarization curves. Figure 3 shows the curves obtained for the three uncoated steels and those coated with NbC, and the Table 1 summarizes the most important parameters obtained in this measurement. It can be observed that the resistance to corrosion of the coated steels decreased, which is clearly manifested in the decrease in the corrosion current and the increase

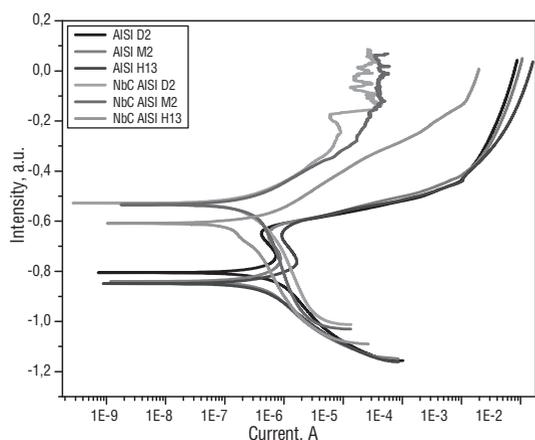


Figure 3. Tafel polarization curves of bare and coated steels.

Table 1. Tafel polarization parameters of the corrosion of bare and coated steels in 3% NaCl. (Corrosion current (I_{cor}) and corrosion potential (E_{cor})).

Substrate	I_{corr} (A)	E_{corr} (mV)
AISI D2	1.19E-06	-807
AISI M2	1.50E-06	-812
AISI H13	9.13E-07	-866
AISI D2 with NbC	3.78E-07	-554
AISI M2 with NbC	3.53E-07	-533
AISI H13 with NbC	3.07E-07	-619

in the corrosion potential of the coatings. The coating produced on the AISI D2 steel exhibited better performance than the coatings produced on the M2 and H13 steels.

The equivalent circuits used to fit the obtained EIS spectra are shown in the Figure 4 and were analyzed with the software Echem Analyst developed by Gamry Instruments.

For the uncoated steel (Figure 4a), a resistance $R_{soln} = R_u$ is proposed, which is the resistance of the solution connected in series with two elements in parallel: a constant phase element (CPE) pair where Y_0 is the capacitor and α is the exponent. An α value of 1 indicates that the proposed element is completely capacitive and if less than 1, indicates that the element has both capacitive and a resistive character; in the figure, R_p represents the polarization resistance. In the case of the coated steel (Figure 4b),

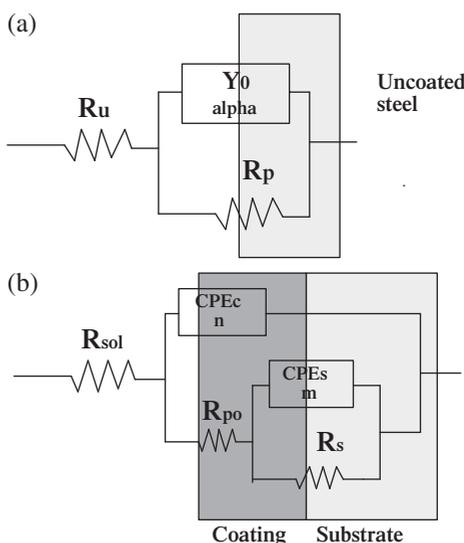


Figure 4. Equivalent circuits for the coatings in 3.5% NaCl solution at different stages: (a) bare steels and (b) coated steels.

$R_{soln} = R_u$ appears again, with a CPE pair made up of C_c that represents the coating capacitance; the value of the exponent m again indicates the capacitive character of C_c . The resistance to charge transfer across the pores, R_{po} , also appears. A second CPE pair is included, made up of C_{cor} , which represents the resistance to charge transfer across the interface (R_{cor}), and the Helmholtz double-layer capacitance. The value of n gives an indication of how capacitive this CPE pair is.

The impedance spectra obtained for exposure times of one hour, one day, two days, and 7 days in a 3% NaCl solution are shown for the uncoated steels in Figure 5 and the values of the parameters obtained after fitting are summarized in the Table 2. The impedance spectra for the coated steel in the same condition than the uncoated steel, are shown in the Figure 6 and Table 3, respectively.

Figure 5 shows impedance values for the substrates between 5,000 and 50,000 Ohms with the presence of a time constant according to Figures 5b, 5d and 5f. The steels coated with NbC have two time constants according to Figures 6b, 6d, and 6f, and these correspond to the coating and the steel time constant, denoted by τ_c and τ_{corr} respectively [17], where:

$$\tau_c = R_{po} C_c \quad \text{and} \quad \tau_c = R_{cor} C_{cor}$$

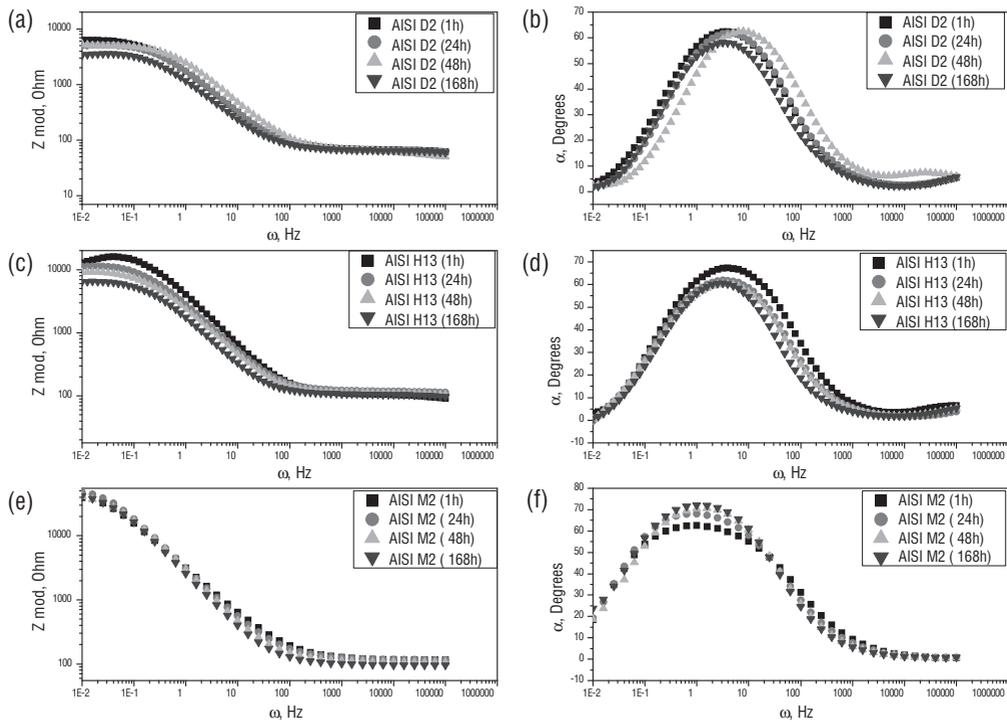


Figure 5. Bode plots of EIS spectra of bare AISI D2, M2, and H13 steels.

Table 2. Electrochemical impedance parameters on uncoated AISI D2, M2 and H13 steels.

System	Exposure time	R_{sol} (ohm)	E_{corr} (mV)	$R_{polarization}$ (ohm)	(CPE) C _{cor}	alpha
AISI D2	1 h	67	-789	6481	1.21E-04	0.8
	1d	65		5290	1.14E-04	0.81
	2d	59		5175	7.46E-05	0.80
	7d	64		3698	1.75E-04	0.79
AISI M2	1 h	116	-820	62980	8.08E-05	0.73
	1d	119		61790	7.20E-05	0.8
	2d	109		46050	7.29E-05	0.83
	7d	98		48890	8.23E-05	0.84
AISI H13	1 h	103	-842	16090	4.89E-05	0.84
	1d	117		11830	7.49E-05	0.81
	2d	109		9505	9.07E-05	0.8
	7d	104		6574	1.17E-04	0.82

It can be noted that the impedance of the coatings is greater (Table 3) with respect to the steels (Table 2). It can also be observed that the impedance decreases as the exposure time increases, which indicates that the coating has a porous character and that the

electrolyte would penetrate the coating through the pores. It is clear that the porosity barely increases with exposure time, which indicates that it would take a long time for the electrolyte to penetrate finer defects, such as microcracks [18].

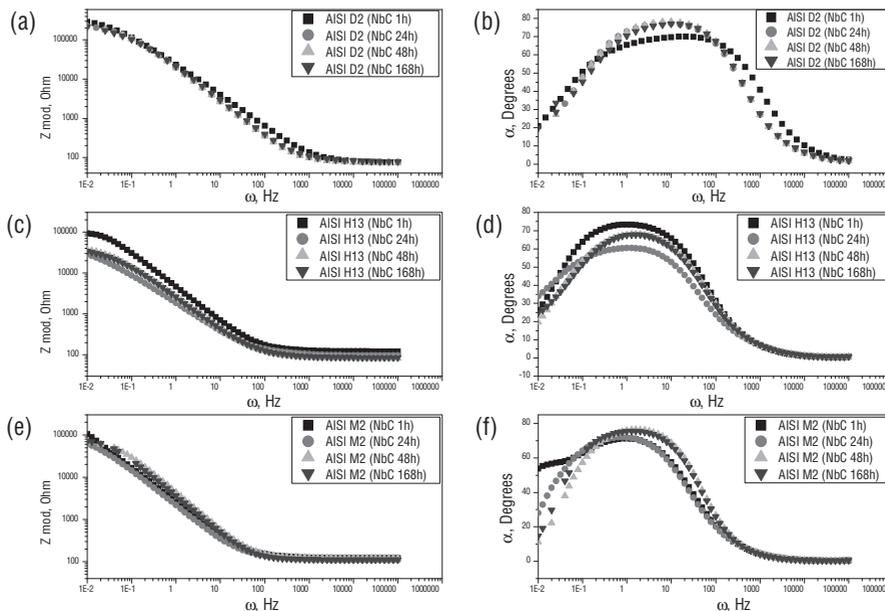


Figure 6. Bode plots of EIS spectra of the coated of NbC on AISI D2, M2, and H13 steels.

Table 3. Electrochemical impedance parameters on bare steels and coated steels.

System	Exposure time	Rsoln (ohm)	Rcor (ohm)	Rpo(ohm)	(CPE) Ccor	N	(CPE) Cc	m
NbC on D2	1 h	74.79	184000	175400	8.30E-06	0.74	9.03E-06	0.81
	1d	79.8	52330	196200	8.56E-05	0.91	9.91E-06	0.88
	2d	75.11	67410	181700	8.88E-05	0.97	9.83E-06	0.89
	7d	81.61	165400	135100	2.53E-05	0.62	9.01E-06	0.88
NbC on M2	1 h	122.9	216000	10280	2.59E-06	0.35	8.39E-05	0.83
	1d	112.1	79180	9650	2.65E-10	0.71	5.30E-05	0.89
	2d	123	80980	189.7	1.76E-06	0	4.36E-05	0.9
	7d	112.1	94130	774.1	2.13E-06	0	5.31E-05	0.89
NbC on H13	1 h	120.8	123300	1230	2.10E-05	0.81	2.41E-05	0.88

The carbide coating deposited on AISI D2 steel exhibited better electrochemical behavior, which can be due to one primary factor: its higher carbon content in the matrix caused the layer thickness which difficult the penetration of the electrolyte through the coating.

CONCLUSIONS

Niobium carbide coatings were obtained using the TRD technique and exhibited excellent uniformity in thickness and high hardness. The coating thickness obtained was proportional to

the amount of carbon in the steel matrix used as a substrate. For this case, it was higher for AISI D2 and lower for AISI H13.

Potentiodynamic polarization curves showed a better performance for the NbC coating deposited on the D2 steel with more electropositive corrosion potentials, which might be because this coating had a lower percentage of porosity, which hampered the penetration of the electrolyte. EIS spectra confirmed the coating performance on the AISI D2 steel, and it was shown that the resistance of the coating was much higher than for the other steels.

Furthermore, the phase-versus-frequency curves exhibited two time constants, for which the dielectric behavior of the coating is evident at high frequencies, and the dielectric behavior of the coating-substrate interface is evident at low frequencies.

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