

Tribological Properties and Corrosion Resistance Enhancement of H13 Hot Work Steel by Means of CrN/TiN Multilayers

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Received: December 01, 2009 / Accepted: December 22, 2009 / Published: June 25, 2010.

Abstract: Steel AISI H13 is used mainly for fabrication of hardened hot work tools; however life time of this steel is limited by its relatively low wear and corrosion resistance, if it would be exposed to an aggressive environment. It is widely known that the performance of tools and parts that undergo high mechanical load can be enhanced by the use of monolayer hard thin coatings. However, the use of such coatings as corrosion barriers is often unsatisfactory, since the deposition processes usually generate small pores and pinholes, which negatively affect the electrochemical behaviour of the coating/substrate system. On the other hand, if a hard thin film covers a less noble material, such as steel, small anodic areas could be generated and exposed to an aggressive environment a galvanic corrosion would take place. Therefore, it is also necessary to optimize the design of the coating system used in order to achieve the better relationship between mechanical and electrochemical properties for the whole system. The intention of the presented work was to enhance the tribological properties and corrosion resistance of steel AISI H13 through the use of a CrN/TiN multilayer coatings system, which were deposited by using the balanced magnetron sputtering technique.

Key words: Magnetron sputtering, multilayers, corrosion resistance, chromium nitride, titanium nitride.

1. Introduction

The phenomena of the wearing down, the oxidation and the corrosion cause millionaire loss in the manufacturing industry, generating in this way an increase of the production costs, affecting unfavorably the price of the end product and the levels of productivity and competitiveness of the companies [1, 2]. An alternative to mitigate the problems of the wearing down and the corrosion of pieces and tools is

the deposition of hard coatings, which at the same time protect against the corrosion, increasing their efficiency and life utility. In this sense the physical vapor deposition of monolayer of CrN, TiN, ZrN, TiAlN, among others, has been used successfully [3-5]. It is known that these coatings possess high hardness, low friction coefficient and good wear resistance, nevertheless its corrosion resistance is diminished by pores and micro fissures, that form in the columnar structure of the monolayer during the deposition process, which can be penetrated by the aggressive means with which the surface enters contact

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generating a galvanic reaction and the damage of the system substrate-coating [6, 7]. A strategy to improve the tribological properties and the corrosion resistance of the steel H13 is the deposition of a multilayer system, which increases the density of the coating; reducing its permeability in front of the liquid or gaseous means surround it. The previous behavior can be generated by one or several of the following effects [8, 10]:

- The increase of the bilayers number diminishes the grain size of the monolayer and increases their density reducing the porosity of the coating system and the penetration of the aggressive means to the substrate surface.
- The alternate layers of different chemical composition can redirect the electric current flow between the coating and the substrate.
- The solid solution of one or more alloy elements and the segregation of nanometric phases that can block the movement of dislocations.
- The nanometric grain size, which prevents the displacement of the dislocation and conduce to an increment of the hardness and Young Modulus of the coating system according to the equation of Hall Petch

$$H = H_0 + kd^{-\frac{1}{2}} \quad (1)$$

Where H is the hardness and d is the grain size.

The contribution of this work aims at the improvement of the tribological properties and the corrosion resistance of steel AISI H13 by means of the use of a multilayer coating system of CrN/TiN. The microstructure, chemical bonds, surface topography, the hardness and wear resistance, as well as the electrochemical behavior and corrosion resistance of the coated samples were evaluated in dependence of the number of bilayers of the coating system. The microstructure of the coatings was analyzed by using

X-ray diffraction; the chemical bonds and surface topography were evaluated by Fourier Transformed Infrared Spectroscopy (FTIR) and Atomic Force Microscopy (AFM), while the hardness and wear resistance were characterized by using the Calo Test Method and Pin on Disc measurements, respectively. The corrosion resistance of the coated samples was evaluated by Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization curves.

2. Experiment

2.1 Hard Coatings Deposition

All coatings were deposited on to AISI H13 steel substrates, which were ultrasonically cleaned with acetone and isopropanol. The used deposition technique was a multi-target r.f. magnetron sputtering set-up at a frequency of 13.56 MHz. During coating deposition, substrates were heated to 250 °C, a r.f. bias of - 100 V was applied and they rotated in front of the targets at a distance of 60 mm. During most runs a thin, pure metal layer (0.3 μm Ti and 0.7 μm Cr, respectively) was deposited onto the metallic substrate prior to the nitride deposition. A 350 W magnetron power was applied to the Ti and Cr targets, which consisted of a single-phase four-inch diameter and 0.16-inch thick Ti- and Cr disk with purity above 99.9%, mounted on a water-cooled Cu holder. The deposition chamber was initially pumped down to less than 5×10^{-4} Pa, using a turbo molecular pump and then a mixture of purified Ar and N gas (93% Ar y 7% N₂), was introduced into the chamber. During the growth, chamber pressure was maintained at 2.1×10^{-2} mbar. Before deposition, the targets and substrates were sputter-cleaning during 20 minutes. For multilayer's deposition, the Cr and Ti target was covered periodically with a steel shutter.

2.2 Coatings Characterization

The crystalline structure and the chemical bonds of the coatings were determined by X-ray diffraction and by Fourier transformed Infrared Spectroscopy. For such aim, an ANTONPAR X-ray diffractometer in the way of grazing angle was used, with an accelerating voltage of 40 kV, current 30 mA and using the Cu K α ($\lambda=1.5405\text{\AA}$) radiation, as well as an infrared spectrometer Shimadzu 8000 ($350\text{-}4600\text{ cm}^{-1}$) in transmittance modus, which employs a ceramic source Nerst type. For the topographic analysis of the coatings an atomic force microscope (AFM Nanosurf easyscan2) was utilized in the contact modus. The hardness of the coatings was determined using the Knoop microindentation technique and applying a load of 150 mN. The wear evaluation of the samples was carried out by means of the Calo Test method (according to norm DIN 1071). Hereby, the samples were subjected to a flat support and it was put under dynamic contact with a steel sphere with a diameter of 42.7 mm, dampened with a highly abrasive diamond solution and turning to 60 rpm during a time of 120 s. During the relative movement of the two surfaces the sample presents a loss of mass by wearing down, leaving on the surface a concentric track in the form of a crater, whose volume can be calculated knowing the diameter of the track and its depth. The corrosion behavior was characterized by means of the electrochemical impedance spectroscopy and by registering of polarization curves at room temperature, using a cell composed of the work electrode with a set out area of 1 cm^2 , a reference electrode of Ag/AgCl and a platinum wire as counter electrode in a 3.5% NaCl solution prepared with distilled water. The diagrams of Nyquist were obtained realizing frequency scanning in the rank of 100 kHz up to 0.001

Hertz, using a sinusoidal signal with amplitude of 10 mV. The polarization curves (Tafel's curves) were obtained at a scanning speed of 0.5 mV/s in a voltage rank of -0.25 V to 0.25 V.

3. Results and Discussion

3.1 Chemical Composition

In Figs. 1a and 1b, the X-ray diffractograms corresponding to the CrN and TiN monolayers are observed, the intense peaks demonstrate that the coatings deposited are stoichiometric and have a high degree of crystallinity. The CrN and the TiN phases present a preferential orientation in the (111) plane, furthermore, the TiN has an intense peak in the (220) plane. This shows that these coatings grew preferentially in the direction (111), where commonly the highest hardness values and Young's Modulus are obtained [11-13]. The peaks in this diffractogram are slightly moved toward higher diffraction angles due to compressive stresses induced by intense bombardment with Ar ions due to bias voltage applied to the substrates of -100 V. These results are consistent with those reported by others research groups [14, 15]. Similarly, the diffraction peaks of the Cr and the Ti are observed in 43.9° and 76.1° angles originated by the respective adherent monolayers previously deposited with a thickness of about 300 nm. FTIR spectra were taken on single layer TiN and CrN coatings deposited on Si with (100) orientation. These spectra were obtained in the transmittance mode, as substrate was transparent to the infrared light.

Fig. 2 shows a FTIR spectrum for the single layer CrN coating deposited using an Ar/N₂ ratio of 93/7, the spectrum was performed in the range from 450 to 1200 cm^{-1} , in which active modes in the infrared are observed. It is mainly found a wide absorption band

centered in 515 cm^{-1} which corresponds to the vibrations of type symmetrical stretching attributed to the single bonds of Cr-N, as well as the presence of three bands around 651 cm^{-1} , associated with Cr-O bonds, probably originates by contamination of the surface with oxygen. Finally, it is observed a wide band centered in 1015 cm^{-1} which corresponds to the vibrations of type symmetrical bending associated to the bonds Cr-N-Cr. These results are consistent with those reported in Refs.[16, 17].

Fig. 3 presents a FTIR spectrum of TiN coating in the range from $500\text{ to }1200\text{ cm}^{-1}$, which was deposited using the same Ar/N₂ ratio of 93/7. A wide band centered in 514 cm^{-1} is observed, which corresponds to the vibrations of type symmetrical stretching attributed to single bonds of Ti-N, as well as the presence of other band around of 1063 cm^{-1} , associated to the bonds Ti-O, like it was found in Ref. [18].

3.2 Physical Properties of the Coatings

In Fig. 4, it is observed the behaviour of the roughness and grain size of the coatings as a function of the number of bilayers, that was characterized using the atomic force microscopy AFM. As it can be seen, the roughness and the grain size decreases from 362 nm and 85 nm for 10 bilayers of CrN/TiN to 116 and 79 nm for 100 bilayers, respectively. This behaviour is consistent with the reduction of the modulation period of the multilayer, which decreases with the number of multilayer from 400 to 40 nm.

The previous fact together with an increase in the hardness with the number of bilayers, which changed from 5 GPa for the uncoated sample to 29 GPa for the CrN/TiN coating with 100 bilayers (Fig. 5) Bejarano et al. (2009) and a probable reduction in the friction coefficient resulted in an increased wear resistance of

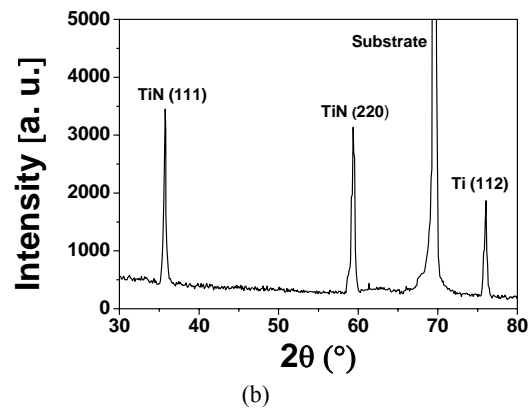
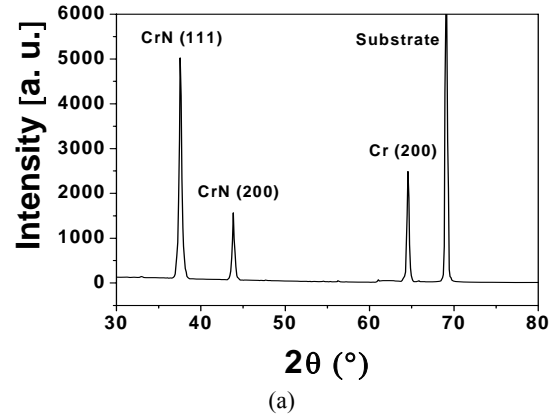


Fig. 1 X-Ray diffractogram for a) CrN single layer and b) TiN single layer.

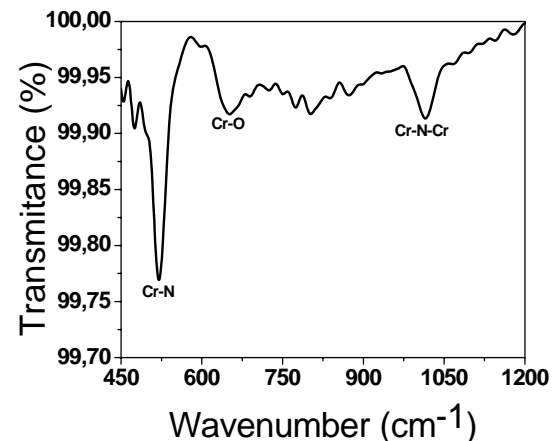


Fig. 2 FTIR spectra of a CrN single layer deposited on (100) Si with an Ar/N₂ ratio of 93/7.

the substrate-coating system represented in a decreased of the wear rate [19-21].

3.3 Tribological Properties

Fig. 6 illustrates the abrasive wear rates obtained during the Calo Test. All our multilayer coatings show

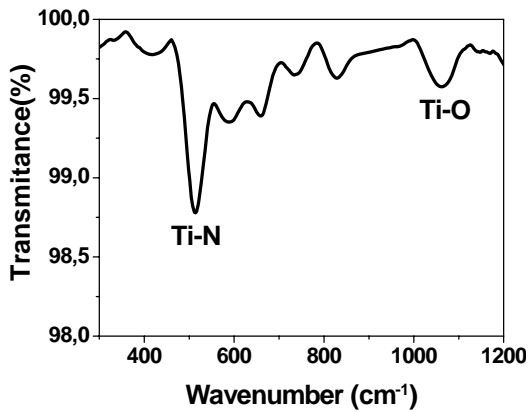


Fig. 3 FTIR spectra of a TiN single layer deposited on (100) Si with an Ar/N₂ ratio of 93/7.

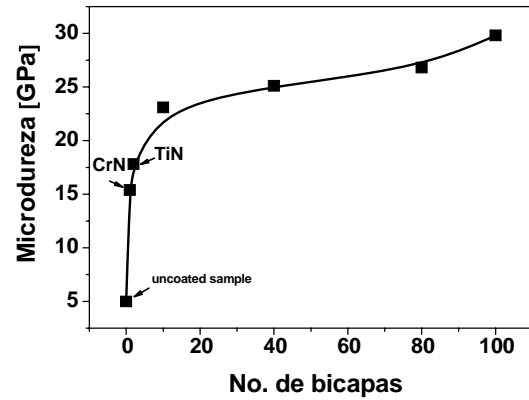


Fig. 5 Hardness of the coating system as a function of the bilayer's number.

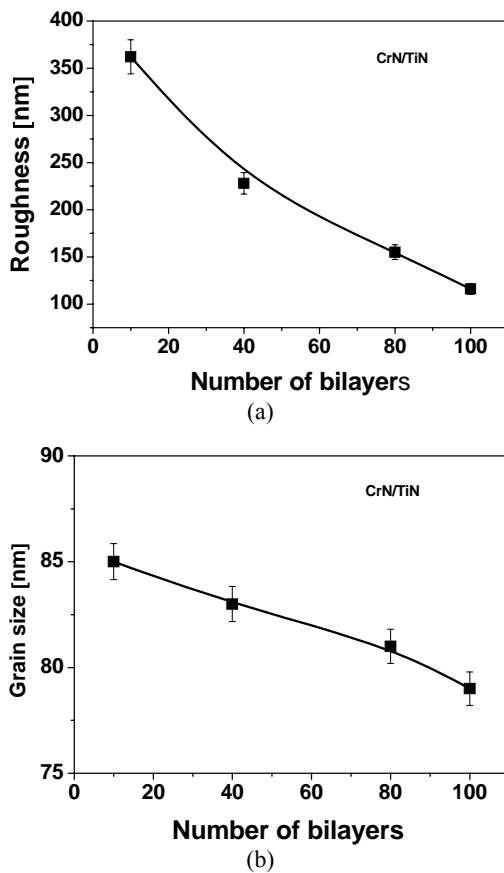


Fig. 4 Roughness (a) and Grain size (b) of the CrN/TiN coatings as a function of the number of bilayers.

similar values of abrasive wear rate, around $4 \cdot 10^{-18}$ m³/Nm, with a significant decrease when the multilayer period decreases. The CrN and TiN single layers show abrasive wear rate forty times higher than the multilayers. The substrate of AISI H13 steel showed the highest abrasive wear rate about of

two hundred times higher than the multilayers. The determined wear rate values of the investigated coating system are lower than those found by other researcher for in Cr/CrN and Cr/CrC coatings system [22-24].

It is known that by nanometric modulation period of the coatings, the plastic deformation of the films take place by sliding throughout of the grain boundaries and not by the sliding of the dislocations, this process requires higher energy and therefore it generates a greater increase of the hardness and Young's modulus of the coating. Other factors that contribute to block the movement of the dislocations as well as the growth and propagation of nano and micro cracks are the multiple interfaces between the single layers, which lead to an additional increase of the coating hardness and wear resistance [8-10, 25].

3.4 Electrochemical Properties

In the case of a perfect coating without pores and micro cracks, the Nyquist plots show an ideal behavior of a barrier against the corrosion; this behavior corresponds to a curve parallel to the imaginary axis. When the coatings have pores or micro cracks allow the attack of the electrolyte to the substrate and a typical Nyquist plot is obtained, in

which the corrosion resistance of the coating-substrate system decreases over the time [25-27]. Fig. 7 shows the Nyquist plot for the substrate and the $[CrN/TiN]_n$ multilayer coatings. To simulate and understand what happens at the interface of all coatings obtained, a circuit that corresponds to the Randles cell is used, which predicts that the capacitance of the double layer is in parallel with the impedance due to the transfer reaction of ions [28].

Tafel polarization curves are presented in Fig. 8, where the values of the anodic and cathodic slopes in each case can be found. It was observed that both $[CrN/TiN]_n$ coatings deposited with bilayers between 10 and 100, have an upward shift compared to H13 steel samples, indicating that it has been generated a

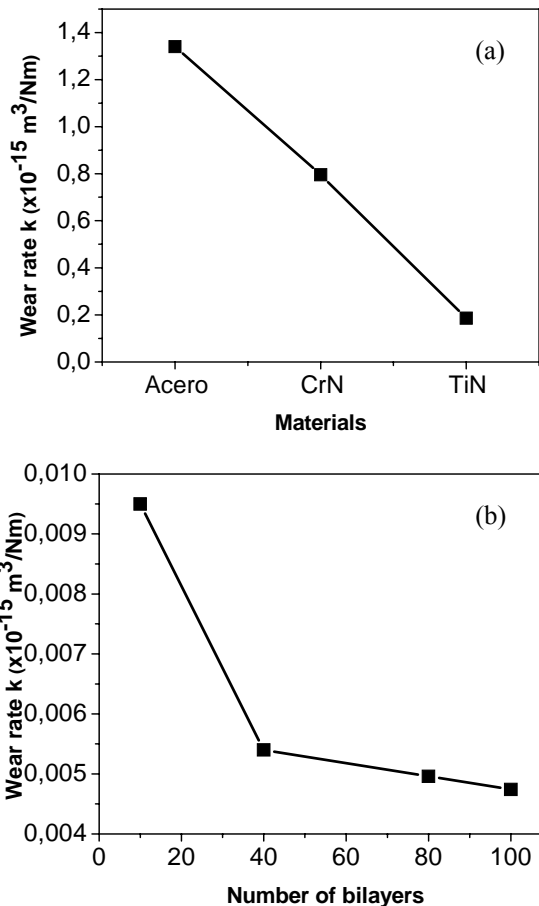


Fig. 6 Wear rate by means of calo test as a function of a) type of materials evaluated and b) number of bilayers.

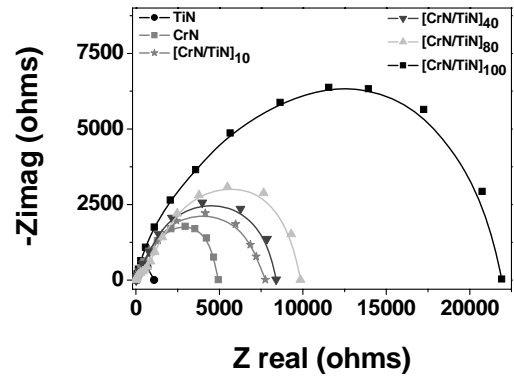


Fig. 7 Nyquist plots for $[CrN/TiN]_n$ coatings with different number of bilayers.

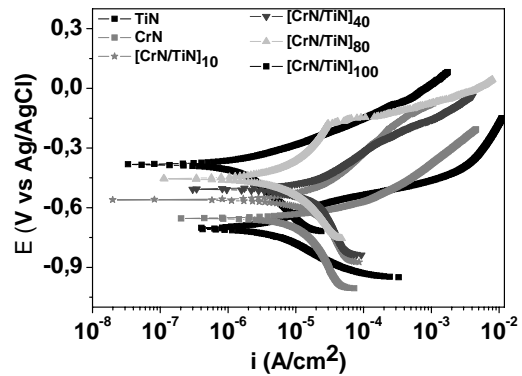
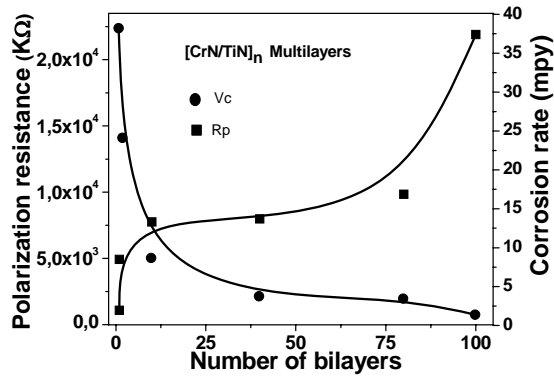


Fig. 8 Potentiodynamic polarization curves of $[CrN/TiN]_n$ multilayer coatings with different number of bilayers.

more protective corrosion potential than the own of the substrate [29]. On the other hand, it was observed that the $[CrN/TiN]_{10}$ coating containing 10 bilayer, shows a wide downward shift indicating a major susceptibility to corrosion in the solution analyzed. This is due to the degree of porosity in the single layers or multilayer with a low period, these porosities can be produced in the coating by a nucleation phenomenon; however the multilayer coatings become passive generating a protective layer obtaining a better corrosion behavior than uncoated AISI H13 steel. The reason of this result is in the nature of the multilayer structures, since increasing the number of bilayers, augment the density of the coating as a result of raising the number of alternating layers of CrN and TiN, but diminishing individual thicknesses, in order to conserve the total thickness of the coating. This leads

Table 1 Electrochemical parameters of the substrate and the [CrN/TiN]_n multilayers.

	TiN	CrN	[CrN/TiN] ₁₀	[CrN/TiN] ₄₀	[CrN/TiN] ₈₀	[CrN/TiN] ₁₀₀
Corrosion rate V _c (mpy)	38.21	24.12	8.676	3.745	3.454	1.375
Polarization R _p resistance (KΩ)	1.09×10 ³	4.93×10 ³	7.75×10 ³	7.98×10 ³	9.85×10 ³	2.19×10 ⁴

**Fig. 9** Polarization resistance (R_p) and corrosion rate (V_c) curves as a function of the number of bilayers of TiN single layer and of the [CrN/TiN]_n multilayer coatings.

to a higher energy required for the free Cl⁻ ions migration from the surface to the interface coating/substrate, which is reflected in a greater corrosion resistance of the multilayer coating system [30, 31].

The values of the polarization resistance (R_p) increase with the increase of the number of bilayers. These values together with the values of corrosion speed (V_c) can be seen in the Table 1. R_p values were found by means of electrochemical impedance spectroscopy and Tafel polarization curves, which were used to calculate the corrosion rates of the multilayer coatings, when they are put under acid or neutral salts solutions containing chloride ions.

Fig. 9 shows the trend of polarization resistance (R_p) and the corrosion rate (V_c) in dependence on the increase of number of bilayers in the coatings. This graph illustrates the systematic augment of R_p up to 2.19×10⁴ kΩ for 100 bilayer of CrN/TiN compared with the value of CrN and TiN monolayer, which are lower than 5×10³ kΩ. On the other hand, the (V_c)

corrosion rate presents a dramatic increase for the single layer of CrN and TiN coatings greater than 25 mpy, while the coating with 100 multilayer a V_c as low as 1.3 mpy exhibit, being consistent with the previous discussion.

4. Conclusions

This work demonstrated, that the corrosion resistance of AISI H13 steel can be improved by the application of a [CrN/TiN]_n multilayer coating system. From the EIS analysis and Tafel polarization curves, it was determined that the [CrN/TiN]_n coatings deposited with 100 bilayers, increased by an order of magnitude the polarization resistance compared to the single layers of CrN and TiN; on the other hand, an increase of the corrosion rate occurs, with 95% and 77% for the TiN and CrN single layer respectively.

The high hardness obtained by the sample coated with 100 multilayer of CrN/TiN together with the achieved reduction of grain size and roughness contributed, under other factors, to a significant increase in wear resistance of the [CrN/TiN]₁₀₀ coatings system, which showed a value two order of magnitude greater than the uncoated steel sample.

The previous analysis make it possible to glimpse an industrial application of AISI H13 steel in light and moderately aggressive environments, and under severe conditions of load, without using expensive stainless steel and/or refractory materials, which can be conduce to a reduction in maintenance and production costs.

Acknowledgments

The authors acknowledge the SENA, COLCIENCIAS and the Sustainability Announcement of the Antioquia University for logistical and financial support to this work.

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