

Comparative Study Between the Electrochemical Behavior of TiN, TiC_xN_y and CrN Hard Coatings by Using Microscopy and Electrochemical Techniques

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Hard thin TiN, TiC_xN_y and CrN films deposited by Physical Vapor Deposition (PVD) techniques onto steel substrates were immersed in an aggressive environment and evaluated by Atomic Force Microscopy (AFM) and Electrochemical Impedance Spectroscopy (EIS). The mechanical and electrochemical behavior, as well as the microstructure of TiC_xN_y depended directly on the contents of carbon and nitrogen in the coating. The best results were obtained with stoichiometric coatings that are presented in this work. Although a small amount of pinholes could be observed, the electrochemical performance of TiN film was poorer than the stoichiometric TiC_xN_y coating. However, the CrN films showed the highest initial and residual corrosion resistance values, probably due to their dense structure.

Keywords: *atomic force microscopy (AFM), electrochemical impedance spectroscopy (EIS), hard coatings*

1. Introduction

It is widely known that the performance of tools and mechanical parts that undergo high mechanical load can be enhanced by the use of hard thin coatings¹⁻³. These coatings generally present high tribological properties, such as hardness and wear resistance. Thus, new characteristics can be achieved by the coating/substrate system, increasing the tools and parts lifetime. In this way, a broad variety of different hard thin coatings are used in industry^{1,2,4}. However, the use of a new coating/substrate system often starts in advance of sufficient knowledge in the field of coatings properties and system characteristics.

The use of hard coatings/steel substrates systems in mechanical applications performed under aggressive environmental conditions brought about an important point of discussion, since despite its tribological properties, a thin hard coating must also be able to improve the corrosion

resistance of the substrate material used. Although the films used as hard coatings are generally chemically inert⁵⁻⁷, their use as corrosion barriers is often unsatisfactory. Since the deposition processes usually generate many small pores and pinholes^{8,9}, the electrochemical behavior of a hard coating/substrate system depends mainly on the extent of these defects. Thus, if a hard thin film covered a less noble material, such as steel, small anodic areas would be exposed to the aggressive environment (electrolyte) and a galvanic corrosion would take place⁸⁻¹⁰. Therefore, it is also necessary to optimize the deposition parameters as a function of the electrochemical behavior of the hard coating/substrate system used. Moreover, the coating used must be chosen in order to achieve the better relationship between mechanical and electrochemical properties for the whole system.

The intention of the work reported here was to compare the electrochemical behaviors of well known hard coat-

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ings/steel substrates systems as generally used for mechanical applications. Among many coatings, CrN and TiN coatings were chosen because both exhibit high hardness and oxidation resistance¹¹. TiC_xN_y was also chosen due to its high hardness, as well as to the known dependence of its mechanical and electrochemical properties on the coating chemical composition^{12,13}. All coatings were produced by PVD techniques, using high speed or stainless steel as substrates. Several mechanical characteristics of the coatings/steel substrate systems presented have also been previously determined¹²⁻¹⁵. The electrochemical evaluation of the coatings was carried out by Electrochemical Impedance Spectroscopy, while Atomic Force Microscopy was used to observe the coatings microstructure, before and after the electrochemical assays.

2. Experimental

Coatings Deposition: Chromium nitride (CrN) coating 304 stainless steel substrates was carried out by Ion Beam Enhanced technique (IBED), at Spire, USA. The coatings thickness was approximately $1.25\ \mu\text{m}$ ¹⁴. Titanium nitride (TiN) coatings, with approximately $4.0\ \mu\text{m}$ thickness, were produced onto high speed steel M2 by Arc Plating technique at Stiftung Institut für Werkstofftechnik, Germany¹⁵. Finally, approximately $3.0\ \mu\text{m}$ titanium carbonitride films (TiC_xN_y) were deposited onto high speed steel M2 by Reactive Magnetron Sputtering technique at Universidade Federal do Rio de Janeiro, Brazil¹². Since the TiC_xN_y coating's mechanical and electrochemical properties depended on the coating chemical composition, a stoichiometric coating (Ti = 50% at.; N + C = 50% at.) was used in this comparative study. All coatings studied in this work have been tested before and presented good tribological properties^{12,14,15}. More details about the PVD techniques used can be found elsewhere^{16,17}.

Electrochemical Analysis: The electrochemical measurements were carried out by using the Electrochemical Impedance Spectroscopy (EIS) technique, which applies electrical concepts to characterize electrochemical interfaces¹⁸⁻²⁰. All samples were electrically linked and then embedded in resin, before being immersed in an electrolyte composed of a solution of sodium sulfate 0.5 M (pH = 5.5). An exposed area of approximately $1.0\ \text{cm}^2$ was kept constant during all the experiments. The electrochemical behavior as a function of time, was monitored by means of the EIS technique, over a period of at least 90 min. The experiments were always performed at the corrosion potential and the frequency range used varied from 40 kHz to 4 MHz, with an amplitude of 10 mV.

Microstructure Analysis: Surface micrographies of CrN, TiN and TiC_xN_y coatings were carried out to observe the microstructure, pores and defects. The samples were analyzed before and after the electrochemical analysis,

using a TOPOMETRIX Atomic Force Microscope (AFM). The samples were prepared by ultrasonically cleaning with acetone and further drying with nitrogen. After the electrochemical measurements, the resin was completely removed from the sample surface, before the cleaning procedures. AFM was used in the non-contact mode. The cantilever oscillation amplitude was used as a feedback signal, in order to obtain both topographic image and changes in phase angle of probe oscillation, which are presented as phase image.

3. Results and Discussion

Before any electrochemical assay, the samples were cleaned and observed by Atomic Force Microscopy. It is possible to note the difference in coatings microstructure by analyzing the coatings topography (Fig. 1). The TiN films presented a honeycomb microstructure typical of TiN Arc Plating produced films¹⁶. Although a small amount of pinholes could be detected, AFM analysis showed a scratched surface, probably due to the steel surface treatment (Fig. 1a). The CrN films showed dense microstructures, although several small pores could still be observed in the coatings (Fig. 1b). AFM observations of stoichiometric TiC_xN_y films showed small grains, and a scratched and irregular coating surface (Fig. 1c). The microstructure, as well the pores and defects observed on the above mentioned surfaces, would certainly determine their performance against an aggressive environment.

Since all the films studied here are usually used as hard coatings, the main results of earlier tests carried out for the three kinds of systems are presented here, in order to illustrate their mechanical properties. Khanna¹⁴ has shown that the CrN coatings deposited on stainless steel presented good performance on mechanical tests, reducing the coefficient of friction and the wear rate of stainless steel, which permitted their use as hard coatings. The stoichiometric TiC_xN_y layers produced onto high-speed steel presented high hardness (approximately 32 GPa), as well high compressive residual stresses^{12,13,21}. Similar results could be observed for the TiN coatings deposited on high speed steel, although the compressive residual stress values were always smaller than the TiC_xN_y ones (-4000 and -7546 MPa, respectively)^{12,15}. Based on these results, all coatings/substrate systems studied in this work were considered adequate to be used on tribological applications. However, none of the above mentioned experiments have been performed in an aggressive environment.

The electrochemical results can now be qualitatively related to the microstructure analysis. In the case of a perfect coating, without pores and micro cracks and without corrosion in the applied medium, the Nyquist diagrams of one experiment show the ideal behavior of a corrosion barrier, which is a curve parallel to imaginary axis. When a coating presents many pores or cracks, which would

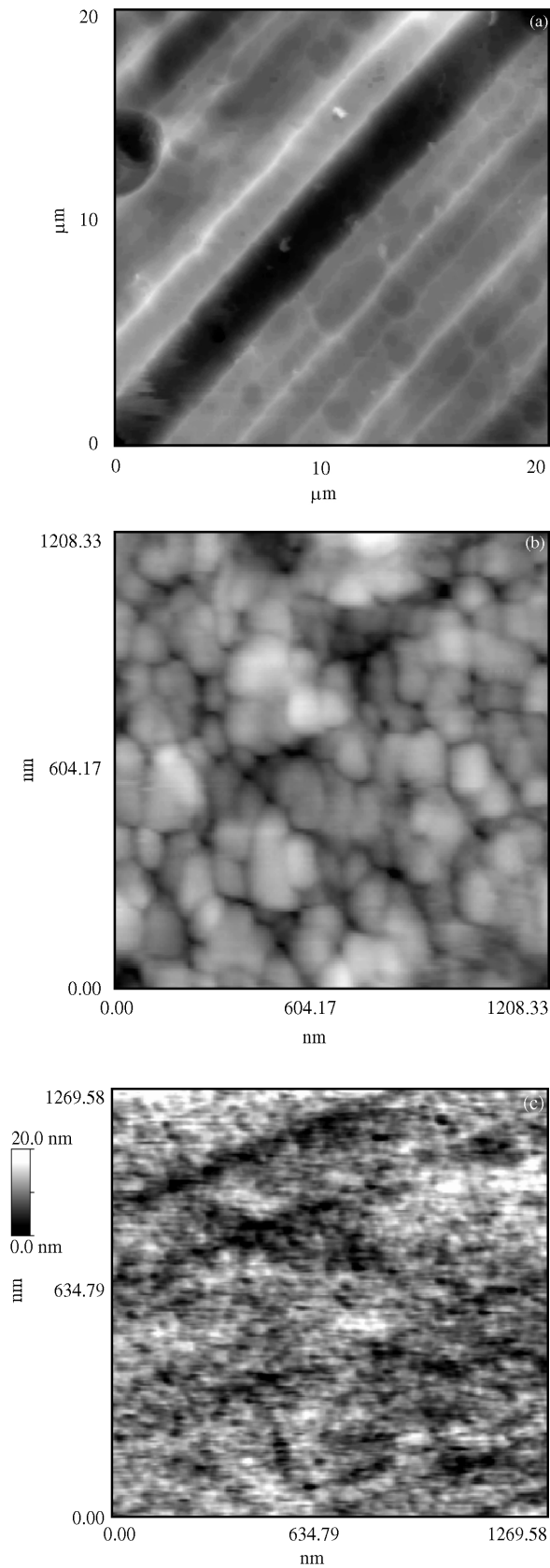


Figure 1. AFM topography images of the coatings before the electrochemical experiments: (a) TiN film; (b) CrN film ; (c) TiC_xN_y film.

permit the attack by the electrolyte on the substrate, a typical Nyquist diagram is obtained. Fig. 2 gives an example, in which the decreasing corrosion resistance (real axis) of the coating-substrate system with increasing time can be seen.

The comparative electrochemical behavior of the TiN, CrN and TiC_xN_y coatings/steel substrate system as a function of the exposition time can be observed in Fig. 3. After approximately 15 min of exposition (Fig. 3a) all coatings behaved as corrosion barriers and presented the expected curve parallel to the imaginary axis. However, it is possible to observe interesting differences among the three coatings comportment after being immersed for 90 min in the electrolyte medium (Fig. 3b). The CrN coatings continued to present a barrier performance, even after a double exposure time (180 min), probably due to their highly dense microstructure, as could be seen earlier in Fig. 1b. After four days of testing, the CrN samples were removed, and showed no significant difference in its corrosion behavior, nor visual deterioration of the coatings. Besides, AFM images of CrN coatings, performed after the EIS analysis, showed a corrosion product at the CrN grain boundaries (Fig. 4a). Khanna¹⁴ carried out a potentiodynamic electrochemical assay for the same kind of CrN samples analyzed in this work and showed that the corrosion potential, as well as the corrosion current, were much lower for the coated system than for the stainless steel alone. Moreover, this author observed that although the CrN coating was very porous before being oxidized in air at high temperature, a uniform thin oxide layer could be seen after oxidation. It is also known that Cr-based alloys generally form a passive oxide coating when exposed to a non-chlorine containing solution²². Thus, the above discussion could support a supposition that AFM could have probably detected the initial formation of a passive chromium oxide on the film surface, since the electrochemical assays were performed at a slightly acid pH (5.5) and in a non-chlorine electrolyte (Na₂SO₄). However, a surface chemical analysis should be executed to confirm this hypothesis. Furthermore, it should be interesting to test these coatings mechanically again

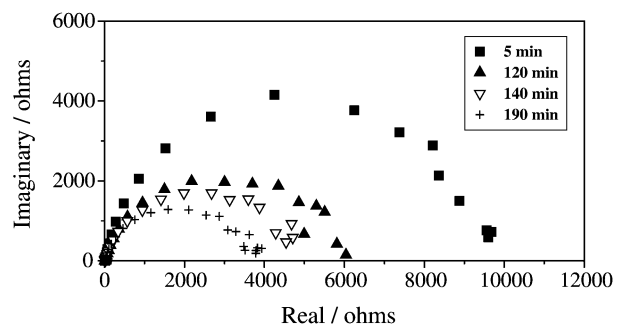


Figure 2. Nyquist diagram of a TiC_xN_y film/M2 high speed steel substrate system as a function of the exposition time to the Na₂SO₄ 0.5M electrolyte.

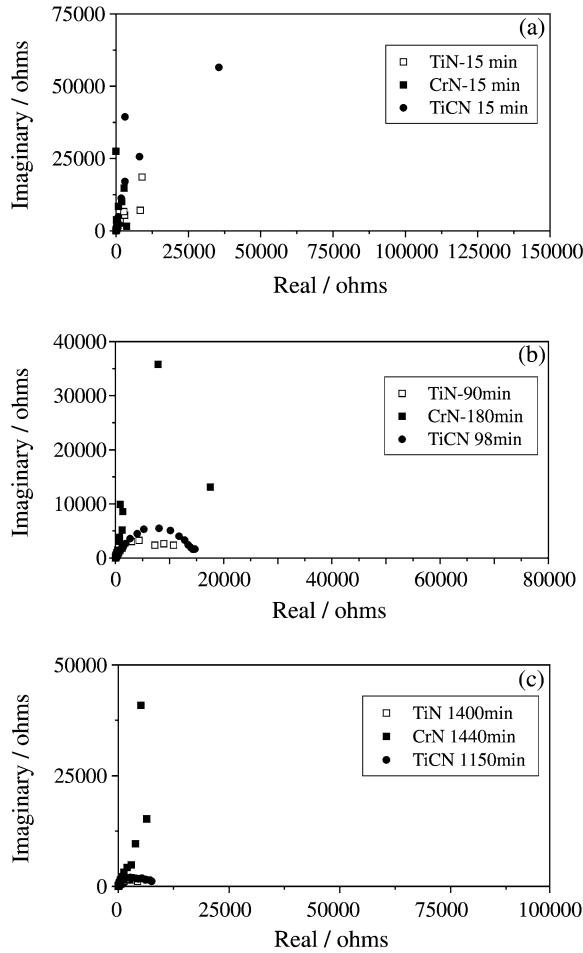


Figure 3. Comparative electrochemical behavior of the TiN, CrN and TiC_xN_y coatings: (a) Exposition time = 15 min; (b) Exposition time = 90 min (TiN and TiC_xN_y) and 180 min (CrN); (c) Exposition time = 1 day.

after the electrochemical studies, in order to know the effect of the observed corrosion product on the mechanical properties of the coating.

The stoichiometric TiC_xN_y coatings presented an intermediate electrochemical behavior among the three coatings. However, after one day of testing there was no difference between the electrochemical results for either TiN or TiC_xN_y coatings, as can be seen in Fig. 3c. No pitting could be detected in this sample. However, the voids observed near the grain boundaries seem to be responsible for the electrolyte attack on the substrate (Fig. 4b). On the other hand, TiN presented the worst corrosion resistance among the analyzed coatings, even exhibiting the highest coating thickness. This behavior was probably due to the pores and defects present in the coating, as shown earlier in Fig. 1a. Moreover, corrosion products could be observed on the coating surface after the EIS experiments (Fig. 4b). Although Massiani *et al.*⁵ showed that there was no attack on TiN films in the corrosion potential, a chemical surface

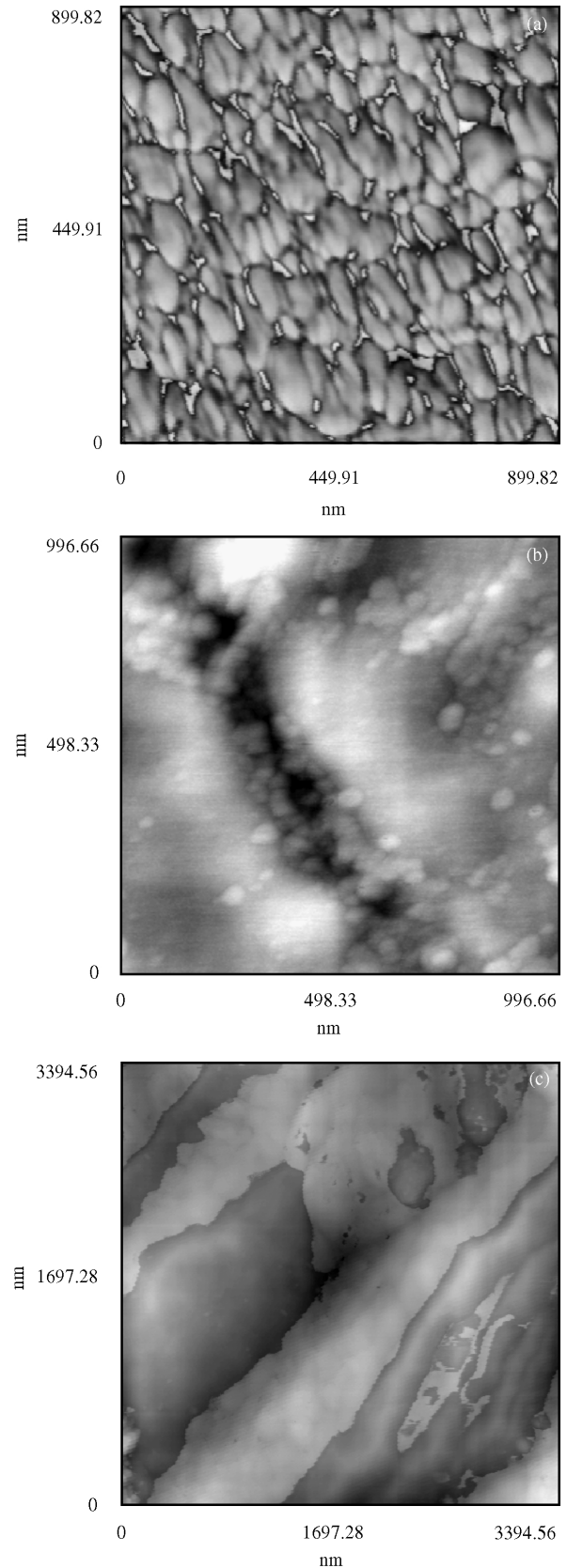


Figure 4. AFM topography images of the coatings after the electrochemical experiments.

analysis should be done in order to know the exact chemical composition of this layer.

4. Conclusion

EIS and AFM techniques were successfully used as complementary tools to evaluate comparatively three usually used hard coating/substrate systems. The electrochemical and morphological study of the coatings permitted both an estimation of their behavior in an aggressive environment and an observation of features of the coatings surfaces after the corrosion attack.

Comparing our results to the earlier mechanical tests, it seems that CrN/stainless steel substrate system could present an adequate mechanical performance under an aggressive environment.

On the other hand, this work showed that although presenting high mechanical performances, TiN and stoichiometric TiC_xN_y films/high speed steel substrate system presented unsatisfactory results as corrosion barriers, due to the amount of pores observed on both coatings' surface. Thus, the use of these coatings in mechanical applications under an aggressive environment cannot be recommended.

References

1. Walkowicz, J.; Smolik, J.; Miernik, K.; Bujak, J. Anti-wear Properties of Ti(C,N) Layers Deposited by Vacuum Arc Method. *Surface and Coating Technology*, v. 81, p. 201, 1996.
2. Weise, P.; Hirsch, T.; Mayr, P. Analysis of Residual Stresses in Hard Coatings on Steel Substrates by a Mechanical Measurement System. *Proceedings of International Conference on Surface Engineering*, Bremen, p. 343, 1993.
3. Bergmann, E.; Kaufmann, H.; Vogel, J.; Schmid, R. Ion Plated Titanium Carbonitride Films. *Surf. and Coat. Technol.*, v. 42, p. 237, 1990.
4. Sproul, W.D.; Graham, M.E.; Wong, M.S.; Rudnik, P. J. Reactive Unbalanced Magnetron Sputtering of the Nitrides of Ti, Zr, Hf, Cr, Mo, Ti-Al, Ti-Zr, and Ti-Al-V. *Surf. Coat. Technol.*, v. 61, p.139, 1993.
5. Massiani, Y.; Medjahed, A.; Gravier, P.; Argème, L.; Fedrizzi, L. Electrochemical Study of Titanium Nitride Films Obtained by Reactive Sputtering. *Thin Solid Films*, v. 191, p. 305, 1990.
6. Massiani, Y.; Gravier, P.; Fedrizzi, L.; Marchetti, F. Corrosion Behavior in Acid Solution of (Ti,Cr)N_x Films Deposited on Glass. *Thin Solid Films*, v. 261, p. 202, 1995.
7. Senna, L.F.; Simão, R.A.; Achete, C.A.; Freire Jr., F.L.; Hirsch, T. Study of the Corrosion Resistance of TiC_xN_y Films by Using Atomic Force Microscope (AFM). *Acta Microscopica*, v. 7, Suppl. A, p. 97, 1998.
8. Elsener, B.; Rota, A.; Böhni, H. Impedance Study of PVD and CVD Titanium Nitride Coatings. *Materials Science Forum*, v. 44/45, p.29, 1989.
9. Brandl, W.; Gendig, C. Corrosion Behavior of Hybrid Coatings. *Thin Solid Films*, v. 290/291, p. 343, 1996.
10. Pourbaix, M. *Lecciones de Corrosion Electroquímica*, Instituto Español de Corrosion y Protección, Madrid, 1987.
11. Esaka, S.; Shimada, H.; Imamura, M.; Matsubayashi, N.; Sato, T.; Nishijima, A.; Kawana, A.; Ichimura, H.; Kikuchi, T.; Furuaya, K. X-ray Absorption and X-ray Photoelectron Spectroscopic Studies of Air-oxidized Chromium Nitride Thin Films. *Thin Solid Films*, v. 281/282, p. 314, 1996.
12. Senna, L.F. Produção e Caracterização de Filmes Duros de Carbonitreto de Titânio. *D.Sc. Thesis*, Universidade Federal do Rio de Janeiro, 1998.
13. Achete, C.A.; Senna, L.F.; Freire Jr, F.L.; Hirsch, T. Characterisation of PVD-TiCN-Layers with Different Chemical Composition. *Final Report Volkswagen Stiftung (VW I 69021)*, Hanover, 1997.
14. Khanna, A.S. Use of Ion Beams to Improve the Oxidation Resistance of Alpha 2 Intermetallics. *Report of the Third Research Co-ordination Meeting of the Co-ordination Research Program on Modification of Materials by Ion Treatment for Industrial Applications*, 1998.
15. Hirsch, T. *Hard Coatings Compound Materials: Properties Detected by X-Ray Diffraction and Mechanical Testing*, Universidade Federal do Rio de Janeiro, 1996.
16. George, J. *Preparation of Thin Films*, Marcel Dekker, Inc., New York, 1992.
17. Konuma, M. *Film Deposition by Plasma Technique*, Springer-Verlag, Berlin, 1991.
18. Mansfeld, F. Electrochemical Impedance Spectroscopy (EIS) as a New Tool for Investigating Methods of Corrosion Protection. *Electrochimica Acta*, v. 35, n. 10, p. 1533, 1990.
19. Jüttner, K. Electrochemical Impedance Spectroscopy (EIS) of Corrosion Process on Inhomogeneous Surfaces. *Electrochimica Acta*, v. 35, n. 10, p. 1501, 1990.
20. Raistrick, I. D. Impedance Studies of Porous Electrodes. *Electrochimica Acta*, v. 35, n. 10, p. 1579, 1990.
21. Senna, L.F.; Achete, C.A.; Freire Jr, F.L.; Hirsch, T. Structural, Chemical and Corrosion Resistance Characterization of TiCN Coatings Prepared by Magnetron Sputtering. *Surface and Coating Technology*, v. 94-95, p. 390, 1997.
22. Marcus, P.; Oudar, J. *Corrosion Mechanisms in Theory and Practice*, Marcel Dekker, Inc., New York, 1995.