Int. J. Electrochem. Sci., 5 **(2010)** 1799 - 1809

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Corrosion of Hot Pressing Titanium Coated Steels for Biomaterial Applications

*F. Barragán, R. Guardián, C. Menchaca, I. Rosales, J. Uruchurtu**

Universidad Autónoma del Estado de Morelos, CIICAp. Av Universidad 1001, Colonia Chamilpa, Cuernavaca, Mor., Mexico
*E-mail: juch25@uaem.mx

Received: 22 September 2010 / *Accepted:* 15 October 2010 / *Published:* 1 December 2010

Titanium diffusion process was applied to three selected steels, namely series AISI 1045, 4140 and stainless steel 304 using the hot pressing technique for a possible biomaterial use. Chemical analyses indicate that Ti diffuses into the steel matrix sample according to time of exposure, obtaining several microns in coating width and producing simultaneously a TiO_2 oxidized layer. Electrochemical evaluation namely linear polarization and electrochemical noise as a function of time, was performed for these different samples under Hank solution immersion conditions. The comparison of test results obtained after electrochemical experiments in Hank solution, indicate that treatment increased the corrosion resistance of steels, specially the AISI-304 stainless steel, presenting the formation and growth of a biofilm.

Keywords: Corrosion, titanium, steels, hot pressing, biomaterials

1. INTRODUCTION

For many years Ti alloys have become traditional biomaterials, which have been used to develop application, in several fields of medicine. It is well known that titanium cannot be used directly. A thin oxide cement layer, known as *osseointegration* must be between the titanium implant and the bone tissue [1]. To increase the performance of this material a big effort has been developed to form a bioactive titanium oxide layer on the metal surface using several ways as chemical, electrochemical, thermal treatment, and anodization methods among others [2-4]. Also titanium offers advantages such as good mechanical properties as well as corrosion resistance under biological fluid conditions, although material high cost is a holdup. Due to material high costs, an alternative for biomedical applications, is to select steels acting as a ductile core with a titanium coating. Similar behavior could be obtained maintaining titanium in contact with bone and body tissue (aqueous solution) without diminishing its mechanical properties, at a lower cost.

The purpose of the present work is to evaluate the corrosion behavior in Hank solution, of Ti diffusion coating over different steels under annealed condition. This treatment can be improved by a controlled heat treatment (Hot Pressing), generating a titanium coating with TiO_2 layers over steel. Good corrosion resistance behavior is expected combining mechanical properties obtained from steel at a lower cost, with enough quality to be applied as biomaterial.

2. EXPERIMENTAL PROCEDURE

A series of three commercial steels supplied by a commercial vendor, were used to perform this study, namely: AISI 1045, 4140 steel and 304 stainless steel. The chemical composition is presented in table 1. Each steel coupon with dimensions of 25.4 mm in diameter, and 5 mm width were cut, abraded by silicon carbide paper in successive grades from 600 to 1200 grit (Leco Corporation, MI), polished to a 0.1 µm finish with alumina powder. The different samples were pressed over with titanium sheets (3mm width by 25.4 mm in diameter) in a metallic holder with a pressure of 200 MPa, and then exposed to a *hot pressing* process, using an electrical furnace for a period of 6h at 900 °C. The samples were post-treated by the application of heating using an oxygen atmosphere at 550°C and then furnace cooled. Also a titanium sample (blank) was also prepared for comparison purposes.

Table 1. Materials chemical composition (wt %).

Material	C	Mn	Si	S	P	Cr	Ní	Mo
AISI1045	0.43-0.50	0.60-0.90		0.050 max.	0.040 max.			
AISI4140	0.38 - 0.43	0.75 - 1.00	0.20 – 0.35	0.040 max.	0.040 max.	0.80 – 1.10		0.15 – 0.25
AISI 304	0.08	2.00 max.	1.00 max.	0.030 max.	0.045 max.	18.00-20.00	8.00-12.00	

For corrosion experiments, specimens of 5x5x3 mm were obtained. After treatment the specimens were encapsulated in epoxy resin and abraded gently by silicon carbide paper using 1200 grit, and then polished up to 0.03 µm using diamond paste and finally rinsed with distilled water and ethanol. Electrochemical experiments were performed using an ACM Instrument controlled by a personal computer for different periods of immersion during 30 days.

The electrochemical free corrosion potential as a function of time of the working electrodes E_{corr}, was measured versus a saturated calomel reference electrode (SCE). Electrochemical noise measurements (EN) in both current and potential were recorded using two *identical* working electrodes and a reference electrode (SCE).

The electrochemical noise measurements were made recording simultaneously the potential and current fluctuations at a sampling rate of 0.5 point per second for a period of 2048 seconds,. A fully automated zero resistance ammeter (ZRA) from ACM instruments was used in this case. Removal of the DC trend from the raw noise data was the first step in the noise analysis when needed. To accomplish this, a least square fitting method was used. Finally, the noise resistance, $R_{n,}$ was then calculated as the ratio of the potential noise standard deviation over the current noise standard deviation ($R_n = \sigma_v / \sigma_i$) [5, 6].

For comparison linear polarization curves were obtained by polarizing the specimens from -30 to 30 mV with respect to the free corrosion potential value, E_{corr}, at a scanning rate of 10 mV/min and corrosion current density values, I_{corr}, were calculated. A typical three electrode arrangement was used with a saturated calomel reference electrode and a graphite rod was the auxiliary counter electrode.

Surface analysis were performed in a LEO-1450VP scanning electron microscope (SEM), as well as the chemical point analysis was performed by using the Energy Dispersive X-Ray Analysis (EDAX) system of the equipment..

3. RESULTS AND DISCUSSION

As an example, figure 1 shows the diffusion profiles obtained after the titanium *hot pressing* process, for the AISI 4140 steel sample.

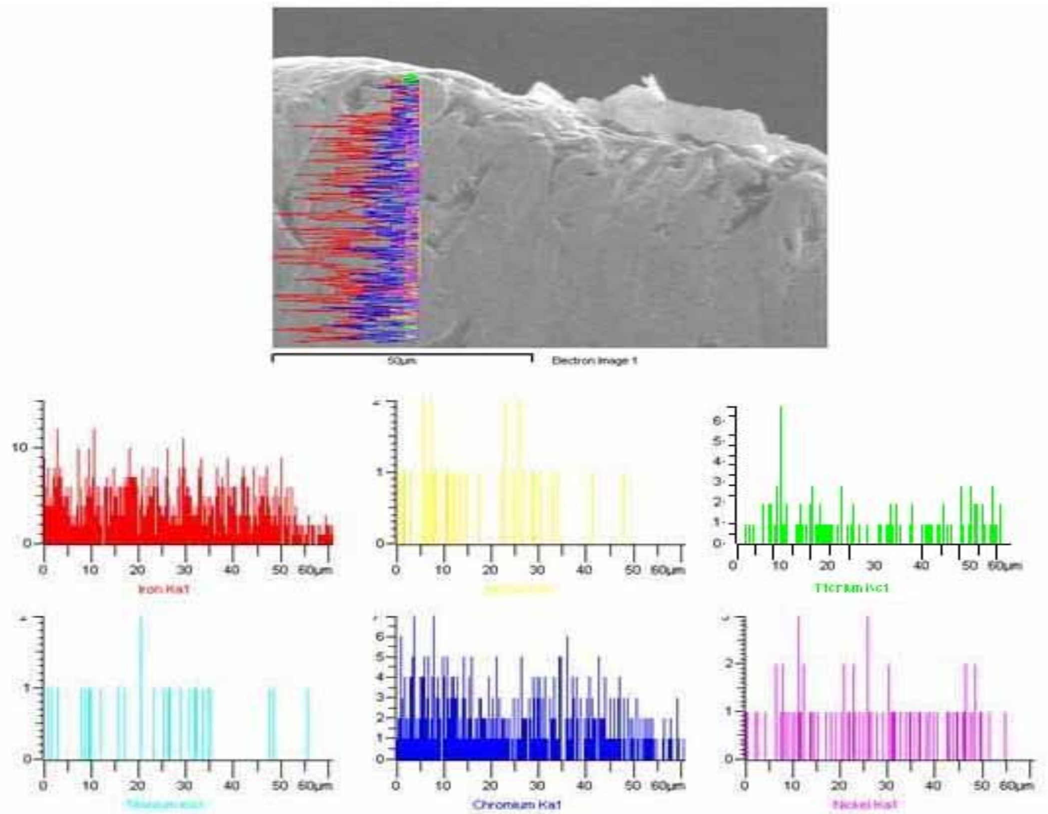


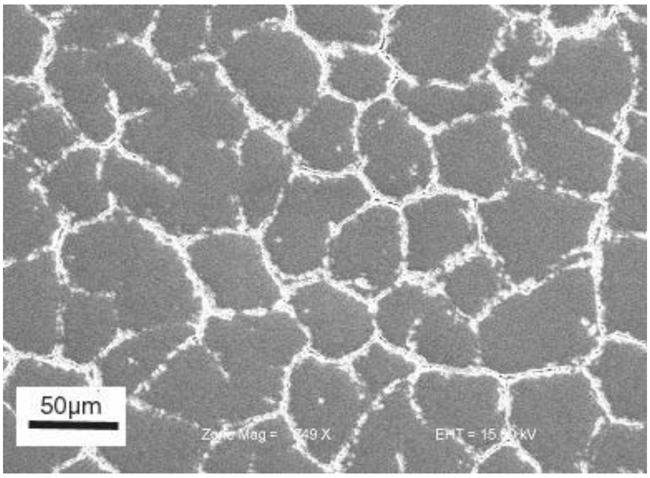
Figure 1. Cross-section lines scan analysis of the AISI 4140 steel Ti treated.

It can be observed that for the steel, the Ti diffusion from the surface sample through the inner sample structure reached the depth value of approximately 40 µm. This resulted film layer can be considered as a good diffusion response of the prepared sample, to accept homogeneously the Ti diffusion.

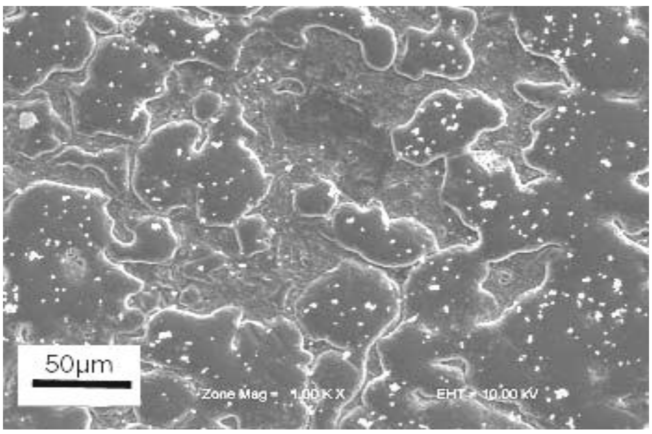
Several authors have reported deviations on the thickness of the formed layer in Cr alloyed steels [7, 8]. The systematic heat treatment application over the steels, evidently contributed to the Ti migration to the inner steel structure, and to the TiO_2 formation.

Nevertheless one of the steel samples showed poor corrosion performance, as evidenced from the electrochemical experimental results obtained, as explained below.

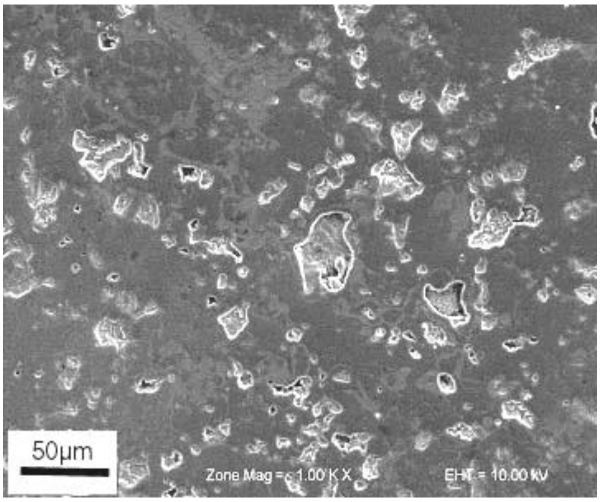
The surface images of the steels after being treated are shown in Figures 2 (a through c). It can be observed on the samples surface that the Ti scale remained present on the total surface of the sample. This fact guarantees that Ti distribution along the surface sample is homogeneous, and therefore the uniform Ti diffusion, corroborating the former result obtained by line scan analysis



(a)



(b)



(c)

Figure 2. SEM micrographs for steel surface treated with titanium: a) AISI 1045 steel b) AISI 4140 steel and c) AISI 304 stainless steel.

Figure 3 presents the corrosion potential as a function of time for the three different samples and for comparison, a titanium (blank) sample was also tested. All samples present a small transient behavior in the anodic direction, reaching a truly steady state condition after a few days. The exception was the 4140 steel sample, presenting a cathodic transient before reaching the steady state conditions. This behavior suggests the formation and the presence of a passive film over the titanium coating surface (TiO_2). The samples free corrosion potential, align according to their potential from: the most positive (-100 mVsce) for titanium, followed by 304 stainless steel (-300 mVsce), 4140 steel (-600 mVsce), and lastly 1045 steel (-700 mVsce), being titanium and the stainless steel samples the least prone to corrosion attack, according to these results.

Figure 4 presents the linear polarization resistance as a function of time results for the different samples, obtained over a thirty days immersion period. Erratic oscillating values were observed for the 4140 steel sample, changing the polarization resistance from 8E+02 ohm-cm^2 up to approximately 1E+09 ohm-cm^2, presenting the highest and lowest values for the samples tested. This behavior suggests localized corrosion conditions confirmed by the electrochemical noise measurements [9-12].

The average steady state polarization resistance values obtained for the other samples with titanium coating were: for 304 stainless steel approximately 1E+05 ohm-cm^2 (the highest value reached), slightly lower for titanium around 9E+04 ohm-cm^2; and less for 1045 steel sample with a low value reaching 1E+03 ohm-cm^2. These results obtained suggest lowest overall corrosion rates for the 304 stainless steel sample, comparable to the titanium blank sample. The highest corrosion rates were for the 1045 steel sample, while variable corrosion rates observed for the 4140 steel sample, could be ascribed to the presence of localized attack over the surface (see below) [11,12].

To follow up possible localized corrosion over the samples during the period of immersion, electrochemical noise tests were performed and results obtained. As an example, figure 5 presents electrochemical noise time series of: (a) potential, (b) current and (c) resistance for 1045 steel sample under different periods of immersion. Noise potential-time series (Figure 5a), present noiseless signals except for: one, two and ten day immersion periods showing slightly oscillating signals.

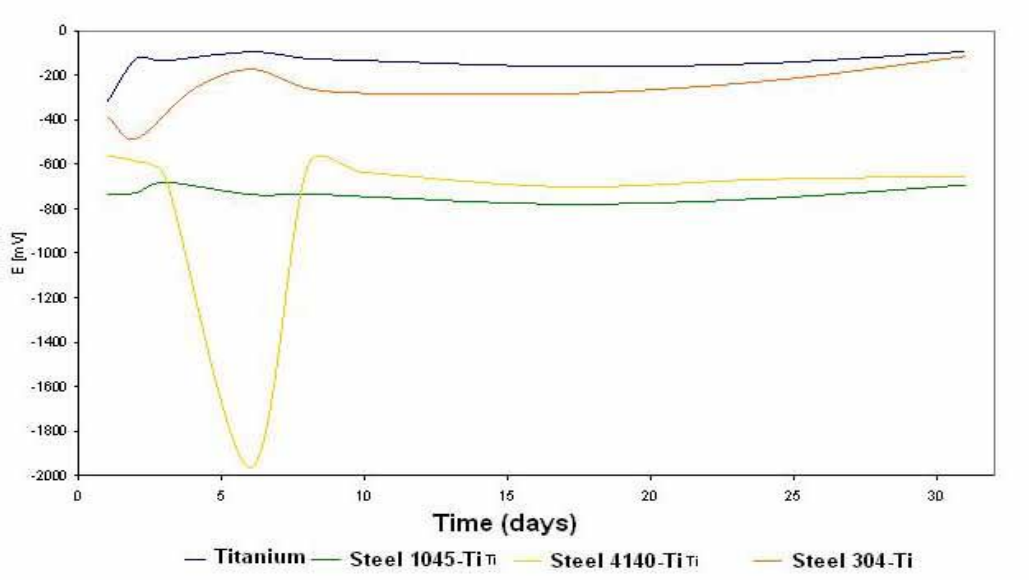


Figure 3. Free corrosion potential as a function of time for the Ti coated samples.

Contrary to this noise current-time series behavior (Figure 5b), large transients were observed for: one, six and twenty four days of immersion. This behavior could be associated to film breakdown-repassivation events in the case of the potential noise signals observed, while large transient behavior observed in the noise current time series could be related to localized attack propagation [11, 12]. The average noise current values lie between 1E-05 and 1E+-6 A/cm^2.

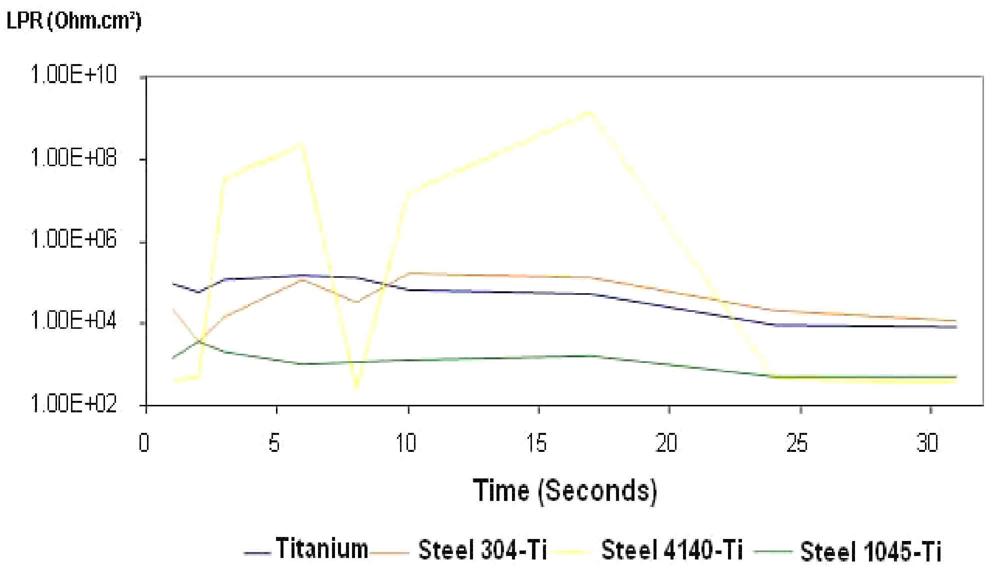


Figure 4. LPR for titanium and steel samples

Figure 5c presents the electrochemical noise resistance time series for different periods of immersion, obtained as the ratio of potential standard deviation over current standard deviation associated to the overall corrosion rates. The signals reflect the conditions of the corrosion surface, depending upon the type of attack present. Variable transient behavior in the noise resistance for: one, six and twenty four days of immersion associated to more localized attack. The average noise resistance values lie between 1E+05 and 1E+06 ohm-cm^2.

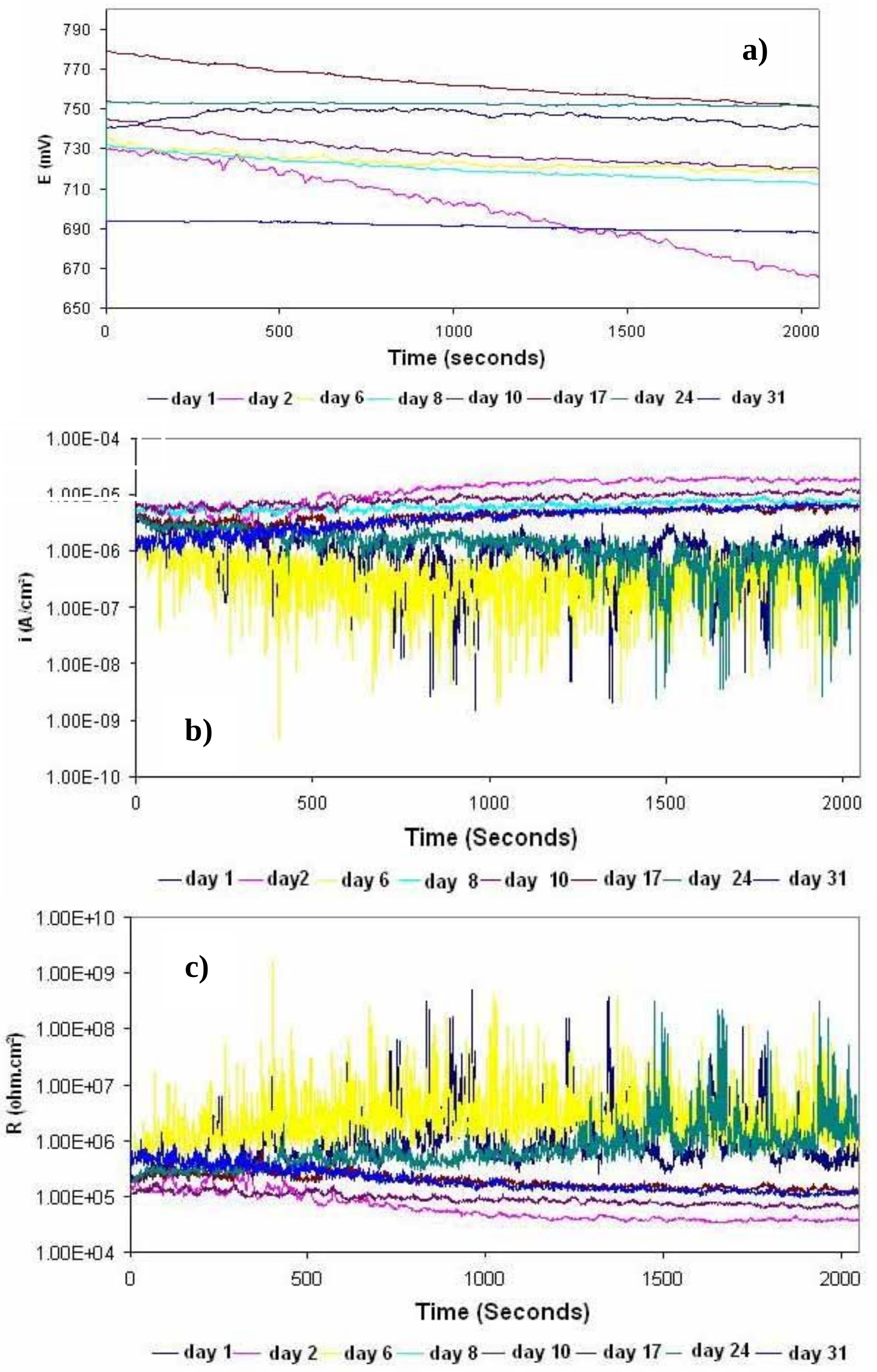


Figure 5. Electrochemical noise: (a)potential, (b)current and (c)resistance for 1045 steel for different periods of immersion.

Figure 6 presents the electrochemical noise resistance values for the steel samples, obtained for different periods of immersion. Noise resistance values vary as a function of time of immersion, reaching the highest transient values around 1E+04 ohm-cm^2, for the titanium (blank) and the 304 stainless steel sample; followed by the 1045 sample (1E+03 ohm-cm^2). All the steel titanium coated samples present variable noise resistance behavior. Exception was the 4140 steel sample with the lowest noise resistance value obtained close to 1E+02 ohm-cm^2, at the end of the experimental period. Also, the sample results present a trend to decrease as a function of time, reflecting the degrading corrosion effects suffered over time by the 4140 steel titanium coating, increasing its corrosion rate over time.

In general, the corrosion behavior of the steel samples, reflect the changing corrosion conditions over the metal surfaces along the period of immersion. They can go from passive conditions, film breakdown and localized attack, according to the electrochemical noise resistance values obtained [6, 12].

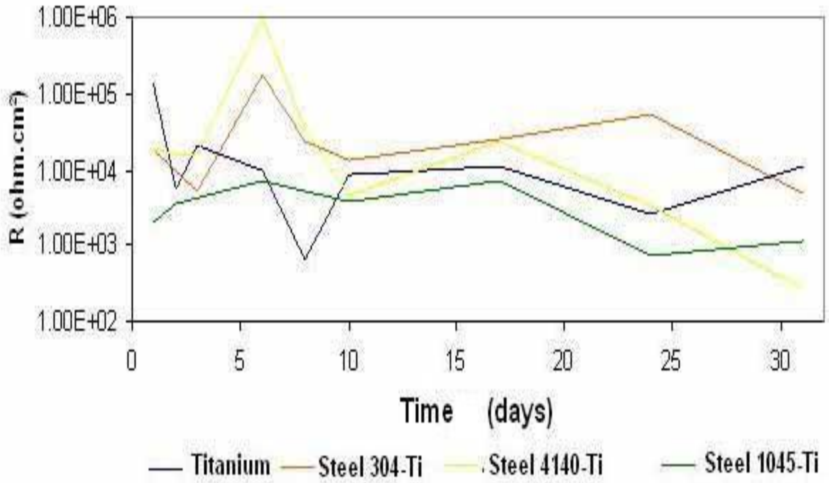


Figure 6. Electrochemical noise resistance for the steel - titanium coated samples for different periods of immersion.

After the end of the experiments, the sample surfaces were gently rinsed in tap water to remove what appears to be a bio-film over the surface. These films were visible after 2 weeks of immersion in the Hank solution, as reported in the literature [13-15]. Good adhesion conditions were observed for these bio-films, a condition regarding biomaterials interacting with body fluids and tissues. Afterwards the samples were prepared for SEM observations of the bio-film growth presence. Figures 7 (a to d) presents SEM micrographs of different areas and magnifications of the metal sample, showing what appears to be a bio-film growth over the 304 stainless steel Ti coated metal surface. Also, cracked metal film could be observed under the bio-film presence.

Figure 8 presents the surface condition of the metal samples: a) titanium sample, b) 1045 steel, c) 4140 steel and d) 304 stainless steel titanium coated samples, after rinsing and gently cleaning the surface with a brush. The blank titanium sample presents a clean surface while AISI 1045 steel sample presents the surface totally covered with iron corrosion products. The AISI 4140 steel sample presents some severe localized crevice corrosion attack at the left hand side and a slight attack at the edges of the metal sample, although the sides were covered with varnish before encapsulation to prevent this attack. Finally the 304 stainless steel sample presents a clean surface with very slight crevice attack quite similar to the titanium surface corrosion condition, as suggested by the electrochemical results obtained (see figures 3 to 6).

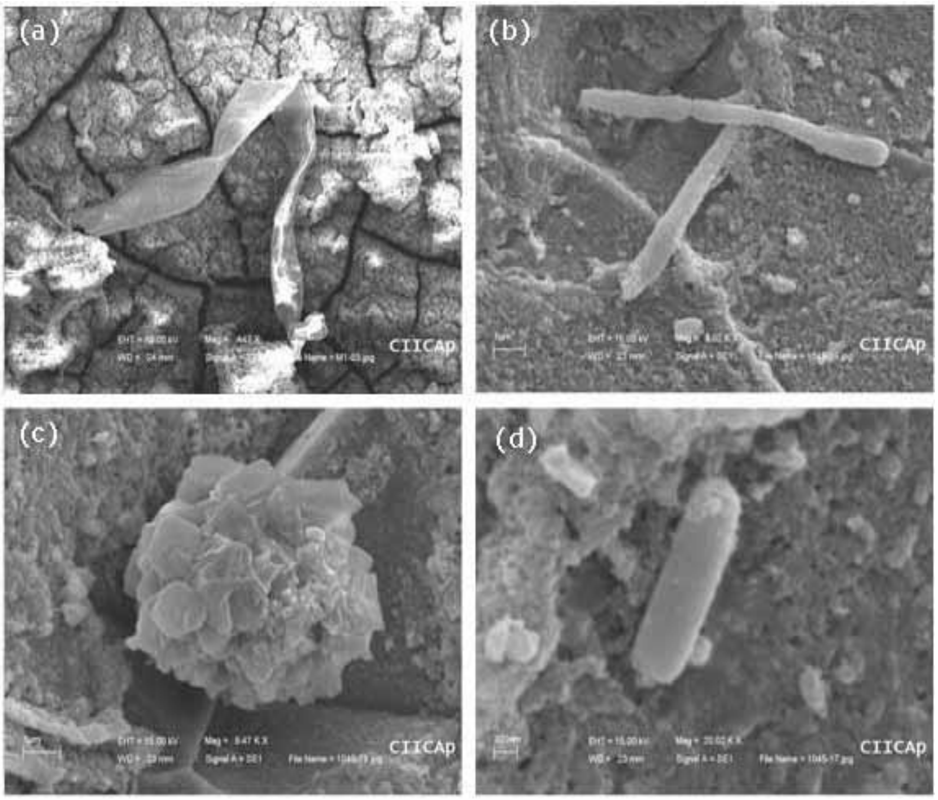


Figure 7. Biofilm formed over the 304 stainless steel Ti coated metal surface.

One possible reason for the corrosion behavior observed were the titanium diffusion process coating, related to the microstructure of the different steel samples. These are characterized, for: 1045 steel by a ferritic and perlite matrix, 4140 steel presents a ferritic matrix, while for 304 stainless steel the microstructure is austenitic type [16, 17]. The AISI 1045 steel presents a particular surface morphology due to the elevated oxidation that was developed during the test. This in turn is responsible for the poor Ti diffusion into the steel and lack of adhesion, which is promoted by the excessive presence of carbon in the steel structure, transforming it into the poor corrosion resistance performance obtained from the electrochemical measurements (see figures 3 and 4) and observed during the corrosion test (see figure 8).

The active free corrosion potential obtained and presented in figure 3, and the low polarization resistance (figure 4), are consistent with the poor corrosion behavior observed in AISI 1045 steel sample (see figure 8). The other two alloyed steel samples present more noble free corrosion potentials and higher polarization resistant values, therefore good corrosion behavior. One of them (4140 steel) presents some scattering in its results, suggesting possible localized corrosion attack [12]. This was confirmed by the electrochemical noise results obtained and presented in figure 5 and 6, and observed over the metal surface and presented in figure 8. Good adhesive properties of the grown bio-film, was obtained for the titanium coated steel samples (except 1045) confirmed by the SEM micrographs presented in figure 7.

Titanium is a well known material and widely used for biological applications, with good mechanical and corrosion properties[9, 18-20]. Titanium develops a passive film over the surface, and this is responsible for its good corrosion conditions. The use of steel provides an alternative cheaper material with good mechanical properties, and the titanium coating with an oxide film developed provides very good corrosion conditions and well proven bio compatibility, thus good bio material properties [18, 21]. The 304 Ti coated is comparable to Ti metal, preventing or inhibiting the formation of Cr^{6+}, that is formed with untreated 304 steel.

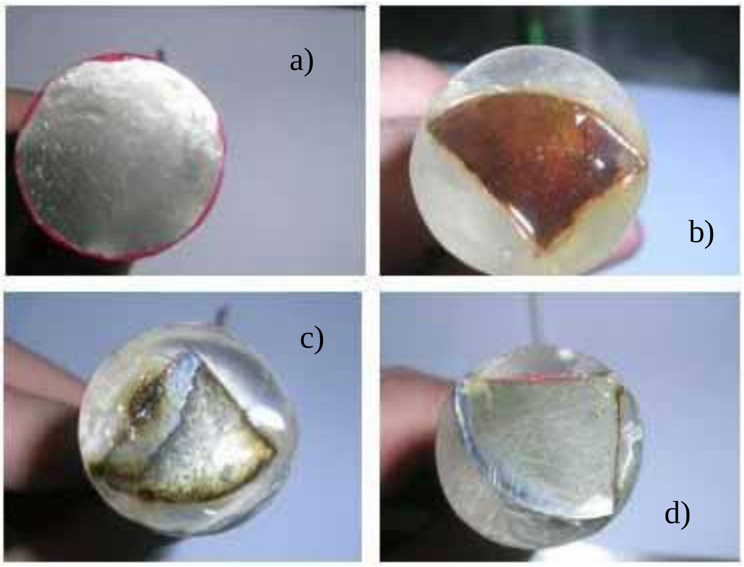


Figure 8. Surface condition of steel samples after cleaning: a) titanium, b) 1045 steel, c) 4140 steel and d) 304 stainless steel titanium coated samples.

4. CONCLUSIONS.

The proposed Ti diffusion by hot pressing coating treatment over steel samples, resulted to be a promissory alternative as a potential biomaterial. The best titanium treated corrosion performance obtained was the 304 stainless steel comparable to titanium; followed by 4140 steel presenting some localized crevice attack. The 1045 steel sample showed the worst performance, presenting a poor diffusion-adhesion conditions and general corrosion attack of the steel substrate.

ACKNOWLEDGEMENTS
The authors are grateful with PROMEP for financial support under grant UAEM-PTC-074 and CONACYT-S53120-Y.Technical support from M.A. Ramon-Garcia and J. Soto-Tapia is recognized.

References.

1. L. Sennerby, P.Thomsen and L. E. Ericson, *Mater. Med*., 3 (1992) 262
2. I. Jonasova, F. A. Muller, A. Helebrant, J. Strnad and P. Greil, *Biomaterial*, 25 (2004)1187
3. P. I. Brenemark, *J. Prosthet. Dent.*, 50 (1983) 399
4. P. I. Brenemark, B. O.Hansson, R. Adell, U. Breine, U.Lindstrom, O. Hellen and A. Ohman, *Scand. J. Plastic Reconstruct Surg.*, 11(1977) 1
5. J. R. Kearns, J. R. Scully, P. R. Roberge, D.L. Reichert, J. L. Dawson , *Electrochemical Noise Measurement, for Corrosion Applications, STP1277,* ASTM (1996)
6. R. Urzua, J. Siqueiros, L. Morales, I. Rosales and J Uruchurtu, *Portugaliae Electrochim. Acta*, 27 (2009) 127.
7. R. Gunzel, M. Betzl, I. Alphonsa, B. Granguly, P. I. John, S. Mukerjee, *Surf. Coat. Technol.* 112 (1999) 307
8. A. Marliska, M. P. Egert, A. R. De Souza, C., V. Spelle, A. N., Klein, *J of Mater Sci.* 23 (1997) 6375
9. A. González, *Control de la Corrosión: Estudio y Medida por Técnicas Electroquímica*, CENIM, (1989)
10. C. Huicochea, I. Rosales, I. E. Castañeda, J.Uruchurtu, *Portugaliae Electrochim. Acta*, 23 (2007)195
11. J. Genescá-Llongeras, *Técnicas Electroquímicas para el Control y Estudio de la Corrosión*, UNAM, (2001).
12. J. Uruchurtu, J. M. Malo, *Técnicas de Monitoreo y Control de Corrosion*, IMICORR, (1997).
13. U. Cano, M. Chavez, J. M. Malo, J. Uruchurtu, *Corrosao y Proteccao de Materiais* 13, 3 (1994) 11
14. M. Katsikogianni and Y. F. Missirlis, *European Cells and Materials*, 8 (2004) 37-57.
15. E, S. Leake, A. G. Gristina, and M. J. Wright, *J. of Clinical Microbiology*, 15, 2 (1982) 320
16. D. T.Llewellyn, *Steels: Metallurgy and Applications*, Butterworth-Heinemann, (1992).
17. D. I. Bardos, *Handbook of Stainless Steels*, McGraw Hill, (1977).
18. A. Ravaglioli, A. Krajewski, *Materials, Properties and Applicatios*, 5 (1992) 261
19. J.A. Ruiz, I. Rosales, J.G. Gonzalez-Rodriguez, J. Uruchurtu, *Int. J. Electrochem. Sci.*, 5 (2010) 593
20. E. Sarmiento, J. G. González-Rodriguez, J. Uruchurtu, O. Sarmiento, M. Menchaca, *Int. J. Electrochem. Sci.*, 4 (2009) 144
21. R. Bhola, S. M. Bhola, B. Mishra, D. L. Olson, *Int. J. Electrochem. Sci.*, 5 (2010) 917