Structural and tribological properties of Ti-TiN coatings obtained with a vacuum arc

L S Vaca¹, A Márquez²,³ and S P Brühl¹

¹Grupo de Ingeniería de Superficies – Facultad Regional Concepción del Uruguay, Universidad Tecnológica Nacional, Argentina
²INFIP, UBA-CONICET, Cdad. Universitaria, Pab. I, C1428EGA
Cdad. Autónoma de Buenos Aires, Argentina
³Member of CONICET

E-mail: laurasvaca@gmail.com

Abstract. In this work TiN and Ti-TiN bilayer coatings obtained with a vacuum arc on AISI 316 samples were proposed in order to improve hardness and tribological properties. The coatings were deposited with a DC cathodic arc running a 130 A current discharge between a Titanium cathode and the vacuum chamber employed as anode. The samples were placed 20 cm away from the cathode surface. TiN films were obtained employing a continuous nitrogen flux of ~20 sccm and a working pressure in the range of 3 × 10⁻² Pa. The structural and tribological properties were characterized by means of an optical microscope, scanning electron microscopy (SEM), x-ray diffraction (XRD), scratch test and fretting. The film thickness was about 0.5µm. Ti-TiN coatings presented better adhesion than TiN coatings and improved the fretting fatigue life compared to the untreated steel.

1. Introduction
The AISI 316L stainless steel is widely used in chemical, nuclear and food industry as well as in medical implants due to its excellent corrosion resistance and good biocompatibility. However, its low hardness, wear resistance and high friction coefficient limit the potential application of this material [1-3].

A way of improving the corrosion resistance and the adhesive wear resistance or the friction coefficient could be to coat the surface with a ceramic film like TiN. These kinds of coatings are widely used for hardening cutting tools made of high speed steels [4-6]. In particular, cathodic arcs have proved to be very attractive to deposit TiN coatings because they promote the formation of dense nanostructured films with a good adhesion and a very high deposition rate. In cathodic arc devices, an electrical discharge of high current (~100 A) and low voltage (~20 V) runs between two electrodes in a vacuum chamber. From the surface of the metallic cathode, a beam of metallic ions is ejected with energies between 20 – 100 eV; the ion current being approximately a 10% of the total discharge current. When a sample is exposed to the plasma, the surface is coated with a metallic film. If a reactive gas flows in the chamber, the substrate is covered with a metallic compound of the cathode material [7-9].
In this work TiN and Ti-TiN bilayer coatings on AISI 316L samples were obtained with a Titanium vacuum arc. Their mechanical properties were investigated and their corrosion resistance was also qualitatively assessed.

2. Experimental procedure

The samples were cut out with a size of 26 mm in diameter from a plate 2 mm in thickness, of AISI 316L whose certified composition is presented in table 1. The surfaces were polished and cleaned using an ultrasonic cleaner in acetone during 10 minutes.

The coatings were deposited with a DC cathodic arc discharge employing a Titanium cathode and the grounded vacuum chamber acting as anode. The arc current was set at 125 A. The samples were placed 30 cm away from the cathode surface and connected electrically to ground.

| Table 1. Chemical composition AISI 316L. |
| C % | Si % | Mn % | P % | S % | Cr % | Mo % | Ni % | Cu % | Ti % | N ppm |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------|
| 0.017 | 0.500 | 1.37 | 0.027 | 0.002 | 16.65 | 2.04 | 10.03 | 0.140 | 0.006 | 216 |

A group of samples was coated with TiN films and a second group of samples with a Ti-TiN bilayer. The samples coated with TiN were exposed to four discharges of three minutes each (a total time of 12 min) with 20 sccm N₂ flow at a work pressure of 3.10⁻² Pa. The Ti-TiN samples received a discharge in vacuum of 1.5 minutes at a lower working pressure, 10⁻² Pa, and then three discharges of three minutes each with a 20 sccm N₂ flow, achieving a working pressure of 3.10⁻² Pa, adding up a total time of exposure to the discharge of 10.5 min. In all cases, the waiting time between two consecutive discharges was 15 minutes.

The deposited mass was determined by weighting the samples before and after the discharges using an Ohaus analytical balance, model AS200. The coating adhesion was evaluated by means of the Tape Test performed with a commercial scotch tape and the Scratch Test employing a Hand Operated Scratch Tester (model 706, Sheen Instrument Ltd.) with a 1 mm tungsten carbide ball with a needle point and with constant loads varying from 5 to 20N. The coating surfaces were observed with a scanning electron microscope Philips SEM 505 (with Soft Imaging System ADDA II (SIS)). Also, the samples were cut and embedded in resin, so as to observe the lateral profile of coatings with a scanning electron microscope Philips 515. The coating structure was studied with X ray diffraction (XRD) employing a Philips diffractometer 1732/10.

Qualitative corrosion tests were performed in order to evaluate the corrosion resistance of the samples. First, the CuSO₄·5H₂O drop test was performed according to ASTM A967 in practice “D” to evaluate the passivity of the material, then the samples were attacked with Marble reagent during 10 s. Marble reagent contains chlorhydric acid (4g CuSO₄, 20 ml HCl, 20 ml H₂O) and it is normally used to reveal structure in austenitic stainless steels.

Wear resistance was evaluated by means of the linear reciprocal sliding and fretting tests. The samples were subjected to a reciprocal sliding wear test, with 2.85 N load, WC counterpart ball of 5 mm in diameter, 953 µm in amplitude and half hour duration. The reciprocal test wear tracks were observed with 50x magnification with an optical microscope Mikoba with Digital Camera DCM500 (USB2.0) Resolution 5 Mixels and the wear scar depth was measured with a roughness tester acting as a profilometer (Mitutoyo Surf test SJ-210). The fretting test was carried out with the same load, counterpart ball and time, but only with 84 µm amplitude, in order to analyze another kind of wear mechanism, mainly plastic deformation and less abrasion. The wear scars were observed with scanning electron microscope (SEM).
3. Results

The deposited mass in the case of TiN coatings was \((0.7 \pm 0.1)\) mg while the gained mass in the samples coated with Ti-TiN was \((1.6 \pm 0.1)\) mg. The big difference in the deposited mass for similar exposure times can be attributed to the fact that the erosion rate of the cathode is higher in vacuum than in the presence of nitrogen. This could be the consequence of the fact that the contamination of the surface not only diminishes the erosion rate, but also changes the conditions of the discharges turning them less repetitive.

The thickness of the TiN coatings can be estimated assuming a density for the film as the tabulated for the bulk material \(\rho_{\text{TiN}} = 5.4 \ \text{g/cm}^3\), then the TiN film thickness was \(\approx 250\) nm. In the case of the bilayers, composed by Ti \(\rho_{\text{Ti}} = 4.5 \ \text{g/cm}^3\) and TiN, both density values were employed and the film thickness was estimated in the range \((630 – 750)\) nm. SEM micrographs with 5000x magnification of lateral cuts of a TiN film and a bilayer film are shown in figure 1. In the SEM images the film cannot be observed along the whole surface; because part of the film was broken when the sample was cut previously to the inclusion in resin. However, the film thickness could be measured and was about 700 nm for the Ti-TiN coating and 300 nm for the TiN coating, agreeing with the calculated values.

![Figure 1. SEM micrograph of lateral cut of samples: (a) Ti-TiN coating and (b) TiN coating.](image)

In figure 2, XRD patterns of the bilayer and TiN coatings are shown. In figure 2(a) the characteristic diffraction peaks of austenite and TiN corresponding to planes \((111)\) and \((200)\) can be distinguished clearly; and the small peak located between TiN peaks at 38.5 degrees can be associated to the Ti \((101)\) plane. In the case of the TiN coating, the same TiN peaks were registered in the diffractogram and also appeared the third TiN peak, corresponding to the \((220)\) plane.

![Figure 2. X-ray diffractograms for: (a) Ti-TiN coating and (b) TiN coating.](image)
The surface morphology of the coatings can be observed in the SEM micrographs presented in figure 3. The Ti-TiN bilayer coatings exhibited an irregular surface with the presence of a few macroparticles while the TiN coatings surface was smoother. Small holes, probably left by the detachment of macroparticles, can also be noticed on both surfaces. However, SEM images with 100kx magnification of lateral cuts of the coatings showed compact films without holes, as shown in the SEM image of figure 4.

The coating roughness was (0.224 ± 0.020) µm for the Ti–TiN bilayer and (0.088 ± 0.007) µm for the TiN film.

The Scratch Test allowed determining that the bilayer coatings had better adhesion to the substrates than the TiN coatings. Pictures of the tracks for the different films are shown in figure 5. For the TiN films some delamination failures on the track were detected with a load of 10 N, while for the bilayer coating no failures were observed in the tested load range, until 20 N. Probably, the better adhesion behavior of the Ti–TiN film could be attributed to its greater thickness but it could be also a consequence of the presence of the Ti interlayer, which generates a graduated hardness profile between the film and the substrate [10-12].

The CuSO₄ 5H₂O drop test and the Marble reagent attack yielded negative results in both types of coatings. Even though these are qualitative experiments; they could indicate that the films are chemically inert like other authors reported for these kind of films [13,14].

SEM images of the scars after performing the fretting test are shown in figure 6. The Ti-TiN coating (figure 6(b)) demonstrated a better behavior than the untreated sample and the TiN coating. Anyway, the scars in both coated samples are of smaller size than in the untreated material. In spite of the surface imperfections, it can be noted that in the Ti-TiN coating the fretting test only produced a
small deformation while in the TiN coating the scar were bigger, a small amount of abrasion was observed such as in the untreated sample and also the film was delaminated around the scar.

![Scratch track](image)

**Figure 5.** Scratch track (a) obtained with a 20N load on Ti-TiN and (b) obtained with 10N load on TiN.

![SEM images](image)

**Figure 6.** SEM images with 200x magnification of fretting scars: (a) untreated sample, (b) Ti-TiN coating and (c) TiN coating.

In the case of the linear reciprocating tests, it can be seen in figure 7 that in the untreated sample the wear track was bigger and deeper, and severe abrasion could be observed, together with a large amount of deformation. Such as in the previous test, both coated samples showed a better wear resistance than the untreated material, but the wear scar in the Ti-TiN coated sample was the smaller. The TiN film presented again some delamination around the scar.

The scar profiles were obtained with the profilometer. For a better comparison, the profile points were copied in an Origin worksheet, they were all aligned and centered, and the final profiles were depicted all together in one graphic (figure 8).

The scar profiles sections have been measured and the values were compared to that of the untreated sample. Assuming this result as the volume loss in the wear test, then in the TiN coated sample the loss was about 57% respect to the value measured for the untreated sample and in the Ti-TiN, it was only 19%. In both films the wear track was deeper than the film thickness, meaning that
the films were lost throughout the test, and as the TiN film was thinner than the Ti – TiN one, its wear resistance was lower.

Figure 7. Micrograph with 50x magnification of reciprocal sliding scars: (a) untreated sample, (b) Ti-TiN coating and (c) TiN coating.

![Micrograph with 50x magnification of reciprocal sliding scars](image)

Figure 8. Reciprocal sliding wear scars.

4. Conclusions
The qualitative corrosion tests showed that both coatings were chemically inert, quantitative corrosion tests should be carried out in the future. In all mechanical tests the scars were greater in the TiN film than in the Ti – TiN film and some delamination was observed around the scars. Also the scratch test revealed the failure of the TiN coating for 10 N load when the Ti-TiN was not broken with 20 N. Both films protected the steel in the tested conditions but it should notice that in the case of the Ti-TiN film, all the scars were very shallow indicating a better wear resistance, especially in the linear reciprocating test, where it was increased 75% with respect to the untreated material.

Finally, it is generally accepted that the presence of macroparticles is a drawback of the cathodic arc process; although in these work the performance of the coatings did not seem to be strongly affected by them, they could be eliminated with the incorporation of filters like a magnetic island.
Acknowledgments
The authors would like to thank J. Tara and M. Sánchez (CINDECA-UNLP) for their technical assistance in DRX and SEM; J. Cimetta, N. García, N. Pecina, G. Schierloh and E. Dalibón (FRCU-UTN) for the collaboration in the wear tests. They would also like to thank the financial support from FRCU and CONICET.

References
[1] Kottel C M, Sprague J A and Smidt F A 1994 ASM Handbook vol 5 (Ohio: ASM International)
[2] ASM International Handbook Committee 1990 Metals Handbook vol 1 (Ohio: ASM International)
[3] Sendriks A J 1996 Corrosion of Stainless Steel 2nd Ed. (New York: Wiley & Sons)
[4] Rybiak R, Fouvry S, Liskiewicz T and Wendler B 2007 Surf. Coat. Technol. 202 1753–63
[5] Wu P-Q, Tang B and Celis J–P 2006 Surf. Coat. Technol. 201 413–7
[6] de Wit E, Froyen L and Celis J–P 1998 Wear 221 124–33
[7] Bruzzone H, Kelly H, Márquez A, Lamas D, Ansaldi A and Oviedo C 1996 Plasma Source Sci. and Technol. 5 582–7
[8] Boxman R L, Martin P J and Sanders D M (eds) 1995 Handbook of Vacuum Arc Science and Technology (New Jersey: Noyes)
[9] Krella A 2009 Surf. Coat. Technol. 204 263-70
[10] Chen L, Wang S Q, Zhou S Z, Li J and Zhang Y Z 2008 Surf. Coat. Technol. 26 456-60
[11] Thao Y, Lin G, Xiao J, Du H, Dong C and Gao L 2011 Appl. Surf. Sci. 257 2683-8
[12] Puchi-Cabrera E S, Martínez F, Herrera J and Berrios J A 2004 Surf. Coat. Technol. 182 276-86
[13] Liu C, Yang D, Lin G and Qi M 2005 Mat. Lett. 59 3813-9
[14] Liu C, Lin G, Yang D and Qi M 2006 Surf. Coat. Technol. 200 4011-6