Corrosion Resistance of Single TiN Layers, Ti/TiN Bilayers and Ti/TiN/Ti/TiN Multilayers on Iron Under a Salt Fog Spray (Phohesion) Test: an Evaluation by XPS

J. F. Marco,[1,]* A. C. Agudelo,[1,]† J. R. Gancedo[1] and D. Hanžel[2]

[1] Instituto de Química-Física 'Rocasolano', CSIC, c/ Serrano 119, 28006 Madrid, Spain
[2] Institute J. Stefan, PO Box 3000, SI-1001 Ljubljana, Slovenia

The corrosion resistance of three different TiN coatings on iron (single TiN layer, Ti/TiN bilayer and Ti/TiN/Ti/TiN multilayer) subjected to a salt (ammonium sulphate and sodium chloride) fog spray (Prohesion) test has been investigated by means of x-ray photoelectron spectroscopy (XPS). The relative intensities of the Fe 2p and O 1s signals in the XPS spectra of the corroded samples increase with their extent of degradation. The results show that the corrosion resistance of these coatings decrease in the order bilayer > multilayer > single layer. Copyright © 1999 John Wiley & Sons Ltd.

KEYWORDS: TiN coatings; XPS; corrosion; salt fog spray test; Prohesion

INTRODUCTION

The applications of titanium nitride-based hard coatings are quite vast and include, just to mention a few, wear protection,[1] diffusion barrier on semiconductors,[2,3] electronic devices,[4] antimultipactor coatings for r.f. superconducting cavity structures,[5,6] decorative coatings[7] or corrosion protection.[1,7,8] The properties of TiN (chemical stability and good adhesion to most steel substrates) make it, in particular, an effective material in the field of corrosion protection. It has also been shown[8,9] that the addition of an intermediate Ti layer between the steel substrate and the TiN layer noticeably improves the corrosion resistance of the latter, particularly in the case of aqueous corrosion. It is thought[8,9] that the addition of an intermediate Ti layer (or the intercalation of several Ti/TiN structures between the steel substrate and the outermost TiN layer) increases the density and improves the adhesion of the overall coating, therefore the possibility of corrosion by mechanisms such as galvanic action, crevice or pitting corrosion or capillary condensation, which could occur if small pores are present in the coating, is reduced. In previous papers[10,11] we have studied the corrosion resistance against humid SO_2-polluted atmospheres that TiN coatings bring about on a pure Fe substrate when they are modified by adding a single layer as adhesion improver, or when different multilayered structures of the Ti/TiN series are produced. These

studies corroborated the conclusions that other authors[9] extracted from electrochemical measurements: the use of multilayered structures of the type Ti/TiN/Ti/TiN results in a better corrosion protection of the steel substrate, even with a much lower total thickness of the coating than the use of single-layer TiN coatings. In this paper we extend the results obtained in SO_2-polluted atmospheres on the corrosion resistance of coatings of the type TiN, Ti/TiN and Ti/TiN/Ti/TiN by subjecting them to a different test called Prohesion (see Ref. 12 and Experimental section for a description). This kind of test was developed to assess the quality of anticorrosive metal paints. X-ray photoelectron spectroscopy (XPS) has been the main analytical technique used in this work to evaluate the extent of degradation of the investigated coatings.

EXPERIMENTAL

The samples used in this work consisted of TiN, Ti/TiN and Ti/TiN/Ti/TiN (see Table 1 for a detailed description) coatings deposited on top of a 100 nm layer of iron previously deposited on silicon wafers of (100) orientation. Each type of thin film was produced in one run without exposure of samples to the air in-between. The Fe and TiN and Ti/TiN layers were deposited by reactive d.c. sputtering (Sputron, Balzers[13–15]) using

* Correspondence to: Dr José F. Marco, Instituto de Química-Física 'Rocasolano', Consejo Superior de Investigaciones Científicas c/Serrano 119, 28006 Madrid, Spain.
   E-mail: jfmarco@iqfr.csic.es
   † On leave from Universidad Nacional Manizales, Colombia.
Current address: Universidad Nacional, Palmira, Colombia.

Table 1. Description of the samples

Sample SL	Si/Fe (100 nm)/TiN (1000 nm)
Sample BL	Si/Fe (100 nm)/Ti (100 nm)/TiN (1000 nm)
Sample ML	Si/Fe (100 nm)/Ti (100 nm)/TiN (100 nm)/Ti (100 nm)/TiN (100 nm)

Table 2. Binding energies obtained from the XPS data recorded from the as-prepared samples

Species	Core level	Binding energy (eV)	Assignment	Reference
Ti1	$2p_{3/2}$	454.8	TiN	18–27
	$2p_{1/2}$	460.6		
Ti2	$2p_{3/2}$	456.8	TiO_xN_y	19, 21, 23–25
	$2p_{1/2}$	462.5		
Ti3	$2p_{3/2}$	458.2	TiO_2	18, 21, 26
	$2p_{1/2}$	463.9		
N1	1s	395.8	N—C, N—O in TiO_xN_y	22; 24, 27 resp.
N2	1s	396.8	TiN	18–22
N3	1s	398.5	N—O in TiO_xN_y	21, 22
O1	1s	529.7	Ti—O	18, 26
O2	1s	531.5	Ti—O bulk, OH	22; 28 resp.
O3	1s	532.7	C—O, H_2O	22; 28 resp.
O4	1s	534.2	H_2O	28

bulk metallic Fe and Ti targets, respectively. During the deposition, no bias voltage was applied and the substrate temperature was kept at 573 K. The base pressure in the preparation chamber was lower than 1×10^{-4} Pa. The TiN layers grow in a fine-grained polycrystalline columnar structure with a 15–20 nm column width, as determined by cross-section transmission electron microscopy (TEM).[16]

Nine square pieces of ~ 10 mm $\times$ 10 mm, three for each type of coating but proceeding from different batches, were the samples subjected to each Prohesion test.[12] This test is basically a kind of salt fog spray test and consists of the following: the samples are exposed slightly tilted from the vertical position in a chamber, where they are sprayed at room temperature for 1 h with a solution containing 0.40 wt.% ammonium sulphate and 0.05 wt.% sodium chloride. Then the spraying is stopped and the temperature of the chamber is raised to 35 °C for 1 h. In a typical Prohesion test this cycle (1 h of spraying and 1 h kept at the elevated temperature) is repeated for 24 h. In our case the test was stopped after four cycles (8 h) because some of the samples showed considerable degradation.

The XPS data were recorded using a Leybold–Heraeus LHS-10 spectrometer under an operating vacuum of better than 1×10^{-6} Pa, using Al Kα radiation (130 W) and analyzer transmission energies of 150 and 50 eV for the wide- and narrow-scan spectra, respectively. The spectra were recorded at take-off angles of 90°. All binding energy values were charge-corrected to the adventitious C 1s signal, which was set at 284.6 eV, and are accurate to ± 0.2 eV. Relative atomic concentrations were calculated using tabulated atomic sensitivity factors.[17]

RESULTS AND DISCUSSION

The characterization of the as-prepared coatings has been carried out extensively in previous papers[10,11] and will not be repeated here. We would only mention that the XPS spectra recorded from the three types of samples were very similar and only showed Ti, N, O and C peaks. The binding energies and the relative intensities of the main species (as well as the N/Ti and

O/Ti atomic ratios) are collected in Tables 2 and 3, respectively.

Visual inspection of the samples after the Prohesion test showed that the appearance of sample BL was very similar to that of the as-prepared sample, except for the existence of very few, small white spots on the surface. However, samples SL and ML showed the presence of a large number of brown spots on the surface, suggesting that they suffered a higher degradation under that test than sample BL.

Figure 1 depicts the wide-scan spectra recorded from one of the as-prepared coatings (as mentioned above, the wide-scan spectra recorded from all three types of coatings were very similar) and the wide-scan spectra recorded from each of these coatings after submission to the Prohesion test. It can be observed clearly that whilst the spectrum corresponding to sample BL is very similar to that of the as-prepared coatings, the spectra of the other two samples show intense lines in the Fe 2p and Fe LMM regions. All the samples showed additional S peaks, as well as Cl and Na signals. We would also mention that the relative intensity of the O 1s signal is larger for samples SL and ML than for sample BL. If, as we have suggested in a previous paper,[11] the relative intensities of the Fe 2p and O 1s signals are

Table 3. Relative intensities and atomic ratios obtained from the XPS data recorded from the as-prepared samples

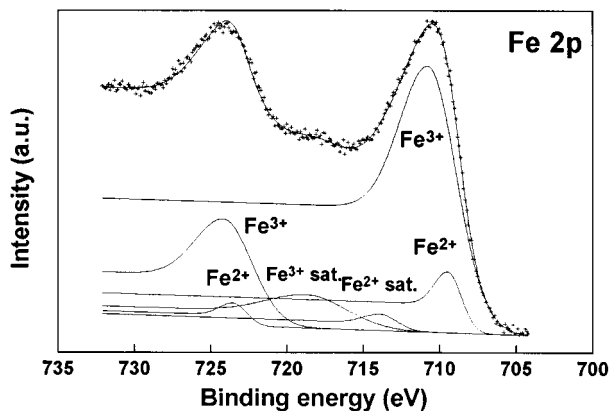| Species	Sample SL	Sample BL	Sample ML
Ti1	48	46	56
Ti2	19	26	16
Ti3	33	28	28
N1	13	15	13
N2	61	60	60
N3	26	25	25
O1	53	61	49
O2	27	24	26
O3	15	11	17
O4	5	4	8
Atomic ratios			
N/Ti	1.08	1.04	1.06
O/Ti	1.00	0.80	0.96
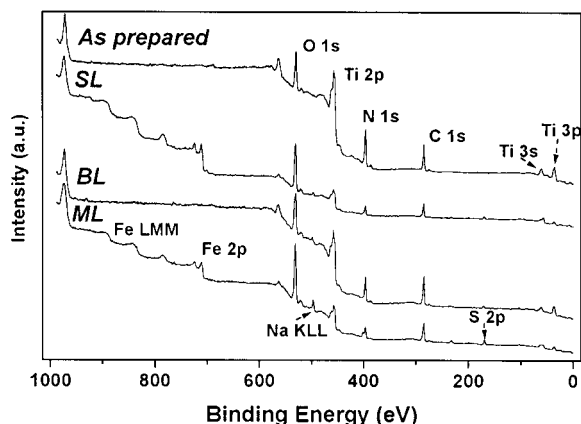
Figure 1. Wide-scan spectra recorded from one of the as-prepared coatings (SL) and from the samples exposed to the Prohesion test.

taken as an indication of the extent of degradation of the samples, it is clear (Table 4) that the corrosion resistance of the studied TiN coatings increases in the order SL < ML < BL. Visual appearance and XPS data of exposed samples were very reproducible for each type of coating.

Analysis of the Fe 2p narrow-scan spectra recorded from samples SL and BL (Fig. 2) showed that most of the iron (80–90%) is in the form of Fe^{3+} (BE Fe $2p_{3/2} = 711.2$ eV, BE Fe $2p_{1/2} = 724.8$ eV, 'shake-up' satellite at 719.3 eV) and the rest (10–20%) is in the form of Fe^{2+} (BE Fe $2p_{3/2} = 709.9$ eV, BE Fe $2p_{1/2} = 723.6$ eV, 'shake-up' satellite at 714.3 eV).[28–30] We associate, then, the brown spots with the presence of oxidized Fe species, possibly in the form of Fe^{3+} oxyhydroxides. The presence of oxyhydroxides is strongly supported by the O 1s spectra, which show (Fig. 3) a strong peak at 531.5 eV (contribution O2) that is characteristic of OH groups.[28] Finally, we would comment that the S 2p (Fig. 4) spectra are fully consistent with the presence of sulphate species (BE S $2p_{3/2} = 169.2$ eV, BE S $2p_{1/2} = 170.5$ eV).[31]

It is also interesting to note that, as observed in a previous work,[11] although samples SL and ML have suffered considerable degradation, as indicated by the presence of a considerable amount of oxidized Fe species in the XPS spectra, the chemical transformations induced by the corrosion test in the coatings

**Table 4.** Atomic ratios calculated from the XPS data recorded from the samples exposed to the Prohesion test

| Sample	Fe/Ti	O/Ti
SL	1.10	3.90
BL	0.00	1.55
ML	0.58	3.63

themselves have not been very large. The Ti 2p spectra recorded from the exposed samples are very similar to those shown by the as-prepared samples, and only the N 1s spectra of samples SL and ML show (Fig. 5) new contributions (N4, N5, N6) in the binding energy range 398–403 eV (Table 5). The nature of these species has been discussed already:[10] they correspond to N species formed during the corrosion process and contain N—H and N—O bonds.[10,11,32,33] However, in the present case we cannot ignore the fact that a certain contribution to the peak at 399.6 eV, which is characteristic of
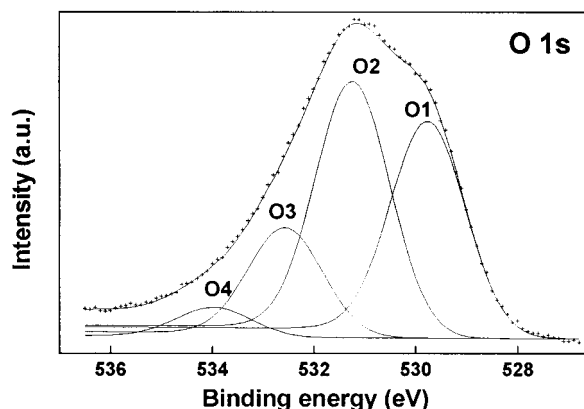
Figure 3. Oxygen 1s spectrum recorded from sample SL after the Prohesion test.

Figure 2. Iron 2p spectrum recorded from sample SL after the Prohesion test.
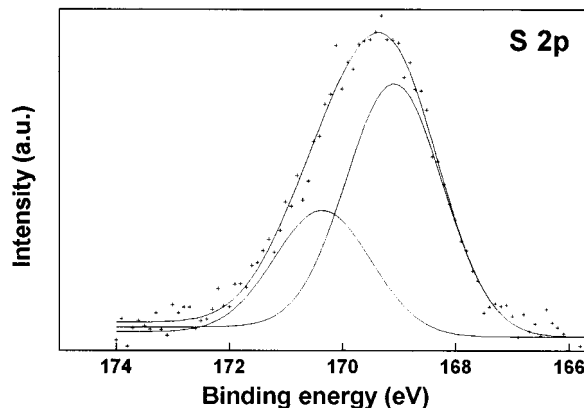
Figure 4. Sulphur 2p spectrum recorded from sample SL after the Prohesion test.
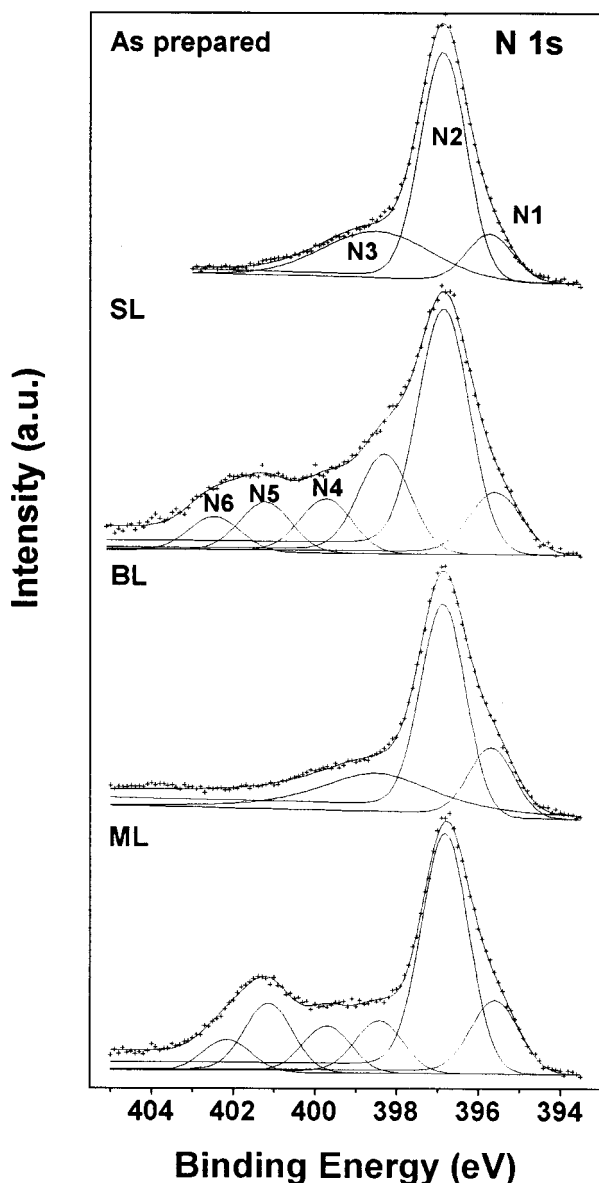
Figure 5. Nitrogen 1s spectra recorded from one of the as-prepared coatings (SL) and from the samples exposed to the Prohesion test.

N—H bonds,[10] can be due to the $NH_4{}^-$ ions contained in the salt fog solution.

It follows that although almost chemically inert, some of these coatings cannot prevent corrosion of the underlying substrate because they allow permeation of the corrosive solution to the iron/coating interface. This permeability should be related to the intrinsic nature of the TiN films, which grow in a columnar form, as well as the possible existence of defects such as micropores.[9] As stated in the Introduction, we have tried to reduce the porosity of the overall coatings by intercalating a single Ti layer or by using a multilayered Ti/TiN/Ti/TiN structure. Under the corrosive conditions used in the present investigation, coating BL presents the best performance. This behaviour presents differences with the behaviour observed in our previous studies[10] in SO_2-polluted atmospheres, where we found that coating ML performs similarly to coating BL, or even better, despite its considerably smaller thickness. It seems that in the very aggressive conditions of the Prohesion test, where additional to sulphate ions there are ammonium and chloride ions, which can accelerate pitting corrosion, the Ti/TiN bilayer exhibits the best corrosion protection. However, it must also be taken into account that the corrosion protection produced by the multilayered Ti/TiN/Ti/TiN structure is noticeably better than that of the thicker, single TiN coating.

CONCLUSION

(1) The corrosion protection brought about on a pure Fe substrate by a TiN coating 1000 nm thick in the simultaneous presence of sulphate, ammonium and chloride ions, under the conditions of a Prohesion test, can be outstandingly improved by adding a 100 nm thick Ti layer between the TiN layer and the Fe substrate. The corrosion protection produced on a pure Fe substrate by multilayered structures of the type Ti/TiN/Ti/TiN, with overall thickness ~ 2.75 times lower than the two mentioned above, under the same corrosion conditions, is noticeably higher than that of the single, thicker TiN coating, but much lower than that shown by the thicker bilayer Ti/TiN structure.

(2) Provided that the cost of a coating is mainly related to its thickness, for the appropriate choice of a particular coating, the degree of required protection against a determined medium has to be tested for different stacking layered configurations.

(3) The suitability of the Prohesion test, primarily intended for organic coatings whose protection performance is mainly determined by the permeability to the aggressive media, appears to be appropriate also for the type of coatings considered in this investigation where the corrosion protection is also related to porosity.

Table 5. Binding energies and relative intensities of the different N contributions to the N 1 spectra recorded from the samples subjected to the Prohesion test

Species	Be (eV)	Assignment (ref.)	Sample SL	Sample BL	Sample ML
N1	See Table 2	See Table 2	11	16	14
N2	See Table 2	See Table 2	45	49	47
N3	See Table 2	See Table 2	18	35	10
N4	399.6	N—H (11)	10	—	9
N5	401.3	N—O (32, 33)	9	—	14
N6	402.8	N—O (32, 33)	7	—	6

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