



Ion beam analysis of TiN/Ti multilayers deposited by magnetron sputtering

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Abstract

TiN/Ti multilayers, 1.74–9.80 μm thick, were deposited on 304 stainless steel substrates by reactive unbalanced magnetron sputtering. It is known that such multilayers can improve the corrosion resistance of the stainless steel. The titanium layers help to reduce the occurrence of pinholes that arise because of the irregularities in substrate surface, and decrease the porosity of subsequent TiN coatings by improving the layers microstructure. A 1400 keV deuterium beam was used to analyse the samples and combinations of RBS/NRA methods were applied to evaluate the sample spectra. The $^{14}\text{N}(d,\alpha_1)^{12}\text{C}$ NR cross sections are well known and were used as way to determine the ^{14}N concentration in the TiN_x layers. The corrosion resistance of the layers was studied by means of potentiodynamic polarization in a 0.5 M NaCl solution. The corrosion test demonstrated that the number of TiN/Ti layers and its total thickness determine the corrosion resistance.

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1. Introduction

If the passive chromium oxide surface layer formed on austenitic stainless steel is damaged, it can suffer from localized corrosion and one way to protect against this is by the use of hard coatings resistant to both wear and corrosion [1]. TiN hard

coatings are intrinsically very chemically stable, however, monolayer films of TiN deposited on steel by PVD techniques, such as magnetron sputtering, generally have a columnar microstructure and when they are exposed to a corrosive environment the defects and pinholes which propagate through the film can act as pathways for corrosive liquids. Moreover, the noble TiN coating and the active metallic substrate form a galvanic pair that can accelerate the pitting corrosion.

TiN/Ti multilayers have been used to reduce the coating porosity since the interfaces between the

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layers act as barriers that restrict the pathways to the substrate and therefore the use of multilayers tends to increase the corrosion resistance. Additionally, it has been reported [2,3] that multilayers with graded interfaces are more corrosion resistant than multilayers with sharp interfaces. When TiN/Ti multilayers are deposited without interruption of the deposition the interface from TiN to Ti is thicker than the interface going from Ti to TiN, with this effect being attributed to residual nitrogen on the target [4]. Furthermore, the degree of ion bombardment, controlled by the magnetic fields of an unbalanced magnetron, can be used to improve the morphology and therefore the corrosion resistance of TiN/Ti multilayers [5].

The aim of this work is to study the corrosion resistance of multilayers of TiN/Ti on stainless steel. The determination of the Ti and TiN_x layer thickness and the N concentration “*x*” are important parameters to measure and IBA methods are appropriate for this purpose.

2. Experimental details

The 304 stainless steel substrates were prepared using 600 and 2000 sandpaper and polished with 1 μm diamond paste. Prior to deposition, the substrates were ultrasonically cleaned; first in acetone and then in isopropanol. The Ti and TiN_x multilayer coatings were deposited by unbalanced magnetron sputtering using a 10.20 cm diameter 99.99% pure titanium target. An argon plasma was used for the titanium layers and a mixture of argon plus nitrogen for the titanium nitride. The temperature of the substrates was maintained at 400 °C and the grounded substrates were placed 5 cm from the target. The deposition pressure for both layers was 0.53 Pa, and the first deposited layer on the substrate was Ti with the last being TiN_x. The change from Ti to TiN_x deposition was achieved by controlling the nitrogen flow without plasma interruption so that a graded interface was generated. The following notation is used to identify the samples: *n*TiN*n*Ti, where “*n*” is the total number of layers. The samples analysed in this work were for *n* = 1, 2, 6 and 7, with total thickness of between 1.74–9.8 μm.

The corrosion resistance of the multilayers was evaluated using the potential–current curves obtained by potentiodynamic polarization scans in a NaCl 0.5 M solution (29.22 g/l). A saturated calomel electrode (SCE) was used as the reference electrode. The electrolyte was a solution prepared from reagent grade NaCl and distilled water and the potential sweep rate was 10 mV/min performed at room temperature (22 °C). The sidewalls of the samples were double-painted with enamel, leaving a 0.9 cm diameter circle in contact with the solution. The corrosion current was estimated by linear fit and Tafel extrapolation to the cathodic part of the polarization curve.

A single ended 5.5 MV Van de Graaff accelerator [6] were used to obtain the atomic composition profiles and the TiN/Ti multilayers thickness. Several possibilities were considered to choose an appropriate IBA method. It is known that a standard 2 MeV ⁴He⁺ RBS method is limited to analyse about the first 2 μm from the target surface and therefore we choose a combination of RBS/NRA methods described below. A 1400 keV ²H⁺ beam was used to bombard the samples so that several NR with positive *Q* values, such as: ¹⁴N(d,α)_i ¹²C and ¹⁴N(d,p)_i ¹⁵N are possible. A surface barrier detector, 1000 μm thick, equipped with standard electronics set at θ = 150° was used to measure the energy of particles. We did not use a particle absorbing foil in front of the detector, and hence the system was able to simultaneously measure the spectrum from the ²H⁺ RBS low energy region and the high particles energy region of the NR particles. A low ²H⁺ beam currents (about 5 nA), were used in order to avoid pile-up pulses and dead time during the data acquisition.

3. Results and discussion

Fig. 1(a) shows the experimental RBS spectrum (dots) from the 1400 keV ²H bombardment on TiN/Ti/SS made of 6TiN6Ti layers. The peaks in this spectrum corresponds to the Ti layers and the valleys corresponds to the TiN_x layers. Fig 1(b)) is part of the corresponding high energy region of the spectrum where the ¹⁴N(d,α)₁ ¹²C* peaks are displayed. Now the peaks corresponds to the nitrogen

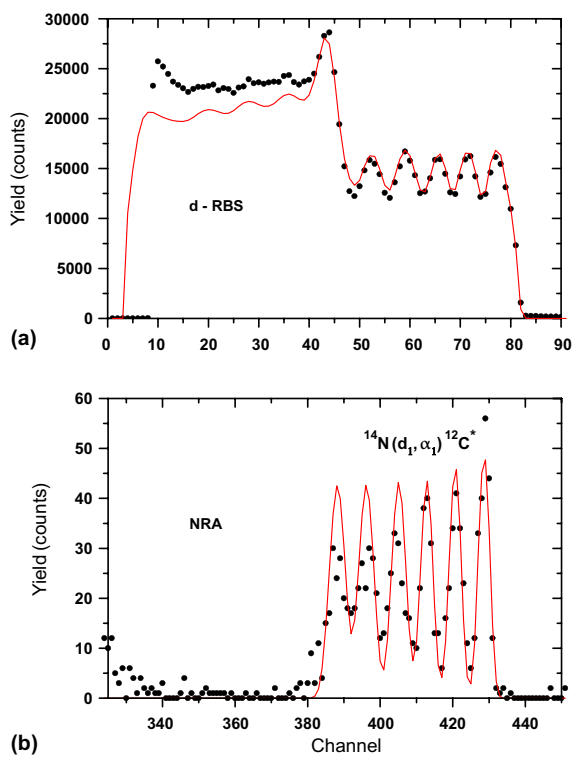


Fig. 1. (a) The experimental RBS spectrum (dots) for a 1400 keV deuterium beam incident on a 6TiN6Ti/SS. (b) The $^{14}\text{N}(d, \alpha_1) ^{12}\text{C}^*$ NR spectrum, the solid line is the WINDF v7.0.47 fit.

in the TiN_x layers and the valleys corresponds to the Ti layers. The task of simulating such type of complex spectra using traditional computer codes such as: RUMP, SIMNRA, etc., is very time consuming. The solid line in the spectrum represent the WINDF v7.0.47 code simulation [7]. The approach of this program tries to answer the question “given RBS or NR data, what is the depth profile”? The $^{14}\text{N}(d, \alpha_1) ^{12}\text{C}^*$ NR cross sections were added to this program to obtain the nitrogen fit in the TiN_x layers from the NRA. The solid line in Fig. 1(b) are the simulation of the $^{14}\text{N}(d, \alpha_1) ^{12}\text{C}^*$ peaks using the nitrogen content “ x ” of each of the TiN_x layers obtained from the RBS simulation. The good fit to the NR spectrum showed that the determination of the nitrogen content by the RBS was correct. Fig. 2 show the depth profiles of N and Ti in the multilayer structures based on the WINDF simulation of the

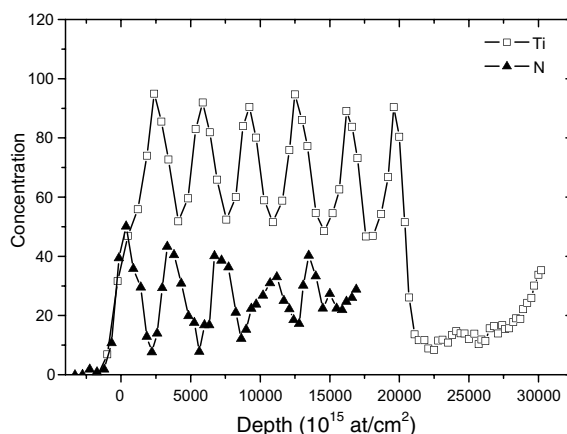


Fig. 2. The depth profiles of nitrogen and titanium in the layers of the coating from the WINDF simulation shown in Fig. 1(a) and (b).

Fig. 1(a) and (b) spectrum. The element profile of this sample, employed 6 layers of TiN_x and 6 layers of Ti, plus the substrate. The IBA methods provide the layer thickness in monolayers units (10^{15} atoms/ cm^2) and the linear layer thickness (in nm) can be calculated if the mass densities of the layers are known. The bulk densities for the TiN (4.51 g/cm^3) and for Ti (5.68 g/cm^3) were used to transform the IBA monolayer thickness to linear thickness (nm). From this, we obtained an average thickness of 278 and 406 nm for the Ti and the TiN_x respectively, giving a total coating thickness of 4122 nm. Ti/N average ratio was 0.88, i.e. these layers were more reach in nitrogen.

Fig. 3 shows the temporal evolution of the open circuit potential E_{corr} or rest potential (E_{rest}) during the electrochemical testing. The three analysed multilayers started with positive potential values that are more noble than the substrate. The potential of 1TiN1Ti showed a decrease similar to the substrate and no indication of passivation was observed. The samples 2TiN2Ti and 7TiN7Ti began with an increase in the potential associated with surface passivation, but after ~ 10 min the potential started to decrease indicating surface activation. All the coated samples had a more noble value of E_{corr} 1 h after the immersion (see Table 1), but the value was not related to the numbers of layers. The 2TiN2Ti sample showed a potential more noble than the thicker sample

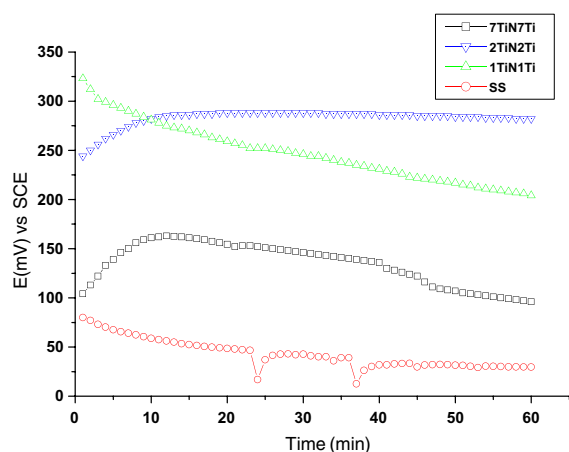


Fig. 3. The temporal evolution of the free corrosion potential of the multilayers in a 0.5 M NaCl solution.

Table 1
Electrochemical parameters

Sample	E_{corr} (mV) after 1 h	i_{corr} ($\mu\text{A cm}^{-2}$)	i ($E = 1$ V) ($\mu\text{A cm}^{-2}$)
304SS	29.6	5.6×10^{-2}	1.62×10^5
1TiN1Ti	282.0	2.0×10^{-2}	933.0
2TiN2Ti	204.0	2.4×10^{-2}	46.7
7TiN7Ti	96.0	7.0×10^{-3}	10.7

7TiN7Ti, and this probably indicates that there was more surface defects in the substrate of the thicker sample. However, these defects did not grow during the polarization, or were closed by corrosion products such as TiO_x , and the 7TiN7Ti sample showed the best resistance to pitting and general corrosion as can be seen in Fig. 3 of the polarization curves for all of the multilayer samples and the substrate.

In Fig. 4 the multilayers 1TiN1Ti and 2TiN2Ti have a current similar to the substrate value in the cathodic region (-500 to -200 mV), so the corrosion current i_{corr} estimated for these samples is only about a half that of the substrate. In the same region, the 7TiN7Ti sample is much better than the others. In the anodic region (0–200 mV), the coated samples are better than the substrate and have a similar behaviour until pitting begins. In this region the currents are different by orders of magnitude depending on the number of layers in

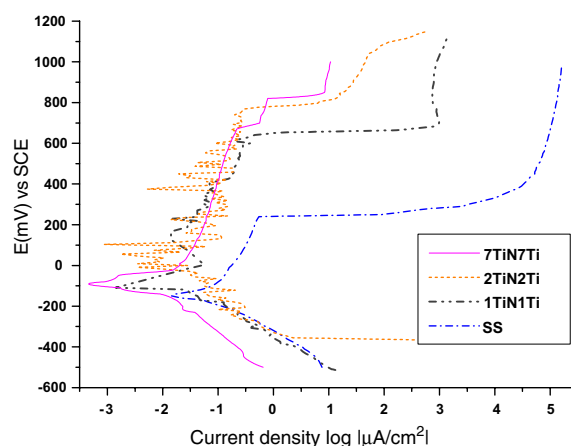


Fig. 4. The polarization curves, in a 0.5 M NaCl solution, of the TiN/Ti multilayers and the substrate, for different configurations as described in the text.

the coating. The sample 2TiN2Ti showed a variation in the current that is an indication of passivation and activation cycles. This behaviour is maintained during almost all of the polarization until a potential value near to the pitting point is reached.

Usually the pitting corrosion potential is defined as the potential at which the current increases abruptly. In Fig. 5, we show the pitting corrosion potential, E_{pit} , as function of the number of layers. There is an obvious improvement with respect to

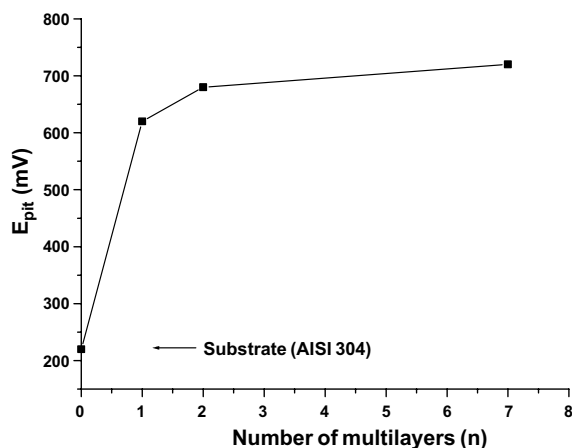


Fig. 5. The pitting corrosion potential, E_{pit} , as function of the number of nTiNnTi layers.

substrate through the use of the multilayers, and the effect is enhanced for the samples with larger numbers of multilayers (or the thickness), but the increase is sub linear.

Table 1 shows the electrochemical parameters obtained in this work. The corrosion current i_{corr} , estimated using the cathodic region, is lower for the multilayers and the lowest is for the thickest coating, or largest number of multilayers. Since the most prevalent corrosion process of coatings is pitting (which occurs in the anodic region), it is possible that this parameter is not the best to estimate the corrosion resistant of the samples. Therefore, an analysis of the pitting potentials and the current response after the pitting was performed as a complimentary manner to compare the corrosion resistance. The current at 1 V, a potential after which pitting has began, is lower for all the coated samples by at least three orders of magnitude and for the thickest sample with 14 layers is four orders of magnitude less than the substrate.

4. Conclusions

Relatively thick (1.74–9.8 μm) TiN–Ti multilayers can be used to significantly improve the corrosion resistance of 304 SS substrates. The

corrosion resistance was found to be dependent on the number of layers in the coating. The improvement in the corrosion resistance was seen to be mainly through a strong reduction in the attack by pitting.

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