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Corrosion behavior of steel coated with thin film TiN/Ti composites

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Thin film multilayered TiN/Ti composites are investigated as a possible alternative for protective coating of steels. Corrosion tests based in cyclovoltametry made in a buffered acetic acid solution reveal that multilayered coatings of this kind with total thickness of 0.5 μm perform as well as 3 μm single layered coatings. A discussion is presented on the influence of the multilayer parameters on this beneficial effect.

I. INTRODUCTION

The success of TiN as a hard coating of steels in many tribocorrosive situations may be attributed to a number of exceptional properties that this material possesses, like hardness, chemical stability and nobility, good adhesion to most steel substrates, and good wear and corrosion resistance.¹⁻³

However, high resistance against aqueous corrosion is only obtained when the coating is fully dense. Small pores in the coating may accelerate the corrosion by many mechanisms, e.g., galvanic action, crevice or pitting corrosion mechanisms, or capillary condensation. Since TiN is an electronic conductor and electrochemically nobler than steels, small pores in the coating will cause rapid corrosion in the area of the pores.^{4,5} The tribologic consequences of this accelerated corrosion are loss of adherence of the coating and consequently loss of wear protection. Since most of the tribologic situations of practical interest involve corrosion or oxidation, porosity of the films always has a deleterious effect.

There are several possibilities for reducing the porosity, the most simple one being the increase of the film thickness. But increasing the thickness too far also has some drawbacks because the stress increases and the dimensions of the substrates change, apart of the increase in the processing cost. Other strategies currently used to promote the densification of TiN films are ion beam assisted coatings, substrate heating, binary and ternary nitrides, and others.^{6,7}

Laboratory and industrial practice have set a lower limit in the thickness of TiN coatings, which are effective in protecting against corrosion and wear. This lower limit is around 1.5–2.0 μm for almost all deposition methods,

which makes TiN technology costly and vulnerable to the effect of interface stresses between film and substrate.

We report here on the use of a new thin film composite structure which is able to overcome several of these difficulties of TiN technology in producing a fully dense coating, like high cost, interface stresses, and others. More specifically, we describe in this article the properties of coating a medium-carbon steel with TiN/Ti multilayers of variable thicknesses with the constraint of having in all cases a maximum total thickness of 0.52 μm , at least three times smaller than the usual lower limit. The idea of using TiN/Ti multilayered composites derives from the already well-established procedure of introducing a Ti intermediate layer between the steel substrate and the TiN coating in order to improve the wear and corrosion protection.^{8,9} It is expected that a TiN/Ti multilayered coating will have considerably lower porosity since open structures reaching from the surface to the substrate in the TiN layers might be interrupted by the Ti intermediate films in the multilayer. Furthermore, corrosion or oxidation processes will oxidize Ti to Ti-oxide, which has a higher volume than Ti, adding one more contribution to the partial closing of the micropores. By using multilayered coatings, it is also possible to relieve interface stresses if couples that develop tensile and compressive stresses are involved. In this case, the relative thicknesses of the two different individual layers have to be optimized to give low interface stresses.

II. SPECIMEN PREPARATION

The TiN/Ti multilayers were prepared by reactive magnetron sputtering using as the cathode a pure Ti target and alternating pure Ar or a mixture of Ar and N₂ in the plasma. The partial pressures were, respectively, 3×10^{-3}

TABLE I. Multilayered TiN/Ti composite coatings of the present work: sample code, number of individual layers, thicknesses of the individual layers in each multilayered sample, and total thickness of each coating. The errors in the thicknesses are 3% and in the N/Ti ratios 5%.

| Multi-layered sample | Number of layers | Thickness of Ti layer (nm) | Thickness of TiN layer (Nm) | Total thickness (nm) | N/Ti atomic ratio in the TiN layers |
|----------------------|------------------|----------------------------|-----------------------------|----------------------|-------------------------------------|
| M1 | 9 | 80 | 30 | 470 | 0.95 |
| M2 | 7 | 80 | 50 | 440 | 0.95 |
| M3 | 5 | 90 | 90 | 450 | 0.90 |
| M4 | 7 | 40 | 80 | 440 | 0.95 |
| M5 | 9 | 30 | 80 | 520 | 0.90 |

mbar of Ar and 0.3×10^{-3} mbar of N_2 . The outermost layer and the one in contact with the steel substrate were always TiN.

The steel sample used as substrates were mirror polished CK45 samples (C:0.42 wt %, Si:0.40 wt %, Mn:0.5–0.8 wt %).

The structure and composition of the multilayered samples were determined by Rutherford backscattering spectrometry and nuclear reaction analyses. The results are given in Table I, where one quotes the number of layers in each multilayer and the correspondent TiN and Ti thicknesses, total thickness and the average stoichiometric atomic ratios of N/Ti in the TiN layers.

The phases that are formed in each multilayered sample were assessed by x-ray diffraction and the main reflection peaks observed were due to the (111), (200), and (220) planes of TiN and the (010), (002), (011), (201), and (002) planes of Ti. Reflection peaks that could be attributed to Ti_2N were not observed.

III. CORROSION TESTS

The samples were submitted to electrochemical corrosion in buffered acetic acid solution (pH 5.6). Multisweep current-potential measurements were carried out, employing a standard calomel reference electrode, and sweeping the potential cyclically between the working electrode and a Pt counter electrode from -1.2 to $+1.8$ V at a sweep speed of 10 mV s^{-1} . From the voltamograms the values of the maximum current density of anodic iron dissolution (critical current density) can be extracted and plotted versus the number of sweep cycles. Multicycling is a severe test and gives a quick estimation of the long term corrosion behavior. The critical current density for the substrate dissolution is also a direct measurement of the microporosity.^{10,11}

Typical cyclovoltamograms for evaluation of the corrosion behavior of coated and uncoated steels have been reported elsewhere in the literature.^{10,11} Figure 1 shows the critical current densities for the anodic iron dissolution as a function of the number of sweep cycles for all multilayer samples, together with a single layer, 500 nm thick, TiN coated sample, and an uncoated CK45 steel sample.

The critical current densities for anodic dissolution of iron on samples M1, M2, and M3 can be compared with those measured for $3 \mu\text{m}$ thick TiN coatings on Fe100 Cr6

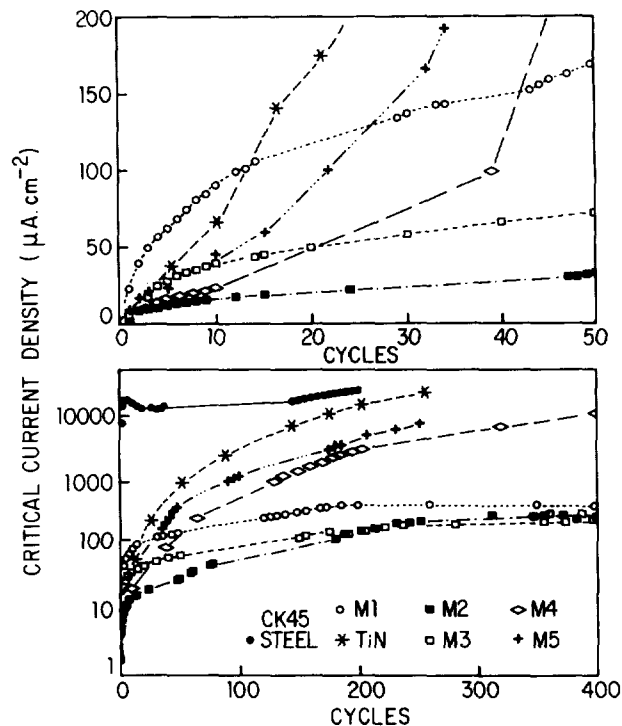


FIG. 1. Critical current densities for the anodic dissolution of iron vs number of cycles. TiN: 500 nm single layered TiN coating; M1: multilayered TiN/Ti composite, Ti = 80 nm and TiN = 30 nm; M2: Ti = 80 nm, TiN = 50 nm; M3: Ti = 90 nm, TiN = 90 nm; M4: Ti = 40 nm, TiN = 80 nm; and M5: Ti = 30 nm, TiN = 80 nm.

steel made by arc evaporation, thermionic evaporation, and magnetron sputtering in similar voltamogram measurements: according to Ref. 12 the critical current densities after 200 cycles fall in the range between 50 and $500 \mu\text{A cm}^{-2}$. So, the present results show that the coating of steels with TiN/Ti multilayered composites can in fact give a competitive coating (at least in terms of aqueous corrosion) with much smaller coating thickness.

IV. MECHANICAL TESTS

It is certainly of large interest to learn about the mechanical properties of these composite coatings, which will complement the corrosion properties in the case of practical use. The Vickers hardnesses of all the multilayered samples and of the uncoated steel sample are plotted in Fig. 2(a). Samples M3 and M4 are the ones displaying higher Vickers hardness at 100 mN load, but all the multilayered coatings have Vickers hardness higher than the CK45 steel substrate. The Vickers hardness measured here are smaller than those measured for thicker ($2 \mu\text{m}$ or more) TiN coatings reported in the literature: according to Refs. 1–3, 8, and 9, the Vickers hardness of TiN coatings fall in the range 1000–3000, depending on the deposition method, coating thickness, and composition. The elasticity of the composite coatings was also assessed by indentation depth versus load plots as shown in Fig. 2(b). These measurements were performed by increasing progressively the load and after decreasing it, and making many stops to measure the indentation depth.

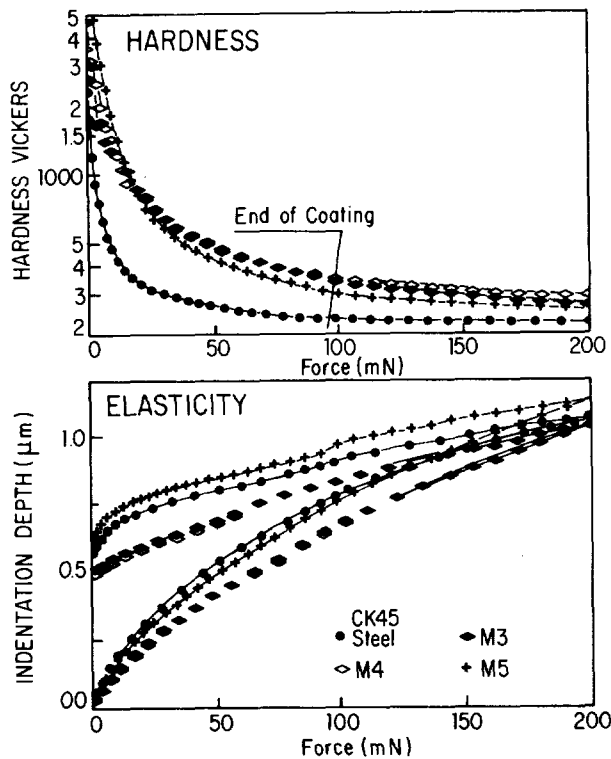


FIG. 2. (Top) Vickers hardness of the CK45 steel and of the multilayered TiN/Ti composites. The hardnesses the M1 and M2 samples are very similar to the M3 and M4 samples. (Bottom) Indentation depth vs load of the CK45 steel and of some of the TiN/Ti multilayers.

V. DISCUSSION

The results given in Fig. 1 allow us to establish some correlations between the structure of the thin film TiN/Ti composites and the reduction in wet corrosion: (i) at the initial stages of the multisweep cycling (up to 10 cycles) all the samples having the TiN layers equal or thicker than 50 nm display a rather small critical current density for anodic dissolution of iron (samples M2, M3, M4, and M5, and the 500 nm TiN single layer coating); (ii) after 40 cycles, the multilayers having the TiN and the Ti layers with thicknesses equal or greater than 40 nm still remain with low or moderate critical current densities (M2, M3, and M4) while those having either the TiN or the Ti layers thinner than 40 nm display higher current densities, including the single layer coating; (iii) the long term behavior, above 200 cycles, shows that the samples having greatly reduced critical current densities are those having thicker Ti interlayers (80 or 90 nm), which are here the samples M1, M2, and M3.

These correlations are evidences that the initial anodic dissolution of iron is inhibited by the action of the TiN layers, and the sample M1 fails because it has a TiN layer too thin (30 nm) to offer any protection. As the corrosion process evolves the Ti layers start to be oxidized to

Ti-oxide, which is a higher volume molecule, that can contribute to partial closing of the micropores. So, after 40 cycles both the TiN and the Ti layers are contributing to inhibit the anodic dissolution of iron, and those layers that do not have thick enough interlayers of either are seen to offer lower protection. Finally, the long term behavior, where only the multilayered coatings with 80 or 90 nm Ti interlayers are still displaying low critical current density, indicates a predominant role of the Ti layers in inhibiting the anodic dissolution of iron, most probably due to the action of the TiO₂ layers formed during corrosion.

Many aspects of the properties of the composite coatings described here remain open to investigation, like the microstructure and composition of the samples before and after corrosion, the influence of interfaces with gradient compositions, the influence of changing from TiN to Ti as the layer in contact with the steel substrate and others. Some of these aspects are presently being addressed and will be reported in a forthcoming publication.

A final comment has to be made concerning the deposition method used to produce the multilayered composite coatings. There is no special reason by which reactive magnetron sputtering would be better than other physical vapor deposition or chemical vapor deposition methods commonly used in TiN hard coating technology. Furthermore, methods that have shown previously to reduce the porosity of single layered TiN coatings should improve even further the performance of multilayered composite coatings. Indeed, in a preliminary investigation, multilayered TiN/Ti coatings deposited by ion beam assisted deposition have shown to be as effective as those shown here, and one expects that the optimization of the IBA parameters will improve this performance.

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