Corrosion of a Zn–Al–Cu alloy coated with TiN/Ti films

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Abstract

TiN and Ti coatings were deposited by d.c. magnetron sputtering on a Zn–Al–Cu alloy. The coatings were deposited at a relative low temperature of 115–130°C. X-ray diffraction showed that the films were crystalline. A pure titanium interlayer was used to improve the adhesion and corrosion resistance of the titanium nitride films. The corrosion behavior of samples in NaCl solutions was studied using polarization curves. Scanning electron microscopy was used to study the corroded samples. It was found that corrosion resistance of coated alloy was higher than the substrate resistance. Furthermore the corrosion resistance is mainly controlled by the presence of defects in the TiN and Ti films. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Corrosion; Sputtering; TiN coatings; Zn–Al–Cu alloy

1. Introduction

Titanium nitride (TiN) can be deposited by reactive magnetron sputtering techniques resulting in appropriate properties for its use as a protective coating to reduce wear and corrosion. Substrate temperatures in the range 400–600°C are commonly used in PVD processes to prepare protective coatings on metallic substrates. These are required to obtain stoichiometric and dense films with good adhesion. However, it is known that TiN films with good properties can be prepared at substrate temperatures of 250°C using magnetron sputtering. Nevertheless, this value is still too high for certain alloys, such as the Zn–Al–Cu material employed in this study.

There have been various papers [1–4] reporting the influence of the substrate temperature on the growth process, as well as the tribological and mechanical properties of TiN coatings deposited by reactive magnetron sputtering. Those studies and our own earlier work [5] indicate that the temperature dependence of the properties of TiN films is not strong even for temperatures of 115°C. That is, TiN coatings can be deposited at substrate temperature of 115°C and still retain most of their mechanical and tribological properties.

This study reports our efforts to improve the corrosion resistance of a Zn–Al–Cu alloy (called Zinalco[TM]) by means of the use of TiN coatings.

2. Experimental details

2.1. Substrate material

Zinalco is a zinc-rich alloy; it has been developed and studied at the IIM-UNAM [6,7]. It is based on the eutectic Zn–Al system modified with copper. The composition of the Zinalco used in this work was 80%Zn–18%Al–2%Cu. This type of Zinalco has a hardness of 100 kg/mm^2 (HV), melting temperature of about 481°C, density of 5.4 kg/cm^3 and thermal expansion coefficient of 25 (10^{-6} K^{-1}) for the temperature range 17–275°C. Its mechanical properties are similar to those of structural steel. These properties and its superplastic behavior make Zinalco a very interesting alloy for many applications, such as automotive accessories. However, the corrosion resistance of Zinalco is poor, specifically in NaCl solutions, because of the reactivity of the zinc component. The principal corrosion mechanism is by dezincification of the alloy.

2.2. Coatings deposition

The TiN and Ti coatings were deposited by d.c. planar magnetron sputtering onto substrates polished using 0.1 μm SiO$_2$ suspension to obtain a mirror-like surface. The substrates were heated in the temperature range of 115–130°C. The sputtering system was operated with a 99.99% pure titanium target of diameter of 10.16 cm (4 inches), and the total gas pressure used throughout was 3.0×10^{-5} Pa (4 mTorr). The Ti interlayer was deposited using a pure argon atmosphere, and the TiN films using a 40% Ar+

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Table 1
Deposition parameters of Ti

Sample	Substrate temperature (°C)	Current (A)	Voltage (V)	Thickness (μm)
M-30	130	0.2	350	0.18
Z-39	130	0.4	400	1.4
Z-43	115	0.4	400	0.3

60% N_2 mixture. The principal deposition parameters for Ti and TiN films are listed in Tables 1 and 2, respectively. The substrate temperature was measured using a chromel– alumel thermocouple connected to the reverse face of the sample. Calibration experiments indicated that this temperature was within 50°C of the temperature of the front surface of the samples.

2.3. Electrochemical testing

Samples of uncoated and TiN/Ti-coated Zinalco were studied in a solution of 0.5 M NaCl by means a potentiostat–galvanostat to obtain the corrosion potential response and polarization curves. The polarization curves were recorded at a polarization rate of 0.010 V/min. The electrochemical testing process was carried out without aeration or deaeration. The samples were in the form of a cylinder of 1–1.9 cm of diameter and 1 cm high. Since only one face of the samples were coated with TiN/Ti the other areas were protected from the solution using an enamel paint. The potential of work electrode was measured with respect to a saturated calomel electrode (SCE).

2.4. Coating characterization

Scanning electron microscopy of the sample surfaces was used to study the effect of the corrosion, following the corrosion tests. The X-ray diffraction patterns of the TiN/Ti were obtained to determine the structure of the coatings as a function of the experimental parameters.

3. Results and discussion

Initial experiments of TiN layers deposited directly onto Zinalco at 130°C showed poor adhesion between the film and the substrate. This was such that the residual stress caused film spalling for film thickness greater than 2 μm. Additionally, spalling of the prepared films was observed during the corrosion tests. However, higher temperatures

could not be used because of the resulting damage to the Zinalco. It is known that, in general, film adhesion can be improved by significant ion bombardment of the substrate during film growth. One method by which ion bombardment can be increased is by increasing the plasma power used. However, we found that plasma powers of more than ~300 W (0.8 A) also caused damage to the Zinalco, probably due to resputtering processes. Therefore the maximum current used was 0.6 A.

The X-ray diffraction studies showed that the films were crystalline and that the preferential orientations were (111) and (200). Films deposited at higher temperatures normally show an orientation of (111). Fig. 1 shows the diffraction pattern of a typical TiN/Ti/Zinalco sample, where the peaks from the TiN and Ti films, and those corresponding to the substrate can be observed.

We found that the inclusion of a interlayer of titanium increased both the coatings' adhesion to substrate and the corrosion resistance, even when both films were deposited at low deposition temperature (115–130°C). Total film thickness of more than 5 μm could be prepared without indications of spalling.

The evolution with time of the corrosion potentials for coated and uncoated samples is presented in Fig. 2. Here we can see that initially the potential of the sample Z-39 is distinct from that of Zinalco, but for long times the potential increases close to that of the Zinalco, indicating that the solution has permeated through the coating and reached the substrate. However, for even longer times a coated sample (Z-39) almost returns to initial potential. For the M-30 sample the change of the potential shows that the solution reaches the substrate fairly rapidly with no evidence of post-passivation. The results shows that there is a minimum thickness for the Ti layer (~0.2 μm) to obtain effective protection.

The polarization curves of the coated and uncoated samples are shown in Fig. 3. The currents corresponding to the coated specimens are somewhat lower than those for the uncoated Zinalco. In cathodic polarization one can see that the coated sample (M30) starts at a current lower than

Table 2
Deposition parameters of TiN

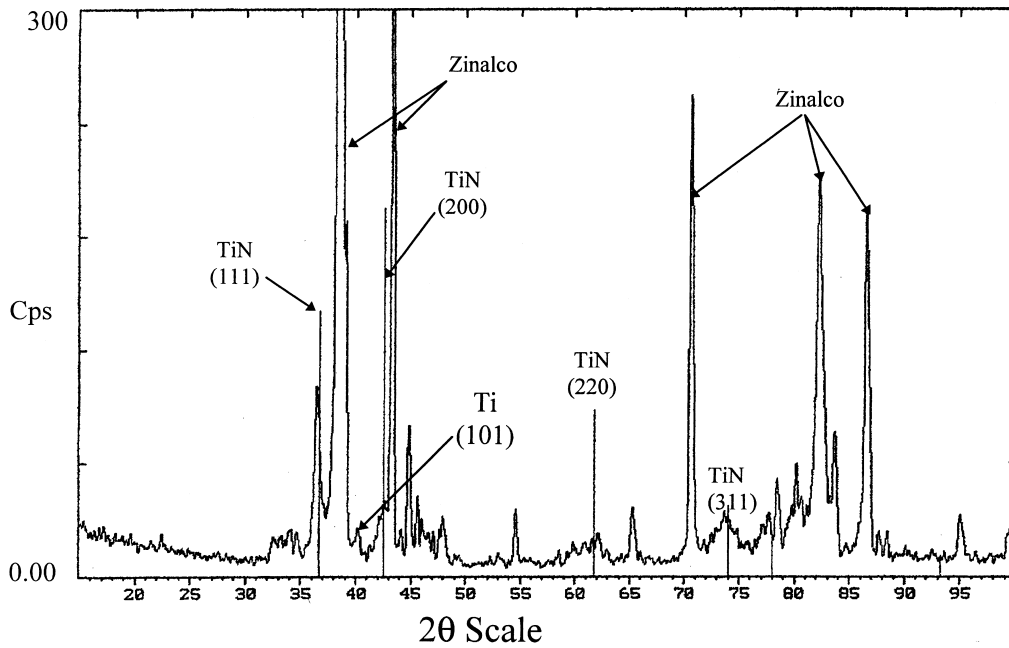| Sample	Substrate temperature (°C)	Current (A)	Voltage (V)	Thickness (μm)
M-30	130	0.4	510	2
Z-39	130	0.6	455	1.8
Z-43	115	0.6	450	1.2

Fig. 1. X-ray diffraction pattern of sample Z43.

the Zinalco case, but near the corrosion potential the coated sample current increases until it becomes almost equal to that of Zinalco. This phenomenon can be explained by pitting of the coatings at defect sites.

Table 3 shows the results obtained from the corrosion study, where the calculation of the corrosion current is based on the cathodic part of the polarization curve. This results shows that current density is lower in coated samples, but the improvement is limited. There are important differences in the corrosion potential (E_{corr}) for the samples that have been immersed in the electrolyte for 1 h with respect to the potential (E) when current is zero, these differences indicate changes in the sample surface.

We have observed that the main limitation of TiN coatings for improving the corrosion resistance of the Zinalco is the presence of structural defects in the films. These defects permit the electrolyte to reach the substrate, accelerating the corrosion rate. Imperfections in the coatings and imperfections in the substrate surface can both generate these defects. This problem can be reduced [8–11] through the use of multilayers of Ti/TiN to build up a thicker protective coat. Multilayers can also help by reducing the residual stress and/or by improving the morphology of the TiN layer. It has been suggested [12] that the grain boundary structure of TiN permits diffusion of the reagents to the surface of the substrate, and that this
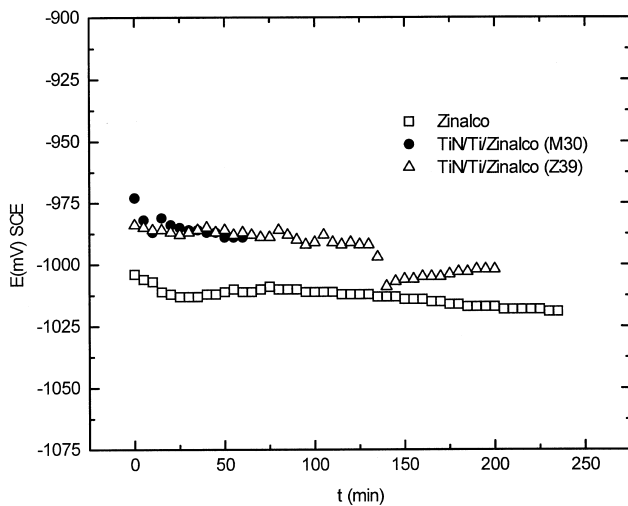

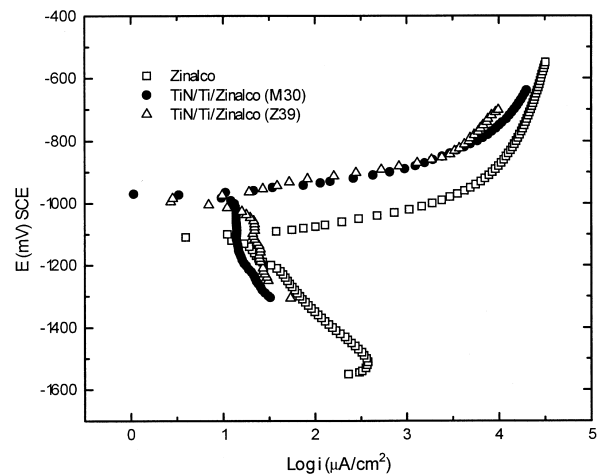Fig. 2. The evolution with time of corrosion potentials.

Fig. 3. Potentiodynamic polarization curves of Zinalco coated and uncoated.

Table 3
Parameters of polarization curves of TiN/Ti/Zinalco and Zinalco in 0.5 M NaCl and potential values of E_{corr} 1 h after the sample was immersed in electrolyte

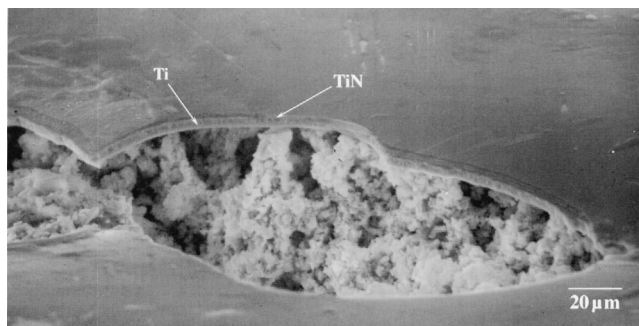| Sample	$E(I=0)$ (V(SCE))	I_{corr} (μA cm^{-2})	E_{corr} (after 1 h) (V(SCE))
M-30 (TiN/Ti/Zinalco)	-0.970	11	-0.989
Z-39 (TiN/Ti/Zinalco)	-1.020	15	-0.970
Zinalco	-1.100	18.6	-1.050

Fig. 4. SEM micrograph showing the attack crater produced by pitting corrosion.

influences the corrosion process. Again multilayer structures can help in reducing this effect and work is in progress to test the effectiveness of TiN/Ti multilayers.

Fig. 4 is a SEM micrograph of the sample Z-38 (polarization curves not included) after the corrosion test. It can seen that the TiN/Ti coating failed due to pitting and that the substrate was undercut below the film. The micrograph also shows that the film was not attacked by the NaCl solution but appears to have been fractured by the formation of the corrosion reaction products. The micrograph of the sample M-30 (Fig. 5), shows that large areas of the film has been lifted off the substrate with little evidence of undercutting or pit formation.

4. Conclusions

The technique of d.c. magnetron sputtering can be used to prepare coatings of TiN at low substrate temperatures. Coatings of TiN deposited on this type of Zn–Al–Cu alloy requires the inclusion of an intermediate layer of Ti to produce a coating with adequate adhesion, improving also the corrosion resistance. The corrosion of the coated samples is controlled by pitting at defect sites in the TiN/Ti layers, a reduction of these defects can be expected to greatly increase the corrosion resistance. The TiN/Ti coatings increases the corrosion resistance of Zn–Al–Cu alloys even when these coatings are deposited at low temperature (115–130°C).
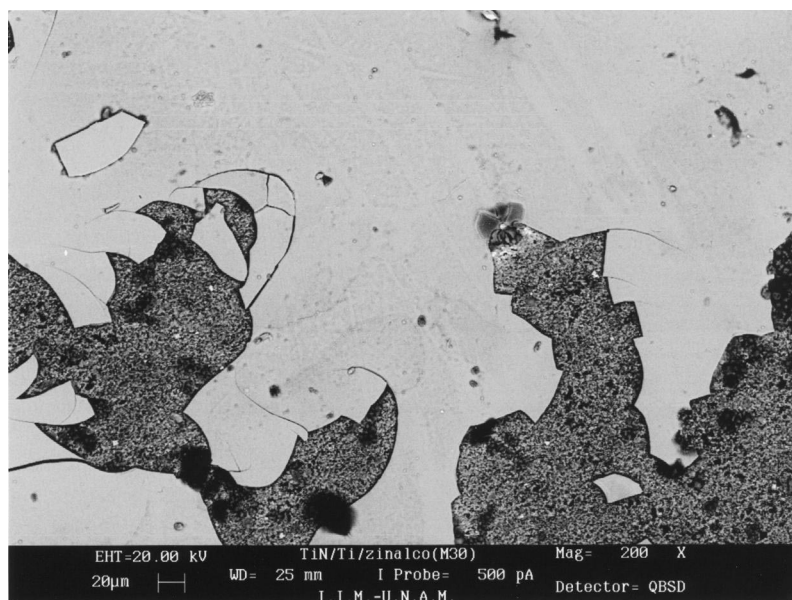
Acknowledgements

Fig. 5. Scanning electron micrograph showing the damages in sample M30 of Zinalco (dark zones) coated with TiN/Ti (gray zones) after corrosion test.

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