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# Influence of C<sub>2</sub>H<sub>2</sub> Flows on Microstructure and Corrosion Resistance of TiCN Films Doped with Carbon Atoms

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**Abstract:** Nanosized TiCN/TiN films were deposited on AZ31 by reactive magnetron sputtering under different acetylene flows. The microstructures of obtained films were characterized, and their corrosion behaviors were also investigated. The films doped with carbon atoms under different acetylene flows own different structures and grain sizes. The grain size decreased to some extent, and the film structure changed from polycrystalline to nanocrystalline, with an increase of  $C_2H_2$  flow. The surface morphology also changed from rough to smooth, with an increase of  $C_2H_2$  flow. The Tafel curves and electrochemical impedance spectroscopy (EIS) demonstrated that the composite films could greatly improve the corrosion resistance of bare substrates in a 3.5% NaCl solution, and the films' corrosion resistance is different, owing to their different structures and grain sizes.

Keywords: ceramic coatings; microstructure; corrosion behavior; acetylene flows; vacuum

## 1. Introduction

Magnesium alloys are prospective to satisfy manufacturing and industrial demands because of their low density, high strength-to-weight ratio, good machinability and electromagnetic shielding, high heat and electrical conductivity, and great recycling potential. These special characteristics cause magnesium alloys to be widely used in microelectronics, automobiles, biomedicine, and aerospace [1–8]. However, magnesium alloys are susceptible to corrosion due to the high chemical activity of the Mg element [6,7]. In order to maintain the inherent property and increase the lifetime of magnesium alloys, surface modification by films can be used to improve the corrosion resistance of magnesium alloys [7–12]. A broad variety of different hard coatings have been used in industry, reducing substantial economic losses in some automobile and aerospace parts. Among these techniques, magnetron sputtering (MS) is a preferred method due to its low temperature, high deposition rate, and strong adhesion.

In recent years, TiCN/TiN composite hard coating has been developed to resist corrosion loss, and has attracted much attention due to its high hardness, high melting points, high chemical stability, and good corrosion resistance. The authors' previous literature [3,13–15] showed that transition metal carbonitride coatings prepared by physical vapor deposition (PVD) play an important role in improving the corrosion resistance of magnesium alloys. However, until now, in view of TiCN/TiN composite film deposited at different acetylene flows on AZ31, there has been little information on the correlation between microstructure and corrosion resistance of bare AZ31 by reducing defects.



However, subsequent annealing not only increases costs, but also takes time. If the structure of the film can be changed directly by atomic doping during preparation, the corrosion resistance must be improved by a certain structure. So far, the authors have not seen the work improve the corrosion resistance of coatings by changing the structure directly. Acetylene is an active gas with high carbon content, and it is the most appropriate alkyne to provide C atoms for fabricating TiCN coating in the way of reactive magnetron sputtering. In this work, the authors produced TiCN films on AZ31 at different  $C_2H_2$  flows by reactive magnetron sputtering, and the correlation between microstructure and corrosion resistance of obtained films was investigated.

### 2. Experimental

#### 2.1. Film Preparation

AZ31 (Mg-3Al-1Zn) with volume of  $20 \times 20 \times 3 \text{ mm}^3$  was polished and ultrasonically cleaned in acetone, ethanol, and DI water before being put into the sputtering chamber; then, the cathode Ti target and AZ31 substrates were pre-sputtered by argon ion to obtain clean surface. Afterwards, a thin Ti buffer layer with the thickness of 200 nm was prepared to reduce residual stress and avoid a failure caused by the large physical difference between the films and AZ31, and a TiCN/TiN film was fabricated by sputtering cathode target in an Ar (99.99%), N<sub>2</sub> (99.99%), and C<sub>2</sub>H<sub>2</sub> (99.99%) mixed atmosphere. The following process parameters were carried out:

- Base pressure of chamber was  $2 \times 10^{-3}$  Pa;
- Substrate bias was -45 V;
- Thickness of TiN was 600 nm, with an average deposition rate of 24 nm min<sup>-1</sup>; TiCN was 800 nm, with an average deposition rate of 20 nm min<sup>-1</sup>;
- DC target current was 0.4 A;
- Total working pressure was 0.5 Pa;
- Ar flow was fixed at 20 sccm; N<sub>2</sub> flow was fixed at 5 sccm; C<sub>2</sub>H<sub>2</sub> flows varied from 2 to 5 sccm; and the films fabricated with 2, 3, 4, and 5 sccm were presented as samples C2, C3, C4, and C5, respectively.

#### 2.2. Characterization of Microstructure

The microstructure of the films was characterized by transmission electron microscopy (TEM, Tecani-F20, FEI, Hillsboro, OR, USA) and glancing angle X-ray diffraction (GAXRD, Bruker-D8, Karlsruhe, Germany). The mean grain size along the vertical direction of the crystal plane was calculated by Scherrer formula, shown as Equation (1) [16–18]. Surface and cross-section morphologies were observed by field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Tokyo, Japan).

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

in which *D* is the grain size; K is a constant, which is equal to 0.89;  $\lambda$  is the wave length of X-ray, which is equal to 1.5407 Å for Cu-K $\alpha$  line;  $\beta$  (rad) is the FWHM of diffraction peak; and  $\theta$  (°) is the peak position of diffraction line.

#### 2.3. Corrosion Behavior

The corrosion behavior was performed by electrochemical workstation (Princeton VersaSTAT3, Ametek, Berwyn, IL, USA) in a 3.5 wt % NaCl aqueous solution. A saturated calomel electrode (SCE) was used as a reference with a platinum counter electrode, and the exposed area was 0.785 cm<sup>2</sup>. The polarization scan ranged between  $\pm 0.5$  V at a rate of 1 mV s<sup>-1</sup> at room temperature, after allowing a steady state potential to develop [19,20]. Procedure of the electrochemical impedance spectroscopy (EIS) measurements was described in detail in [8]. The corrosion morphologies were also observed by SEM

equipped with energy disperse spectroscopy (EDS, EDAX-Falcon, Mahwah, NJ, USA); the scanning area of SEM micrographs before and after electrochemical test was the same.

#### 3. Results and Discussion

#### 3.1. Microstructure

XRD patterns of the as-deposited films and electrochemical test films are shown in Figure 1. From Figure 1, the as-deposited films present a mixed phase of TiN and TiCN; peaks of cubic TiCN corresponding to the planes (111), (200), (220), (311), and (222); and diffraction peaks of TiN corresponding to the planes (111), (220), and (311). The as-deposited films also show that both TiCN and TiN have a (111) preferred orientation in all samples, as the (111) is the most densely packed plane in the film structure, and the (111) preferred orientation gradually decreases with the increase of acetylene flows.



Figure 1. XRD patterns of all samples (a) as-deposited films; (b) electrochemical test films.

According to Scherrer formula, all the grain sizes are nanometers, obtained by determining the full width at half maximum. The grain sizes decrease as the  $C_2H_2$  flow increases from 2 to 4 sccm, then the grain sizes begin to increase when the  $C_2H_2$  flow increases to 5 sccm, as shown in Table 1. The slight shift of diffraction peaks indicates a decrease in the lattice parameter and is often considered to be the substitution of C atoms with the smaller N atoms in the solid solution and a change in the stress state [21,22]. After the electrochemical test, shown in Figure 1b, the TiCN (111), (200), (220), and TiN (111) diffraction peaks can still be observed from XRD spectra. All the coatings still have a (111) preferred orientation; the decrease of peak intensities indicates that the films experienced the electrochemical reaction, and some corrosion products have been generated. After further confirmation, characteristic peaks of corrosion products are TiO<sub>2</sub> and Mg(OH)<sub>2</sub>.

Table 1. The grain size values of coatings (nm).

Coatings	Grain Size (nm)
C2	33.67
C3	30.03
C4	25.51
C5	25.95

Figure 2a reveals the high-resolution TEM (HRTEM) image of C4 as-deposited film, where the inset at the top right is the corresponding selected area electron diffraction (SAED). It is clear that the TiCN film exhibits a typical nanocrystalline phase embedded in an amorphous matrix, and the

multi-ring pattern is not clear, indicating the grains are nanocrystalline and very small. The lattice fringes with  $a_{(111)} \approx 2.453$  Å and  $a_{(220)} \approx 1.510$  Å can be found. Figure 2b reveals the HRTEM image of C5 as-deposited film; C5 presents polycrystalline phases with small grains and is confirmed as the cubic TiCN phase, and the lattice fringes are  $a_{(111)} \approx 2.462$  Å and  $a_{(220)} \approx 1.513$  Å. The grain size of C5 is bigger than C4, SAED pattern, indicating that the crystallinity of C5 is better than C4, which is consistent with XRD.



**Figure 2.** High-resolution transmission electron microscopy (HRTEM) image observation of (**a**) C4 and (**b**) C5.

#### 3.2. Morphologies and EDS Analysis

Figure 3 shows the SEM morphologies of as-deposited coatings and examined coatings by electrochemical test. It is noted that the defects like pores and pinholes are intrinsic to the physical vapor deposition (PVD) process, and this is almost impossible to completely avoid [23–25]. C2 is compact, but coarse with many particles; C3 is smooth but presents some tiny particles and pinholes; C5 is coarse with some tiny pores; only C4 presents flat and smooth surface with some small white spots. The defects may be produced by particle recoil of the film surface or the bombardment of charge particles, and the number and size of particles could contribute to the particles charging and the repulsive force in the plasma sheath near the substrate surface. It is clear that the  $C_2H_2$  flow has great influence on surface morphology of films; the film gets smoother as the acetylene flow increases from 2 to 4 sccm. According to the authors' inference, it is because carbon atom doping refines grains. As the acetylene flow increases to 5 sccm, the excess reaction gas may poison targets during the TiCN deposition process, which makes the sputtering process unstable and produces some granular defects and pores. Therefore, the roughness of C5 increases.

Figure 3k,l exhibits cross-sectional observations of C2 and C4 samples in order to further explore the film structure. It can be observed that the film structure is dense and compacted; C2 film shows a dense columnar structure grown perpendicular to the AZ31 surface, and C4 sample shows a smoother structure with a columnar-free feature. It is deduced that the smooth surface and columnar-free structure are caused by the formation of small size nanocrystals.

After electrochemical test, some corrosion pits, pores, and corrosion cracks are observed on the surface, but no part of the film is missing. C2 exhibits some pits, C3 presents some cracks, C4 exhibits a few pores, and C5 presents some cracks and pores. The corrosive attack is due to the columnar crystal structure and defects of the film, because chloride ions in the solution can penetrate the film through small pores or columnar crystal structure. Since TiN/TiCN coatings are more electrochemically stable than AZ31 substrate, and the exposed area begins to experience anodic dissolution with the reaction of hydrogen evolution, the corrosion compounds are formed at the same time. The structure and grain size of TiCN film were changed by the increase of  $C_2H_2$  flow, such as columnar crystal

to nanocrystalline, larger grains to smaller grains, and rough surface to smooth surface, which all improved the corrosion resistance and enlarged application of the substrates.

The values of the EDS analysis for samples as-deposited are given in Table 2. From EDS analysis in Figure 3c–i, the carbon content increases with the increase of  $F_{C2H2}$  from 2 to 5 sccm; it is the same as the as-deposited film. The oxygen is from the atmosphere after the film has undergone electrochemical corrosion. The oxygen content decreases with an increase of  $F_{C2H2}$ , indicating the corrosion resistance was improved by carbon atoms doped. The Cl and Na elements are from NaCl solution; the Mg and Al are diffused from substrate during the electrochemical reaction. From Table 2, it can be seen that the Ti content decreases after electrochemical corrosion, and the N element has the same rules.



Figure 3. Cont.



**Figure 3.** SEM morphology of as-deposited films, electrochemical test films, and EDS analysis after electrochemical test: (**a**–**c**) C2, (**d**–**f**) C3, (**g**–**i**) C4, (**j**–**l**) C5, (**m**) and (**n**) cross-section of deposited film of sample C2 and C4; (**o**) cross-section of electrochemical test film of sample C2. The films fabricated with 2, 3, 4, and 5 sccm were presented as samples C2, C3, C4, and C5, respectively.

**Table 2.** The values of the energy dispersive X-ray spectroscopy (EDS) analysis for samples as-deposited (wt %).

Samples	Ti	С	Ν
C2	49.13	18.55	32.32
C3	46.26	22.99	30.75
C4	44.97	25.89	29.14
C5	42.08	28.74	29.18

#### 3.3. Corrosion Behavior

Figure 4a shows the potential-time curves, and stable octacalcium phosphates (OCPs) are obtained for all five electrodes after immersion for 1800 s. As shown in Figure 4a, the OCP of bare AZ31 in 3.5 wt % NaCl solution has the most negative potential value (-1.565 V vs. SCE), whereas the C4 has the most positive potential value (-1.245 V vs. SCE). The more positive potential indicates the less corrosion tendency of the electrode system. Figure 4b shows the potentiodynamic polarization curves of films; it is observed that the curves of the coated AZ31 shift in the direction of lower current density and nobler corrosion potential. According to the mixed potential theory [26], the films are more cathodic than AZ31. Therefore, the corrosion resistance of the coated samples is improved.



Figure 4. Cont.



**Figure 4.** (a) Open circuit potential curves of the bare AZ31 and films as a function of time; (b) Potentiodynamic polarization curves of the bare AZ31 and films; (c) Nyquist plots; (d) Bode plots of log |Z| vs. frequency; (e) Bode phase angle plots.

For convenience of comparison, the values of corrosion potential ( $E_{corr}$ , V) and corrosion current density ( $I_{corr}$ , A cm<sup>-2</sup>) derived from the polarization curves by Tafel region extrapolation are shown in Table 3. The corrosion current density is related to the corrosion rate;  $C_R$  (mm/day) can be obtained by using the following Equation (2) [27,28]:

$$C_{\rm R} = \frac{22.85}{365} I_{\rm coor}$$
(2)

According to the Equation (2), C2 presents the highest corrosion rate, but all the corrosion rates of films are greater than bare AZ31. C4 film presents the lowest rate ( $4.43 \times 10^{-5}$  mm/day), owing to the little defects and fine grain, as well as less columnar structure, and it is much lower than other coatings, such as conversion coating in literature [29]. Among all samples, the corrosion potential of C4 increases from -1.562 to -1.129 V and the corrosion current density decreases from  $8.15 \times 10^{-4}$  to  $7.07 \times 10^{-7}$  A cm<sup>-2</sup> due to its smooth surface, nanometer grains, and columnar crystal-free structure. It is also evident that the C2 film has poorer corrosion resistance compared with the rest films due to its greater number of defects, larger grain, and columnar structure. Comparing C4 and C5, it is found that the C5 film has poorer corrosion resistance due to its relatively rough surface and larger grains. Comparing C3 and C4, it can be inferred that SEM morphology of electrochemical test films seems very different, but corrosion rates are similar. This phenomenon can be explained as follows: the corrosion resistance of C3 is not as good as C4 film. When C3 experienced electrochemical corrosion, it could form small galvanic cells in some local defect areas and generate corrosion products. These corrosion products will accumulate in the defect area, and thus prevent the outside invasive ions from entering the internal. Therefore, the corrosion rate of C3 is similar to C4 in a short time.

Samples	Corrosion Potential E <sub>corr</sub> (V)	Current Density $I_{\rm corr}$ (A cm <sup>-2</sup> )	Corrosion Rate C <sub>R</sub> (mm/day)
Uncoated AZ31	-1.562	$8.15  imes 10^{-4}$	$5.1 \times 10^{-2}$
C2	-1.188	$4.78 imes10^{-6}$	$2.99 imes10^{-4}$
C3	-1.151	$7.65 imes10^{-7}$	$4.79  imes 10^{-5}$
C4	-1.129	$7.07 imes10^{-7}$	$4.43 imes10^{-5}$
C5	-1.173	$1.05  imes 10^{-6}$	$6.57 \times 10^{-5}$

Table 3. Electrochemical data of substrate and films obtained from potentiodynamic polarization curves.

Figure 4c–e shows the results of EIS plots of the coatings. As shown in Figure 4c, the Nyquist plots are characterized by a capacitive loop in high-frequency and an inductance loop in low-frequency, and the C2 coating exhibits the smallest diameter, while the C4 coating presents the biggest one, implying that the C4 sample has a better inhibitive property. As shown in Bode plots of Figure 4d,e, the impedances of all films are higher than AZ31 immersion in the electrolyte and increase by one order compared with the bare AZ31. These indicate that the films provide an effective barrier against corrosive electrolyte ingress during EIS tests. It is clearly shown in Figure 4e that the phase angle value of the C4 sample is higher than other samples, suggesting the good barrier behavior of C4 film. However, C2 film only provides a little and limited protection effect on AZ31 due to its defects and columnar crystal structure.

Two factors can explain the enhanced corrosion resistance of coatings. First, fine grains and nanostructure were obtained, and the columnar crystal was inhibited by increasing the  $C_2H_2$  flow. Second, few defects and smooth surface are other important factors to improve corrosion resistance. The two factors could reduce a direct path for the corrosive medium to pass through the film, and the corrosion path is longer than single TiCN film and blocked by the interface of a duplex structure, resulting in enhanced corrosion resistance.

#### 4. Conclusions

In summary, the structures of TiN/TiCN composite films have been changed through alteration of  $C_2H_2$  flow, and the corrosion resistance improved greatly. The smooth surface, small grain size, and equiaxial crystal structure should be explored to obtain good corrosion resistance. As is known to all, corrosion resistance of film is greatly influenced by surface defects and structure. However, surface defects are impossible to avoid completely; thus, changing the structure of film is another effective way for us to improve the corrosion resistance of coatings.

**Author Contributions:** H.L. wrote the paper and led the team to carry out the investigation; P.S. and Y.Z. have done the experimental details and analyzed the data; M.W. has designed the layers of coating and process parameters; Q.W. has investigated the corrosion behavior of obtained films.

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