

# Investigation of VN/TiN Multilayer Coatings on AZ91D Mg Alloys

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**Abstract**—To develop AZ91D magnesium alloys with improved properties, we have applied TiN and VN/TiN multilayer coatings using DC magnetron sputter technique. Coating structure, surface morphology, chemical bonding and corrosion resistance of coatings were analyzed by x-ray diffraction (XRD), scanning electron microscope (SEM), x-ray photoelectron spectroscopy (XPS), and tafel extrapolation method, respectively. XPS analysis reveal that VN overlayer reacts with oxygen at the VN/TiN interface and forms more stable TiN layer. Morphological investigations and the corrosion results show that VN/TiN multilayer thin film coatings are quite effective to optimize the corrosion resistance of Mg alloys.

**Keywords**—AZ91D Mg alloys, High corrosion resistance, Transition metal nitride coatings, Magnetron sputter.

## I. INTRODUCTION

THERE is an increasing need of light material in automotive, aerospace, biomedical application and electronic industries. Due to the low density and low price, magnesium (Mg) and Mg alloys have been widely used as structural materials in these industries [1], [2]. Mg offers tremendous potential for dramatic increases in the fuel efficiency of automobiles, with corresponding reductions in CO<sub>2</sub> emission due to its high strength to weight ratio. Although Mg has fairly good mechanical properties, it shows relatively poor wear and corrosion resistance which limits its applications [3], [4]. Forming magnesium alloys with a mixture of high purity elements helps to improve corrosion resistance [5]. However, it does not change galvanic corrosion problems if Mg alloys are in contact with another metal or an electrolyte. A method that is often used to improve the corrosion resistance of metallic surfaces is coating. Due to extreme chemical reactivity of Mg, air or oxygen contamination during the coating process might cause damaging effects on coating adhesion and uniformity. Thus, in-situ processing plays a critical role in the development of a good protective coating on magnesium and its alloys.

Coating metal surfaces with transition metal nitrides based on Ti, Cr, Al and V using magnetron sputter is an effective method to overcome these problems [6]-[8]. Especially,

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multilayer coatings of transition metal nitrides have been used extensively for coating of cutting tools and protection of medical implant surfaces because of their good mechanical properties, such as great wear and corrosion resistance, and extreme hardness. Since automotive parts are subject to both corrosion and impact damage, metal nitride multilayer structures that show enhancement in hardness and fracture resistance come into prominence as coatings to these materials. Recently, TiN, AlN, CrN, and their alloy and multilayer coatings were applied on magnesium alloys and improved the corrosion-resistance, adhesion and hardness of these alloys [9]-[14].

The aim of this study is develop TiN and VN/TiN multilayer coatings with improved corrosion properties of AZ91D Mg alloys. While TiN coatings show excellent corrosion resistance, VN coatings can easily oxidize at relatively low temperatures by forming V<sub>2</sub>O<sub>5</sub> containing oxide which reduces friction on the surface [15]. In order to investigate the microstructure of TiN and VN/TiN coatings and their effect on the corrosion resistance of Mg alloy, TiN and VN/TiN coatings were deposited by DC magnetron sputter technique. The characterization of TiN and VN/TiN coatings on AZ91D alloy was carried out by structural, morphological, chemical bonding and electrochemical investigations.

## II. EXPERIMENTAL TECHNIQUE

TiN and VN/TiN multilayer coatings were deposited onto commercially bought AZ91D Mg alloys using a UHV growth and analysis system. Before deposition process, the 15mm×15mm×3mm AZ91D Mg alloy surfaces were mechanically polished using 800, 1200 and 2400 grid SiC papers sequentially and subsequently polished with diamond suspension (average size 1 μm and 3 μm). This process has been conducted for smoothing of the surface and removal of the surface oxide layer for improved chemical bond strength between the coating and Mg alloy. Before mounting in the vacuum chamber, substrates were ultrasonically washed in first water and then isopropyl alcohol to remove all contamination caused during polishing. In order to achieve a better surface, we checked the polished surface using reflected-light on an optical microscope for polishing defects.

The TiN and VN/TiN multilayer thin films were deposited at room temperature by DC magnetron sputtering from a high purity Titanium (%99.9) and Vanadium (%99.9) targets with 2 inch diameter and 5 mm thick. Before deposition of each film, the targets were presputtered in pure argon atmosphere for 10 min in order to remove oxide layers if any on the surface of

the targets. The deposition rates were obtained by calibration samples grown under identical conditions as the sample series by using x-ray reflectivity.

The base pressure of the deposition chamber was below  $3 \times 10^{-9}$  Torr and the pressure of Ar and N<sub>2</sub> gases, with a purity of 99.9999 %, was kept at  $1.9 \times 10^{-3}$  mbar (Ar:N<sub>2</sub> = 1:2) during the deposition. The pressure in the sputter chamber was measured using digital Pirani–capacitance gauge combination. The sputtering conditions maintained during the growth of the films are given in Table I. We have observed that high plasma power has negative impact on the corrosion resistance of coatings, thus coatings were developed using 15W plasma power. When the alloys were exposed to high plasma power or plasma dose, corrosion resistance decreased and morphology of the coatings worsened. The effect of sputtering power on the morphology and mechanical properties of coatings was investigated in details elsewhere[16].

	Power	Ar/N <sub>2</sub> Rate	Pressure	Thickness
TiN Coating	15 W	4/8 sccm	$1.9 \times 10^{-3}$ mBar	220nm TiN
VN/TiN Multilayer Coating	15W	4/8 sccm	$1.9 \times 10^{-3}$ mBar	2x(55nm TiN /55nm VN)

Surface morphology of the films was investigated after and before corrosion tests by scanning electron microscopy (SEM, Phillips XL 30 SFEG). The chemical nature of the films was obtained by X-ray photoelectron spectroscopy (XPS) using Specs Phoibos 100 analyzer. All samples were fabricated and transferred *in-situ* using a UHV transfer chamber which is connected to the deposition chamber and the x-ray photoelectron spectrometer so that no surface contamination was expected during transfer. XPS measurements were performed at a base pressure of  $1 \times 10^{-10}$  mbar using Al K $\alpha$  x-ray source without removing the films out of vacuum.

Corrosion tests of the coatings were done using “Volta Lab PGZ 402” potentiostat system using a three-electrode cell with a saturated calomel electrode as the reference electrode and a platinum electrode as the counter electrode at 25°C. Corrosion tests were performed in a solution containing distilled water and 3.5 wt% NaCl. The exposed surface area of the sample to the corrosive medium was approximately 1.1 cm<sup>2</sup>. Potentiodynamic polarization studies were performed with a scan rate of 1 mV/s in the potential range from –2000 to –1000 mV relative to the corrosion potential. To evaluate the corrosion resistance of coating samples, the Tafel polarization curves of the coatings and AZ91D Mg alloy (as a reference) were measured.

### III. RESULTS

X-ray diffraction spectra for nanoscale TiN and VN/TiN multilayer coatings deposited on AZ91D magnesium alloys presented in Fig. 1. The uncoated alloy shows peaks attributed to the solid solution phase of Mg ( $\alpha$ -Mg) and the intermetallic compound phase Al<sub>12</sub>Mg<sub>17</sub> ( $\gamma$ -Mg)[17]. Peaks related to TiN

and VN are not observed in the XRD patterns of the coated Mg alloy. The only observed peaks belong to the substrate ( $\alpha$ -Mg phase dominant), indicating that the TiN and VN crystals become too tiny to detect or the films are mostly amorphous in the as-grown state consistent with the similar results reported in literature[10], [18]. Since the coating is carried out at room temperature, highly immobile low energy particles do not prefer a crystallographic orientation.

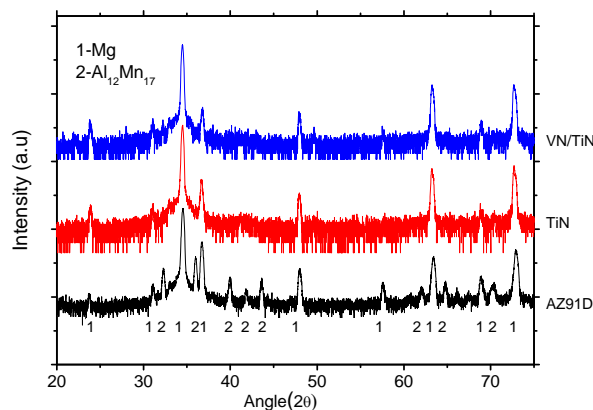


Fig. 1 XRD pattern of VN/TiN multilayer coated, TiN coated and uncoated AZ91D alloy

In order to investigate the chemical bonding environment of Ti, V and N, XPS measurements have been carried out. Fig. 2 focuses on the XPS core level signatures at the VN/TiN interface, with the evolution of Ti 2*p*, V 2*p* and N 1*s* core levels plotted in the course of stepwise VN/TiN multilayer deposition. Four elements (Mg, Zn, Al, C and O) were identified from the full-survey-scan spectrum of uncoated AZ91D, with no other impurity being detected. The background was subtracted using Shirley’s method [19]. After the first 10nm thick TiN growth, Gaussian fitting of the Ti 2*p*<sub>3/2</sub> peak indicated (line 1 in Fig. 2 (a) that it consisted of two peaks centered at 455.4 eV and 457 eV. Jaeger et al. reported that the Ti 2*p*<sub>3/2</sub> position of thick TiN films deposited by PVD is at 455 eV [20]. Considering very thin TiN coating and high oxygen contamination on the substrate surface, electronegative O involves in the film formation and that would slightly increase the binding energy of TiN. Thus, the 455.4 eV and 457 eV peaks correspond to the TiN and TiON bonds, respectively [21]. In fact, with the increase of TiN thickness as shown as line 2 in Fig. 2 (a), contribution from TiN component increases. However, TiON component is still present because highly active Ti atoms preferentially attract O more than N atoms. The source of oxidation may be the nitrogen gas. The commercial nitrogen gas was used and it may have considerable percentage of oxygen impurities [21]. During the deposition of VN overlayer, we investigated the intensity evolution of Ti emission until it is completely attenuated and intensity TiON relative to TiN decreased indicating that some of the oxygen from underneath TiN layer may have moved (line 3 in Fig. 2 (a). On the other hand, the intensity of TiN peak increased and TiN film became more

stable by removing some of the trapped oxygen inside the film. Although the deposition was performed at room temperature, local heating of energetic particles hitting the surface might have caused the diffusion of oxygen atoms. In order to investigate the oxygen diffusion mechanism, a comparison is made between the V 2p3/2 spectrum taken from VN/TiN interface and VN surface, indicated in the inset of Fig 2 as region 5 and 6, respectively. Two components are required to fit the V 2p spectra presented in Fig. 2 (b). The first component is the sharper peak exhibiting at 513eV binding energy, which is attributed to VN. While the second component at 516eV has been attributed  $V_2O_5$  [15], [22], and it was found that intensity of this peak is higher at the VN/TiN interface. This suggests that the oxygen is more likely to diffuse into the VN overlayer and forms  $V_2O_5$  overlayer after each TiN.

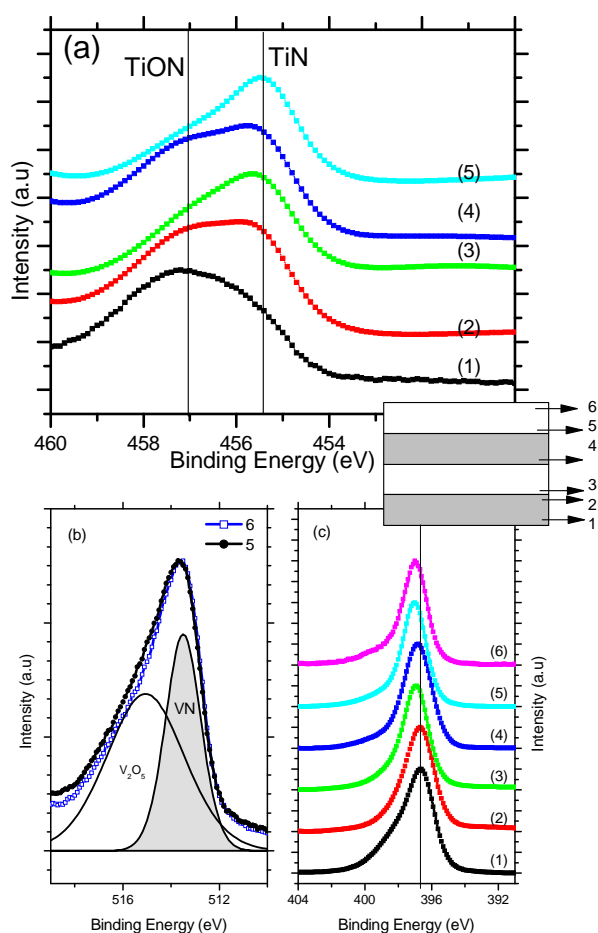


Fig. 2 TiN coating of XPS spectrum (a) Ti 2p and (b) V 2p and (c) N 1s. The inset shows schematic diagram of the multilayer coating and representative spectra from each layer

Evolution of N 1s spectrum with increasing multilayer thickness is shown in Fig. 2 (c). For about 10nm TiN layer growth, a shoulder is evident on the N 1s spectrum. The occurrence of a shoulder around 398 eV might be explained by oxynitride formation around the interface due to the oxygen

contamination of AZ91D surface [12]. With the increase of coating thickness, shoulder of N 1s has mostly disappeared. The main N 1s peak has centered at 397eV, associated with the TiN and VN[22].

Fig. 3 shows the polarization curves of the VN/TiN multilayer coated, TiN coated and uncoated AZ91D alloys after 1 hour of immersion in 3.5% NaCl aqueous solution. The corrosion current densities and the corrosion potentials were obtained by the intersection of the extrapolation of anodic and cathodic Tafel curves and summarized in Table II. It can be seen that the measured corrosion potential value of the TiN coated alloy is much more positive than that of the uncoated substrate, indicating that the coating the surface provides more resistant to corrosion. More noble potential (-1384.7 mV) has been observed in the case of VN/TiN multilayer coated sample. In addition, the corrosion current density decreased about one order of magnitude in coatings compared to uncoated alloy. The reduction in the corrosion current density ( $i_{corr}$ ) in TiN and VN/TiN multilayer coated Mg alloy indicates the effective corrosion protection performance of these transition metal nitrides. It is well known that TiN is chemically inactive in many solutions and corrosion occurs through defects which forms a path for corrosion agent transfer to the substrate. Thin layer of VN/TiN and TiN coatings on Mg alloys surface acts as a barrier against corrosion and reduces the corrosion rate from 60 mm/y to 3 mm/y.

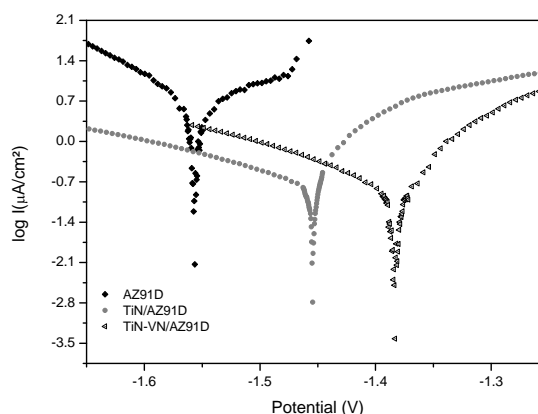


Fig. 3 Tafel curve of VN/TiN multilayers and TiN coated and uncoated AZ91D alloy

TABLE II  
ELECTROCHEMICAL PARAMETERS RELATED TO POTENTIODYNAMIC POLARIZATION CURVES

	E <sub>corr</sub> (mV)	I <sub>corr</sub> (μA/cm <sup>2</sup> )	C.R (μm/y)
Uncoated	1556.6	5.1233	59.92
TiN	-1454.5	0.2624	3.069
VN/TiN Multilayer	-1384.7	0.3031	3.545

As can be seen from Table II, the corrosion potential is slightly more positive in VN/TiN multilayer coating compared to the TiN coating. This means that the multilayer coatings need more energy to initiate the corrosion reaction due to the

inclusion of  $V_2O_5$  overlayer and formation of more stable TiN with reduced oxygen contamination. However, the corrosion current values and corrosion rates for coatings are similar. This can be explained on the basis of the effect of VN on the structure and surface morphology of the coating.

Fig. 4 shows the surface morphology of the coated and uncoated samples after corrosion test performed. It could be seen that certain regions of the surface of uncoated alloy show severe degradation and the formation of large and deep pits. This is due existence of secondary  $\beta$ -phase ( $Al_{12}Mg_{17}$ ) in AZ91D alloy which have higher galvanic corrosion rate compared to  $\alpha$ -Mg phase [23]. In the case TiN coated sample, surface showed shallow cracks and few small pits related to a barrier effect of the coating. Whereas, with the incorporation of VN into coating, the extent of corrosion to Mg alloy was reduced gradually and the smallest visible surface layer destruction is observed for AZ91D Mg alloy after VN/TiN multilayer coating. However, some tiny cracks were observed on the surface region. Although corrosion potential increases, no further reduction in current density compared to TiN coating may be attributable to these cracks.

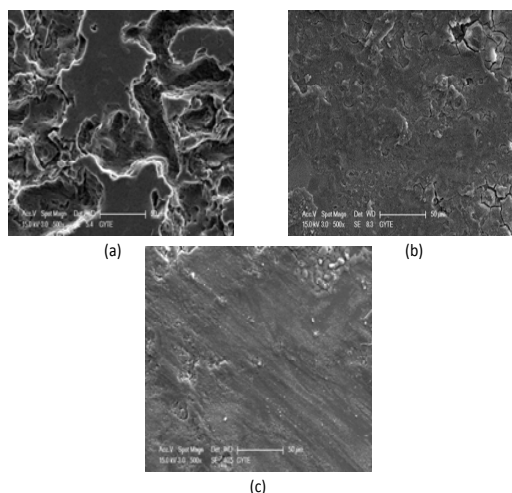


Fig. 4 SEM micrographs of (a) uncoated (b) TiN coated (c) VN/TiN multilayer coated AZ91D alloy after corrosion test

#### IV. CONCLUSION

TiN and VN/TiN multilayer thin films were prepared on AZ91D Mg alloy by magnetron sputtering method. The corrosion results and surface morphology investigations show that, compared with uncoated alloy, TiN coating can provide a good protection for AZ91D alloy in 3.5% NaCl solution due to surface passivation and suppression of chemical activities. Moreover, corrosion potential VN/TiN multilayer coatings shows more improvement than that of the single layer TiN, which is correlated with enhanced microstructure in TiN with reduced oxygen content.

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