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Corrosion behavior of AZ91 Mg-Alloy coated with AlN and TiN in NaCl and Hank's solution

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Abstract. Magnesium alloys create increasing interest in structural application where weight reduction is vast concern. However, its low corrosion resistance especially in atmosphere environment restricts their wide application. In this study, AlN and TiN were coated on AZ91 Mg alloy using PVD magnetron sputtering. AlN and TiN existence is confirmed via grazing angle x-ray diffraction (GA-XRD). The corrosion behaviors of uncoated and coated AZ91 Mg alloy in3.5% NaCl and Hank's solutions were investigated using a potentiostat during electrochemical corrosion test. AlN and TiN coated samples showed better performance in Hank's solution with TiN coated samples have the least corrosion rate (penetration rate=0.040mm/yr and mass loss rate=0.191g/m^{2}d) in Hank's solution. These create interest to further works on exploring the potential of coated AZ91 Mg alloy in biomaterial application.

1. Introduction

AZ91 (9 % Al–1 % Zn), among all magnesium alloys is the most widely used because of its good castability and mechanical properties with good corrosion resistance for the high purity version of the alloys [1]. However, Mg alloys have poor resistance to wear and corrosion which is a serious barrier against wider application of Mg alloys [2, 3]. It is because Mg alloys is thermodynamic instable that makes Mg alloys highly reactive. The interaction of oxygen with Mg leads to the formation of a thin, protective oxide layer. However, temperatures as well as moisture accelerate the transition to less protective films. At elevated temperatures the MgO film rapidly attains a critical thickness and starts to crack, thus allowing further oxidation [4].

Surface modification by coatings has become an essential step to improve the surface properties such as wear, corrosion and oxidation. Coatings can protect a substrate by providing a barrier between the metal and its environment and/or through the presence of corrosion inhibiting chemicals in them [5]. Nitride based hard coatings like TiN, (TiAl)N, BN and etc. have proved their capability to increase tool lifetime when exposed to abrasive and corrosive environments found in plastic transformation processes [6]. Thus, hard surface coating on Mg alloys substrate improved and overcome the drawbacks of Mg alloys such as poor corrosion and wears resistance [7]. However, it is also observed that in a coating-substrate system, the degradation of the corrosion properties is a result of galvanic corrosion between the magnesium and the coating material itself [8]. At coating defects like pinholes, inclusions and microporosity, the electrolyte can reach the substrate material which causes a high current density at the anodic magnesium, causing accelerated dissolution of the metal [9].

In this paper, the corrosion behavior of AlN and TiN coating on AZ91 Mg alloy deposited via PVD magnetron sputtering in two different corrosion medium which are 3.5% NaCl and Hank's solution are reported. The assessment of the corrosion behavior in Hank's solution is an effort to improve current understanding on the performance of AlN and TiN coating which is commonly limited only in NaCl medium. The results would contribute towards exploring the potential of coated AZ91 Mg alloy in biomaterial area application.

2. Materials and methods and characterization

2.1 Sample preparation

For coating deposition, AZ91 Mg alloy samples were ground successively with 400–1200 grit SiC paper and were polished with Al_2O_3 paste 1μm and 3μm; they were degreased in acetone and washed with distilled water ultrasonically in 10 minutes and dried with high pressure.

All coatings were carried out using a SNTEK DC and RF magnetron sputtering model PSP5004. A high-purity (99.99%) aluminum target was used in the AlN coating deposition and for TiN coating deposition, high-purity titanium (99.99 %). The substrate to target distance was 14cm. The AlN films were deposited using the following process parameters; power 200W, gas composition nitrogen: argon 6 sccm: 19 sccm and deposition time was 90 minutes whereas the TiN films were deposited using the following parameters; power 400W, gas composition nitrogen: argon 3 sccm: 10 sccm and deposition time was 45 minute. Both coating depositions are conducted at 180ºC due to temperature stability of mg alloy with -60V bias voltage and 10mTorr working pressure. Prior to deposition, ion cleaning using inert argon gas was carried out to avoid contamination and to improve adhesion [1]. Grazing-angle x-ray diffraction (GA-XRD) Diffractrometer XPERT-PRO system (copper anode, K® radiation, wavelength =1.54 A°) was utilize for phase constituent determination.

2.2 Electrochemical tests

For electrochemical tests, coated samples were mounted in epoxy resin to an expose area of 3.142 cm^2. The potentiodynamic polarization scans were performed according to ASTM G 5 (Standard Reference Test Method for Making Potentiostat and Potentiodynamic Anodic Polarization Measurements) using Gamry Instrument for the uncoated and coated samples in a 3.5 wt. % NaCl and Hank's solution. Table 1 shows the chemical composition of NaCl and Hank's solution used in this work. The electrodes for this purpose were prepared by connecting a wire to one side of the sample that was covered with cold setting resin. One side of the specimen, whose area was 3.142 cm^2, was exposed to the solution. The polarization measurements were carried out in corrosion cell containing 500 ml solution at room temperature for the 3.5 wt. % NaCl solution and 37°C for Hank's solution. The specimens were immersed in the test solution, and a polarization scan was carried out towards more noble values at a rate of 1 mV/s, after allowing a steady state potential to develop.

Table 1: The chemical composition of NaCl and Hank's solution used in this work

Solution	Chemical composition in terms of substance that make up the solution (mmol/L)								
	NaCl	$Mg(OH)_2$	$CaCl.2H_2O$	$MgSO_4$(anhydrous)	KCl	KH_2P_4(anhydrous)	Na_2PO_4 (anhydrous)	D-Glucose	$NaHCO_3$
Hank's	137	-	2.5	0.8	5.4	0.4	0.3	5.6	4.2
NaCl	550	8.6	-	-	-	-	-	-	-

3. Results and Discussion

3.1 Phase Analysis

3.1.1 Grazing-angle x-ray diffraction (GA-XRD)

Figure 1 shows the GA-XRD patterns of AZ91 uncoated sample (substrate), AZ91-AlN coated and AZ91-TiN coated samples. AlN phases with hexagonal structures (ICDD: 00-025-1133) were identified by the presence of the diffraction peaks at $2\theta=35.9^{\circ}$, 37.8° and 49.8° assigning to the [101], [102] and [103] planes. Diffraction peak with the highest intensity were observed at $2\theta=35.9^{\circ}$. These confirm the presence of AlN. The presence of TiN phases (ICDD: 03-065-5744) was characterized by diffraction peaks at $2\theta=42.65^{\circ}$, 62.13° and 78.36° assigning to the [200], [222] and [311] planes. The presence of diffraction peak (though with a very low intensity) at 62.13° and 78.36° confirmed the presence of TiN.

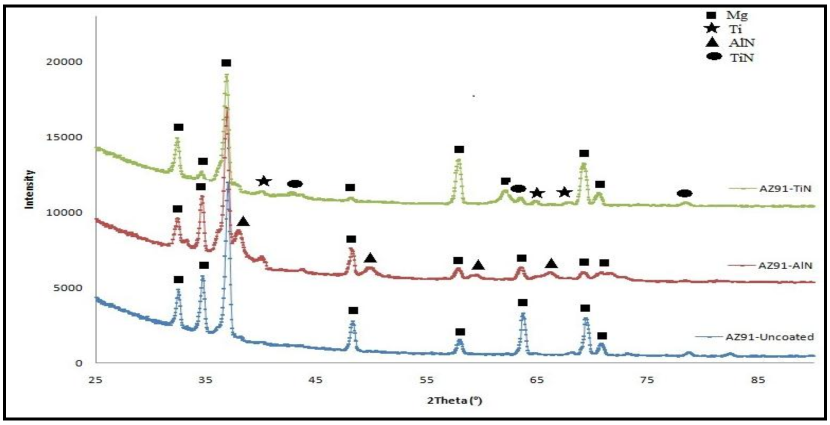

Figure 1: GA-XRD patterns of AlN and TiN coated on AZ91 magnesium alloy substrate

3.2 Electrochemical test

Figure 2 shows the polarization curves of uncoated and coated AZ91 Mg alloy in3.5wt. % NaCl and Hank's solution. From Figure 2a, it was observed that the anodic branches of the polarization curves for all sample (uncoated and coated) in NaCl solution were almost the same. Thus, the corrosion potential and current density are very close to each other. The corrosion potential and the current density of AZ91-uncoated are -1.56 mV and 250.35μA/cm^2; AZ91-AlN is -1.49mV and 35.22μA/cm^2 and AZ91-TiN is -1.44 mV and 16.10μA/cm^2. In contrast, the polarization curve of all samples in Hank's solution (Figure 2b) is slightly differences in anodic branches. The corrosion potential and current density for each sample are; AZ91-uncoated is -1.48 mV and 67.75μA/cm^2; AZ91-AlN is -1.47 mV and 15.08μA/cm^2 and AZ91-TiN is -1.43 mV and 1.75μA/cm^2 respectively.

Based on the polarization curves observed in both solutions, it can be seen that AZ91-TiN shows better corrosion performance compared to AZ91-AlN. It could be deduced that the better performance of TiN is generally due to the formation of TiO_2 in the interlayer of the deposited coating whereby TiO_2 act as a protective layer reducing the potential of corrosion of the coated sample. Furthermore, a pure metal interlayer of Ti that could exist in the TiN coatings may contribute to the improve corrosion protection; substantially due to the corrosion resistance properties of Ti itself [10]. In contrast, for the AlN, the formation of Al_2O_3 layer may reduce the potential of corrosion protection due to low corrosion resistance of Al [10]. Nevertheless, further investigation is needed to properly justify this corrosion behavior.

The penetration rate and mass loss rate calculated based on the corrosion potential and current density obtains during the electrochemical test is summarized in Table 2. The corrosion rates of uncoated and coated AZ91 Mg alloy in both solutions increased according to the following: AZ91-TiN < AZ91-AlN < AZ91-uncoated. For example, penetration rate and mass loss rate in

Hank’s solution for AZ91-TiN is 0.040mm/yr and 0.191g/m^{2}d respectively; while it is 0.344mm/yr and 1.641g/m^{2}d for AZ91-AlN in Hank’s solution. The low current density is correlated to the better corrosion resistance of metals [11].

Overall, AZ91-TiN shows better corrosion performance in Hank’s solution compared to 3.5wt.% NaCl solution due to the least aggressive of chloride ions in Hank’s solution. It should be noted that TiN penetration rate 0.040mm/yr and mass loss rate 0.191g/m^{2}d in Hank’s solution whereby the penetration rate 0.367mm/yr and mass loss rate 1.752g/m^{2}d in 3.5wt.% NaCl solution. This is related to the fact that the presence of chloride ions in the solution affects the passivity of Mg alloy substrate [12]. The higher chloride ionsconcentration leads to higher tendency for the protective surface film (the layer formed on the coated sample during the electrochemical) to breakdown and allowing microgalvanic corrosion acceleration hence increased rate of corrosion [13, 14, 15].

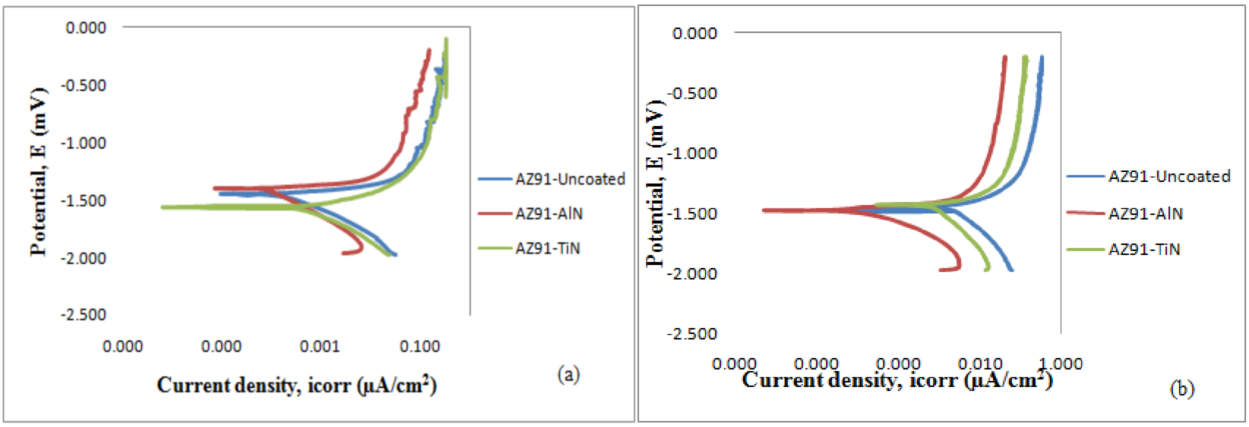

Figure 2: Polarization curves of uncoated and coated AZ91 Mg alloys in (a) NaCl solution (b) Hank’s solution

Table 2: Penetration rate and mass loss rate in NaCl solutionand Hank’s solution

Samples	**Sodium Chloride (NaCl)**		**Hank's solution**	
	Penetration rate (CR)	Mass Loss rate (MR)	Penetration rate (CR)	Mass Loss rate (MR)
AZ91-Uncoated	5.716	27.235	1.547	7.371
AZ91-AlN	0.804	3.832	0.3444	1.641
AZ91-TiN	0.368	1.752	0.040	0.191

4. Conclusion

AlN and TiN was successfully deposited via magnetron sputtering technique and its presence is confirmed by GAXRD analysis. AlN and TiN shows better performance of corrosion behavior in Hank’s solution. Overall TiN show the least mass loss rate and penetration rate in Hank’s solution. Thus, it was suggested that the corrosion behavior of coated samples (AlN and TiN) of AZ91 Mg alloy substrate should be subjected to further investigation in order to look into the potential of this metal in the area of biomaterial.

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Reference

[1] A. Němcová, J. Zapletal, M. Juliš& T. Podrábský: Materials EngineeringVol. 16 (2009), No. 4

[2] K.W. Guo, 'A review of magnesium/magnesium alloys corrosion and its protection', *Recent Patent on Corrosion*, Vol. 2 (2010), p. 13-21

[3] B.L. Mordike& T. Ebert, 'Magnesium Properties — applications — potential', Materials Science and Engineering, vol. A302 (2001), p. 37–45

[4] Li-jingYang, Ying-huiWei , Li-fengHou and DiZhang: Corrosion ScienceVol. 52 (2010), p. 345–351

[5] L.Zhu and G. Song:Surface & Coatings Vol. 200 (2006), p. 2834– 2840

[6] H. Altun and H. Sinichi:Materials Characterization Vol. 58 (2008), p. 266-270

[7] N.I.Z. Abidin, A.D Atrens, D. Martin and A. Atrems:Corrosion Science Vol.53 (2011), p. 3542-355

[8] H.Hoche, C. Blawertand E. Broszeit:Surface Coating TechnologyVol.193 (2005), p. 223-229

[9] M-C. Zhao, M. Liu, G-L. Song and A. Atrens:Corrosion ScienceVol. 50 (2008), p. 3168-3178

[10] L. Chunha, M. Andritschky, L. Reboutaand R. Silva, 'Corrosion of TiN, (TiAl)N and CrN hard coatings produced by magnetron sputtering'.

[11] A. Pardo, M.C. Merino, A.E. Coy , R. Arrabal, F. Viejo and E. Matykina:Corrosion Science Vol.50 (2008), p. 823–834

[12] Y. Xin, C. Liu, K. Huo, G. Tang, X. Tian and P.K. Chu: Surface & Coatings Technology Vol. 203 (2009), p. 2554-2557

[13] H. Altun and S. Sen: Surface and Coating Technology Vol. 27 (2006), p. 1174-1179.

[14] C. Rebholz, A. Leyland, A. Matthews, C. Charitidis, S. Logothetidisand D. Schneider: Thin Solid Films Vol. 514 (2006), p. 81-86

[15] H. Altun and S.Sen: Materials Characterization Vol. 58 (2007), p. 917-921