



# Corrosion behaviour of magnesium alloys coated with TiN by cathodic arc deposition in NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions

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#### ABSTRACT

Magnesium-based light-metal alloys belong to a class of structural materials with increasing industrial attention. Magnesium alloys show the lowest density among the engineering metallic materials, low cost and large availability. However, the limitations according to mechanical strength and the low corrosion resistance restrict their practical application. In this study, TiN was coated on magnesium-based AZ91 magnesium-aluminium-zinc alloy using cathodic arc PVD process. The corrosion behaviours of uncoated and coated magnesium alloys in 1% NaCl, 3% NaCl and 3% Na<sub>2</sub>SO<sub>4</sub> solutions and the influence of the coatings on the corrosion behaviour of the substrate were investigated utilizing potentiodynamic polarization tests. A potentiostat for electrochemical corrosion tests, a cathodic arc physical vapour deposition coating system for coating processes, a scanning electron microscopy for surface examination and elemental analysis of the coatings were used in this study. It was determined that corrosion resistance of magnesium alloys can be increased with TiN coating on the alloys using cathodic arc PVD process.

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#### 1. Introduction

The need for weight reduction, particularly in portable micro-electronics, telecommunication, aerospace and automobile sectors has stimulated engineers to be more creative in their choice of materials. Magnesium and its alloys, with one quarter of the density of steel and only two-thirds that of aluminium, and a strength to weight ratio that far exceeds either, fulfils the role admirably, as an 'ultra light' alloy [1]. Magnesium is the lightest of the structural metals, which makes it one of the favoured materials to minimize vehicle weight and therefore to reduce exhaust gas emissions in transport applications [2]. Although Mg alloys have the highest strength-to-weight-ratio of all the structural metals, several drawbacks, above all the below average corrosion properties, restrict the application of unprotected magnesium alloys [3,4]. Their poor corrosion resistance has hindered its widespread use in many applications [5].

One of the most effective ways to prevent corrosion is to coat the base materials. Surface modification by coatings has

become an essential step to improve the surface properties such as wear, corrosion and oxidation. Various conventional techniques are utilized for depositing the desired material on to the substrate to achieve the surface modification [6]. 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 [7].

It is very important that the protection of magnesium alloys from corrosion using surface treatments for their much more widespread usage. Many studies related to the surface modifications carried out on magnesium alloys and their protection ability against corrosion have been made in recent years. Due to process cleanliness and environmental comprehensively, research into physical vapour deposition (PVD) coatings has been an essential task to develop various advanced surface modification materials for industrial manufacturing [8]. There are a few studies [9–18] in the literature about the effect of PVD coatings on the corrosion behaviour of magnesium alloys, but the researches have increased more

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	l – The che weight %)	mical com <sub>l</sub>	position of	AZ91 magı	nesium
Al	Zn	Cu	Ni	Mn	Si
8.46	0.83	0.07	0.01	0.09	0.08

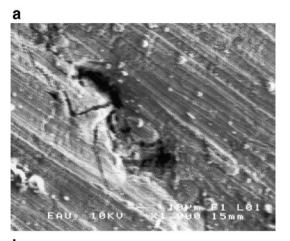
and more. At almost all of the studies, sputtering process has been used as PVD technique. In contrast to sputtering, cathodic arc deposition process is a recent developed PVD technology which has a rapider coating rate and also plays an important role in PVD coating methods [19]. In addition, the cathodic arc process for the deposition of hard coatings is well known for its high ionization efficiency in the plasma and allows the deposition of dense coatings [20]. To date, it has not been met any study related to the effect of cathodic arc PVD coatings on the corrosion resistance of magnesium alloys. In addition, nearly all of the mentioned above studies in the literature related to the effect of PVD coatings on the corrosion behaviour of magnesium alloys have been focused on the corrosion behaviours in solutions including Cl- ions such as NaCl. However, the corrosion behaviour of magnesium alloys in the solutions including (SO<sub>4</sub>)<sup>-2</sup> ions also is a serious attractive area [21]. But, it also has not been met any study about the effect of (SO<sub>4</sub>)<sup>-2</sup> ions on the corrosion behaviour of the PVD coated magnesium alloys. Therefore, the purpose of this study is to deposit TiN coating on the magnesium alloys by cathodic arc deposition process, and then to evaluate the effect of the coating on the corrosion behaviour of the alloys in NaCl and Na2SO4 solutions.

#### 2. Experimental Details

In this study, AZ91 alloy which is one of the most commonly used magnesium alloys was used as the substrate material. The chemical composition of the alloy is reported in Table 1. Before coating, the surfaces of the samples were ground by SiC emery paper with grits of 400, 800 and 1200 and were polished by  ${\rm Al}_2{\rm O}_3$  paste. Then, they were rinsed in distilled water and acetone, and dried in warm air. TiN coatings were deposited on the substrates by cathodic arc PVD technique according to the parameters listed in Table 2.

The electrochemical evaluation was carried out at room temperature using a standard three-electrode (reference, counter and working) configuration, with an Ag/AgCl electrode as the reference electrode, a platinum plate as the counter electrode and the specimen as the working electrode. The experiments were performed using a potentiostat controlled with a computer. The potentiodynamic polarization tests were conducted in 500 ml solutions of 1% NaCl, 3% NaCl and 3% Na<sub>2</sub>SO<sub>4</sub> at a constant scan rate of 1 mV/s. Prior to polarization, the samples were allowed to stabilize to obtain a stable open circuit potential (OCP). A scanning electron

Table 2 – The cathodic arc PVD parameters for TiN coating						
Bias voltage	N <sub>2</sub> pressure	Cathode current	Coating time			
-200 V	4 mtorr	70 A	30 min			



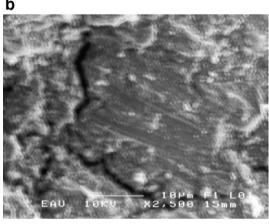


Fig. 1 – SEM images of small structural coating defects on TiN coated AZ91 magnesium alloy, a) a pinhole b) a crack.

microscopy (SEM) for surface examination and elemental analysis of the coatings were used.

#### 3. Results and Discussion

In Fig. 1a, SEM image of a small structural coating defect on TiN coated AZ91 magnesium alloy were given. As seen in the figure, the width of the defects could reach to about 25–30  $\mu m$ . In

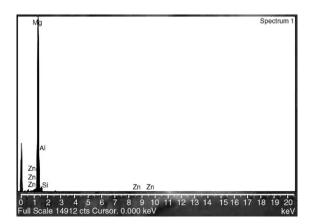


Fig. 2-EDS graphic of uncoated AZ91 magnesium alloy.

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