STRUCTURE AND CORROSION RESISTANCE OF FLUORIDE COATING PREPARED ON MAGNESIUM MATERIAL

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Abstract

Fluoride conversion coatings are perspective surface treatments for reducing corrosion rate of magnesium and its alloys. This work focuses on the preparation of fluoride conversion coating on magnesium material prepared by powder metallurgy. The base material was prepared by compacting powder magnesium into cylinders 20 mm in diameter and 5 mm thick using 400 MPa of uniaxial pressure. The green compacts were sintered in argon atmosphere at 600 °C for 12h. The coating was prepared by dipping the magnesium materials in molten $Na[BF_4]$ salt at 430 °C, the preparation times were 1, 2, 4 and 8 h. The effect of fluoride coating preparation time on thickness and structure of the coating was investigated by mainly two methods. Corrosion resistance was measured by potentiodynamic polarisation in NaCl solution, the structure and thickness of the coating was measured by SEM-EDS (Scanning electron Microscope – Energy Dispersive Spectroscopy) method. The corrosion current decreased significantly with increasing preparation time of the coating. This finding is in correlation with SEM-EDS observation, which confirmed thicker coating layer with increasing preparation time. The structure of the coating was not uniform; however, the coating was predominantly formed on the surface of the individual powder particles from which the base material was formed.

Keywords: Magnesium, Powder metallurgy, Corrosion, Fluoride conversion coatings

1. INTRODUCTION

An important issue related to the use of magnesium is its corrosion resistance. Magnesium readily corrodes on contact with oxygen and water, even at normal temperatures, which prevents its wider use and thus poses a significant problem. In order to prevent corrosion, magnesium materials must be protected [1]. One way to prevent or at least slow down corrosion is to form a conversion coating on the surface of the material. This is formed by combining the substrate with another element with which the substrate is able to react chemically. The resulting coating forms a protective layer that prevents the substrate from reacting with the surrounding environment and corroding. The present work focuses on the fluoride conversion coating. The advantage of the fluoride coating is that it is non-toxic to the body, like magnesium, and is biodegradable, unlike other conversion coatings. Magnesium material with a fluoride conversion coating could therefore find further applications, for example in medicine [2,3].

A hydrofluoric acid solution is used to form a fluoride conversion coating on magnesium material, this method is referred to as conventional. Other effective methods are electrodeposition in a KF solution and immersion of the metal in a $Na[BF_4]$ salt melt, these methods are referred to as non-conventional [3-5].

The conventional method of preparing fluoride conversion coatings produces a protective layer of amorphous $Mg(OH)_2$-xFx. These layers generally improve the corrosion resistance of magnesium alloys. In the case of $Na[BF_4]$, the coating consists of two different layers. A primary one, consisting of MgF_2, and a secondary one, consisting of $Na[MgF_3]$. The mechanism of coating formation is probably based on the decomposition of $Na[BF_4]$. At temperatures above 384 °C this salt decomposes into NaF and BF_3. BF_3 can react with the

magnesium alloy to form a primary layer of crystalline MgF_2. NaF is soluble in the melt of the $Na[BF_4]$ salt and could be involved in the formation of the secondary layer of $Na[MgF_3]$. The secondary layer is probably toxic and can be removed by boiling the coated sample in distilled water. The primary MgF_2 layer is not toxic and acts as a corrosion protection for the magnesium alloy. Unconventional coatings achieve better resistance to electrochemical corrosion than conventional ones. The unconventional coating was successfully prepared on wrought alloys, yet preparing the coating on powder metallurgy prepared magnesium was not tested [6-8].

2. MATERIALS AND METHODS

2.1. Sample preparation

The work with magnesium powder was carried out in a glove box in a nitrogen atmosphere to prevent oxidation or ignition of the powder. 2.5 ± 0.1 g of magnesium powder was weighed into steel dies and the preparation of 20x5 mm cylindrical samples were prepared by applying 400 MPa of uniaxial pressure for 60 s. The pressed tablets were placed in a graphite mould. The mould was placed in a furnace with argon atmosphere. The samples were sintered in an argon atmosphere at 600 °C for 12 hours.

After cooling, the samples were ground with 1200 and 4000 grit SiC paper and subsequently polished on polishing wheels with diamond paste down to 1 µm.

2.2. Coating preparation

A melt of sodium tetrafluoroborate salt ($Na[BF_4]$) was used to form the coating on the samples.

The salt was weighed in a quantity of 80 g into a corundum crucible with a lid and placed in a laboratory furnace, which was subsequently heated to 420 °C. The crucibles were left in the furnace for 2.5 hours to melt the salt completely.

Samples (2 per crucible) were placed in the melt and coated for 1, 2, 4 and 8 hours. After removal from the melt, the samples were boiled in distilled water for 10 minutes to remove any salt residue on the sample surface. After boiling, the samples were rinsed with distilled water, ethanol and dried with hot air.

2.3. Electrochemical characterisation

The corrosion tests were performed using a potentiostat VSP-300 using potentiodynamic polarization (PDP). The measurements and evaluation were performed in EC-Lab.

The measured samples were placed in a corrosion in three-electrode setup. The sample was connected via a copper plate as working electrode, a saturated calomel electrode was used as reference electrode and a platinum mesh was used as auxiliary electrode. Measurements were carried out in 0.15 $mol \cdot l^{-1}$ NaCl solution after one hour of stabilization. The voltage applied to the samples ranged from -0.15 V to 0.5 V with a constant rate of 1 $mV \cdot s^{-1}$ and a reaction area of 1 cm^2. After the measurements were completed, the pH and temperature of the NaCl solution used were measured.

2.4. Metallographic preparation

The samples were cut and moulded into polymer resin for metallographic preparation. Grinding of the crosscuts was done up to 4000 grid sand papers, after this step polishing was carried out up to 1 µm using diamond paste on polishing cloths. The samples crosscuts were observed using a JEOL JSM-7600F electron microscope with an Ultim Max EDS analyser.

3. RESULTS AND DISCUSSION

3.1. Electrochemical behaviour

The corrosion behaviour of the samples was tested using PDP. After one hour of stabilization, the polarization curve, which consists of cathodic and anodic parts, was measured. The evaluation is performed by extrapolating the linear (Tafel) region of both the cathodic and anodic curves. The intersection resulting from the extrapolation determines the values of the corrosion potential Ecorr and the corrosion current Icorr, which are quantities characterising the corrosion behaviour of the sample.

In the case of the measurements in this work, the cathodic part of the curve is mainly used because the anodic part did not have an ideal waveform (see **Figure 1**), which could be due to the influence of dissolved corrosion products in the electrolyte. Similar polarization curves were also observed in [9] and [10], so it could be assumed that the mentioned behaviour is typical for magnesium and it is therefore appropriate to start from the cathodic part of the curve.

From **Figure 2** it can be seen that the corrosion resistance increases with increasing coating time. The polished sample has the highest value of corrosion current, which is not surprising. The decrease of corrosion current is probably connected to increasing thickness of the coating. There is only negligible drop in corrosion current between the 4 h coating and 8 h coating. This small difference is to be expected as the rate coating creation decreases significantly in time. The pH values of the used NaCl solution after the measurements (**Table 1**) correlate well with the PDP data. Decreasing corrosion rate means less dissolved magnesium, in form of $Mg(OH)_2$, in the solution, therefore higher pH values correspond to lower corrosion resistance.

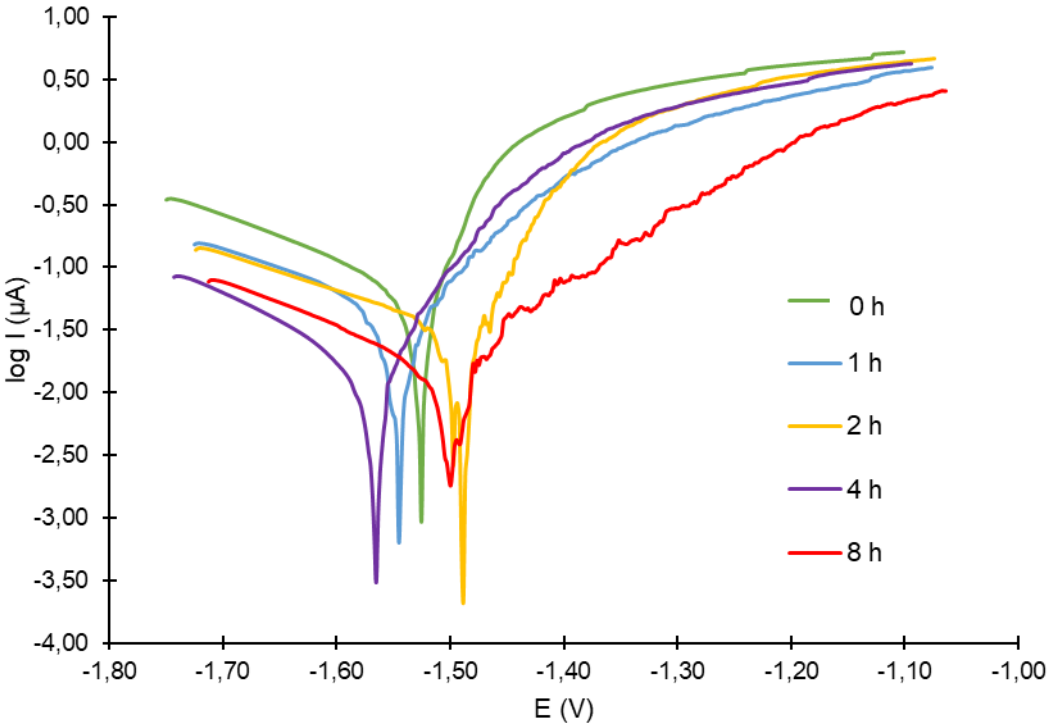

Figure 1 Measured potentiodynamic curves of coated and uncoated samples

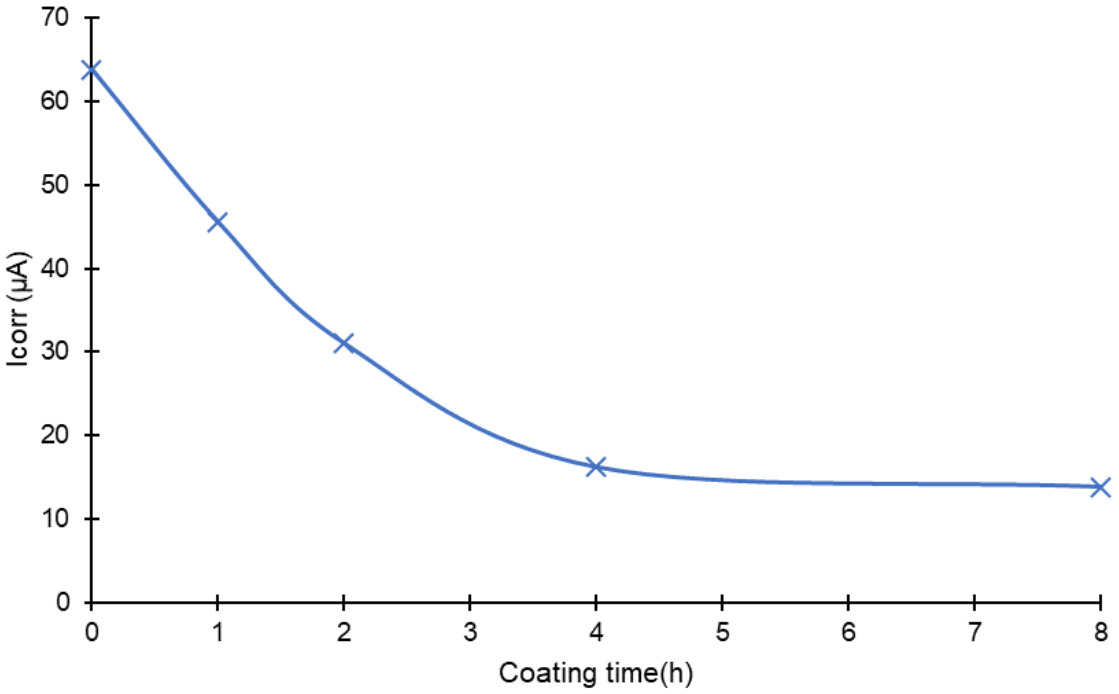

Figure 2 Dependence of corrosion current on coating time

Table 1 pH values of the used NaCl solution after poteciodynamic measurement

Coating time (h)	0	1	2	4	8
pH	8.39	7.33	7.44	7.27	6.8
Solution temperature (°C)	23.6	24.4	24.5	24.7	25

3.2. SEM-EDS analysis

Figure 3 shows fluorine elemental map from the crosscuts for all coated samples. The maps shows increasing penetration depth of fluorine into the microstructure of the samples. This is different when compared to the coating preparation on wrought alloys [8]. Powder metallurgy samples have different morphology than wrought alloys, because they are prepared from individual magnesium particles, which have small amount of oxygen on the surface. This oxygen can prevent perfect bonding of the powder particles so a microporosity may be present in these samples. This porosity however does not provide a way for the salt melt penetration as no boron or sodium were detected in the samples. The higher depth of fluorine penetration is probably caused by reaction of fluorine with oxidized powder particle surfaces.

It can also be observed from the elemental maps that a thin (only few microns thick) continuous coating layer formed on the sample surface. Although the fluorine extends to a depth of tens of microns in some cases, it does not completely coat the magnesium powder particles and thus does not form an additional barrier in the sample volume to prevent corrosion. Similar phenomenon was found in [11]. Even if the whole surface of the initial powder particles is covered with fluoride coating the corrosion is not sufficiently hindered. Once the conversion coating on the surface of the material is breached the degradation of the whole component will take place.

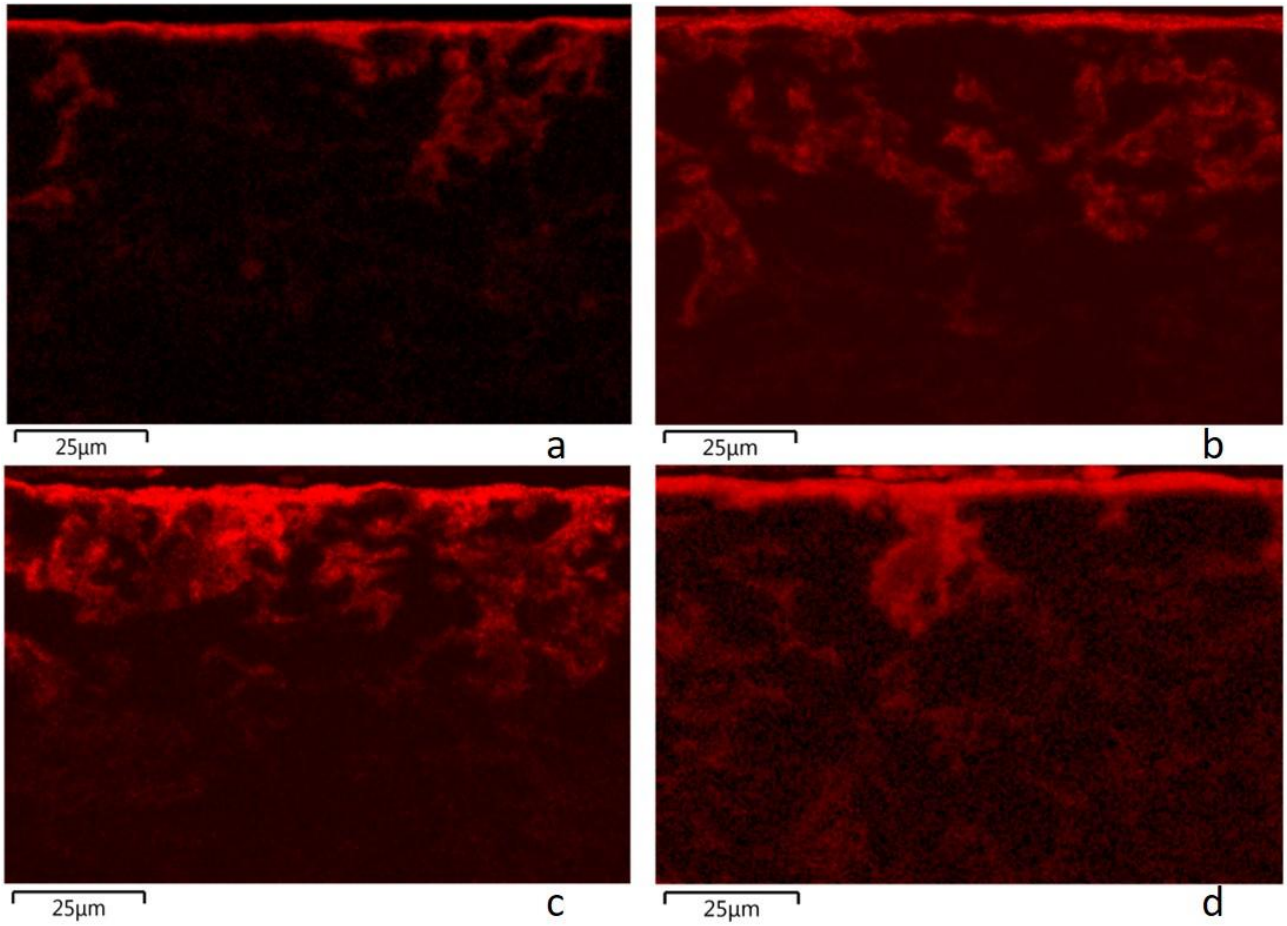

Figure 3 Distribution of fluorine content from the surface into the substrate material with different coating times, a – 1 h, b – 2 h, c – 4 h and d – 8 h

4. CONCLUSION

- Potentiodynamic measurements were used to test the corrosion behavior of the samples and from the resulting corrosion current values it was concluded that the corrosion resistance of the samples increases with increasing coating time. The 4 h coating time was sufficient to reduce the corrosion current to approximately third in comparison with uncoated material. Further coating time led only to minimal decrease of corrosion current.
- From the EDS analysis, it was also found that the thickness of the coating layer increases with increasing coating time. The porous nature of powder metallurgy prepared substrate enabled deeper penetration of fluorine into the material when compared to wrought alloys, however it did not lead to better corrosion protection.

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