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Effect of process conditions for the preparation of a manganese-based coating on the surface of AZ31 magnesium alloy

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Manganese-based coatings on AZ31 magnesium alloy with $Mg(OH)_2$ interlayer were prepared by hydrothermal reaction under different process conditions (temperature, time, and concentration). The harsh reaction conditions provided coatings with defects. These defects enabled the corrosive environment penetrated to the magnesium alloy which impaired the corrosion properties of AZ31 alloy. Optimal conditions included a temperature of 120 °C, 0.25 M $MnCl_2$, and a reaction time of 1 h. The prepared coating was mainly composed of Mn_3O_4, which consisted of nanosized crystals of polyhedral shape. Potentiodynamic polarization measurements showed that the coating had very good corrosion resistance in 0.15 M NaCl. Future work will focus on the potential use of the manganese-based coating in biomedical applications.

INTRODUCTION

Magnesium and its alloys have high application potential and could become some of the most important engineering materials of the 21st century. At present, magnesium materials are finding applications in the automotive, aerospace, and electronics industries, as well as in biomedicine [1]. The attractiveness of magnesium and its alloys is due to their favourable properties, such as low density, high specific strength, favourable thermal and electrical conductivity, biocompatibility, and biodegradability [2]. Unfortunately, their main drawback is their poor corrosion resistance, which limits the wider use of magnesium materials in practice. In order to overcome this problem, various coatings, including fluoride coatings, Ni-P coatings, superhydrophobic coatings, plasma electrolytic oxidation coatings, calcium phosphate coatings, HVOF-sprayed Fe-based coatings and layered double hydroxide coatings, are being developed and investigated [3–9]. Fluoride coatings have high corrosion resistance and are simple to prepare. However, their use in practice is questionable due to the presence of fluoride. Similarly, a wider interest in the use of Ni-P coatings on magnesium alloys is the limited occurrence of nickel. Much more interesting potential (especially in the medical field) is represented by phosphate-based coatings (CaP coatings) and LDH coatings. An alternative to these coatings may be manganese-based coatings, which are still rather on the periphery of research. Jian et al. [10] published a work in which they reported the preparation of a conversion coating on AZ31 alloy from a permanganate solution. The coating was mainly composed of MnO_2, MnO, and $Mg(OH)_2$ and formed a continuous nearly crack-free layer providing improved corrosion resistance of AZ31 alloy. Umehara et al. [11] used permanganate solution with HNO_3 or HF for the preparation of the conversion coatings which improved corrosion resistance of AZ91D alloy. The effect of an aqueous $MnSO_4$ solution on bare AZ31 alloy was described by Xun et al. [12], who showed that the $MnSO_4$ solution preferentially dissolved magnesium of the alloy to form $Mn(OH)_2$ resulting in an increase in corrosion resistance in the simulated body fluid. This etching method is often used to roughen the surface for subsequent superhydrophobization process [8]. The positive effect of manganese-based compounds on the corrosion properties has also been demonstrated in the case of sealing PEO coating pores on magnesium alloys using a permanganate bath [13].

The aim of this work was to prepare a manganese-based coating on AZ31 alloy using $MnCl_2$ solution under hydrothermal conditions. Attention was paid to finding the optimum reaction conditions (temperature, time, $MnCl_2$ concentration) for the preparation of the coating. The corrosion behaviour was tested in 0.15 M NaCl using potentiodynamic polarization measurements.

EXPERIMENTAL

Material and coating preparation

Material and its pre-treatment

Rolled sheet AZ31 magnesium alloy was used in this work. The elemental compositions of the alloy were determined using a Glow-Discharge Optical Emission Spectroscopy (GDOES; Spectrumat GDS 750, Spectruma Analytik GmbH, Hof, Germany) and is listed in Tab. 1. This GDOES data were measured on Faculty of Mechanical Engineering on Brno University of Technology. Samples of AZ31 alloy with dimensions of 20 × 20 × 5 mm were ground with 800 and 1200 grit SiC paper, rinsed with deionized water and isopropanol, and dried with hot air. The ground samples were hydrothermally treated in 2 M NaOH solution at 120 °C for 12 h. Then, the pre-treated samples were rinsed in deionized water and isopropanol, and dried with hot air.

Tab. 1. The elemental compositions of AZ31 magnesium alloy (GDOES analysis)

Content (wt.%)	Al	Zn	Mn	Si	Fe	Sn	Zn	Mg
AZ31	3.60	1.34	0.28	0.03	0.002	0.01	–	Bal.

Coating Preparation

The pre-treated AZ31 alloy sample was placed in a 250 ml PTFE-lined autoclave stainless steel reactor containing 100 ml of $MnCl_2$ solution. The autoclave reactor was placed in a preheated oven to allow the hydrothermal reaction to take place. The following conditions were used:

0.5 M $MnCl_2$, 160 °C, 2 h

0.5 M $MnCl_2$, 120 °C, 1 h and 2 h

0.25 M $MnCl_2$, 120 °C, 0.5 h, 1 h, 2 h and 4 h

0.25 M $MnCl_2$, 90 °C, 1 h, 2 h and 4 h

The reactors were taken out of the furnace and opened after one hour of cooling in air. The samples were rinsed in deionized water and isopropanol, and dried with hot air.

Characterization

Macroscopic analysis

Macroscopic surface characterization of the samples was performed using a light microscope (Zeiss Stemi 2000-C, Zeiss, Oberkochen, Germany).

SEM-EDS analysis

A scanning electron microscope (SEM, JEOL JSM-7600, Tokyo, Japan) with an energy dispersive X-ray spectroscope (EDS, Oxford Instruments plc, Abingdon, UK) was used to characterize the surface morphology and elemental composition of samples.

PDP measurements

Potentiodynamic polarization (PDP) measurements were performed using a Bio-Logic VSP-300 potentiostat (BioLogic, Seyssinet-Pariset, France). Measured samples with an exposed area of 1 cm^2 served as the working electrode. The saturated calomel electrode (SCE) was used as the reference electrode and Pt mesh as the counter-electrode. A 0.15 M NaCl solution without pH adjustment served as a corrosive medium in the corrosion cell with a volume of 200 ml. Open circuit potential (OCP) variations with time were recorded during 60 min of exposure. Afterwards, PDP measurements were performed in the potential range from −300 mV to 750 mV vs. OCP at a scan rate of 1 mV/s.

XRD analysis

The phase composition was analysed by X-ray diffraction (XRD; Panalytical, Malvern, UK). The X-ray source was Cu Kα1 radiation (λ =1.540598 Å), which was operated at a voltage of 40 kV and a current of 30 mA within the range of 5° and 90° 2θ at a scanning rate of 0.01313° 2θ time per step of 46 s.

RESULTS

Effect of process conditions

The silver-gloss surface of AZ31 alloy was pre-treated in NaOH solution, resulting in a dark brown appearance of the $Mg(OH)_2$ coating (Fig. 1). This coating was characterized by a layer of very fine $Mg(OH)_2$ crystals, see Fig. 1. The pre-treated sample was subjected to a hydrothermal reaction in 0.5 M $MnCl_2$ at 160 °C for 2 h. As can be seen in Fig. 2, the surface was covered with a brownish orange coating which contained defects visible to the eye. This fact indicates that the reaction conditions used were aggressive for the preparation of the coating.

In the second experimental procedure, the pre-treated samples were hydrothermally reacted with 0.5 M $MnCl_2$ at a lower temperature of 120 °C for 1 h and 2 h. Fig. 3 shows the surfaces of the prepared coatings. By extending the reaction time from 1 h to 2 h, it was clearly seen that the colour appearance of the coating changed from light brown to reddish brown. On the basis of SEM analysis, this colour shift is probably related to the greater density arrangement of crystals and their smaller size in the sample prepared for 2 h, because the thickness of the coating was around 0.9 μm for both reaction times (1 and 2 h). However, both coatings prepared in 0.5 M $MnCl_2$ at 120 °C contained defects (observed as black or white areas). The white areas were attributed to $Mg(OH)_2$, which filled the holes (observed

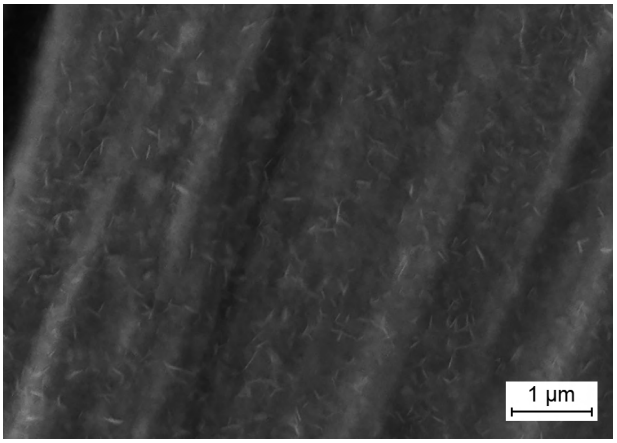
as black dots) after the corrosive environment penetrated the magnesium alloy. These results indicated that the concentration of $MnCl_2$ used was high.

In the next experimental procedure, the hydrothermal reaction of the pre-treated sample with 0.25 M $MnCl_2$ at 120 °C was carried out for 0.5, 1, 2, and 4 h. The surface of the prepared samples is shown in Fig. 5. The appearance of the surface prepared at 0.5 h corresponded to that of the pre-treated sample ($Mg(OH)_2$ coating on AZ31 alloy), see Fig. 1 and Fig. 5. This indicates that the reaction time was too short to form a manganese-based coating on the surface. Conversely, a reaction time of 4 h was too long as it led to the formation of a coating with defects that were manifested as black dots. The coatings prepared at 1 and 2 h did not differ from each other. Both surfaces were orange in colour and without visible defects.

The effect of the temperature of 90 °C on the preparation of the coatings in 0.25 M $MnCl_2$ was monitored at times of 1, 2, and 4 h. The coating surfaces obtained are shown in Fig. 6. As can be seen, the reaction time of 1 h was insufficient as the coating was in the early stages of formation. On the other hand, a reaction time of 4 h caused the appearance of defects. An orange-coloured coating with the absence of corrosion defects was observed at a time of 2 h.



a) light microscopy



b) SEM

Fig. 1. Surface of the pre-treated sample using light microscopy (a) and SEM (b)

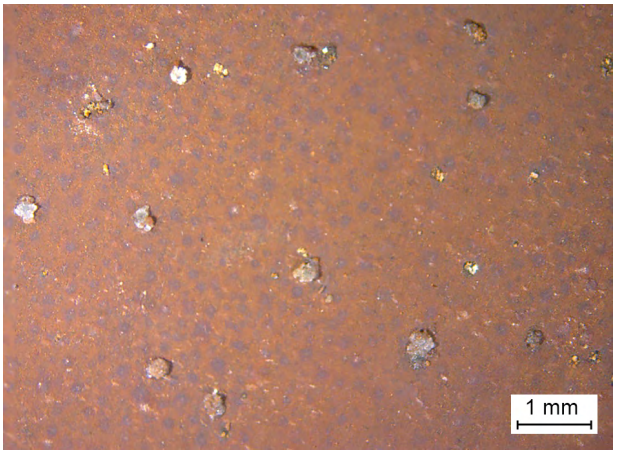
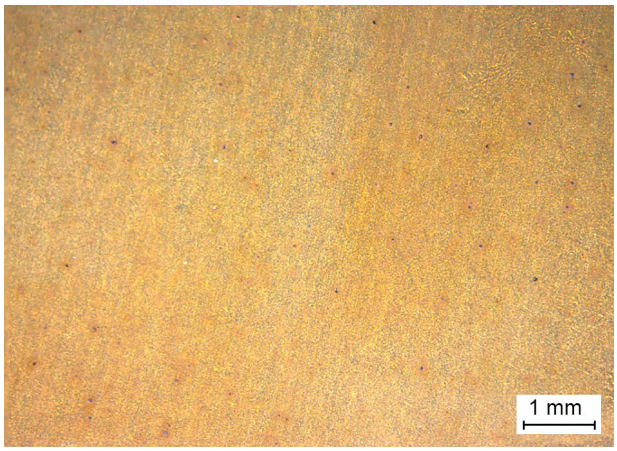
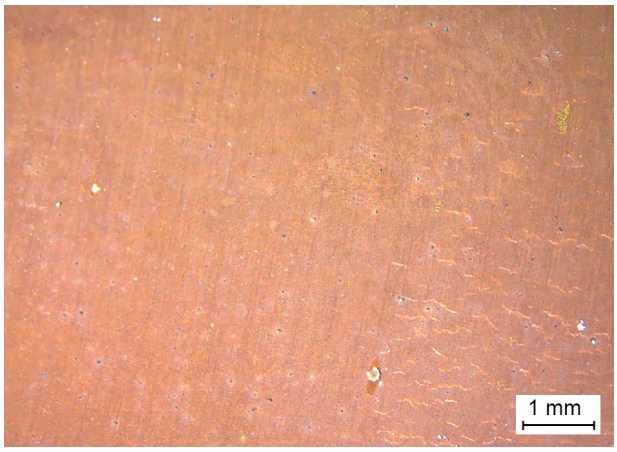


Fig. 2. Coating prepared in 0.5 M $MnCl_2$ at 160 °C for 2 h



a) 1 h



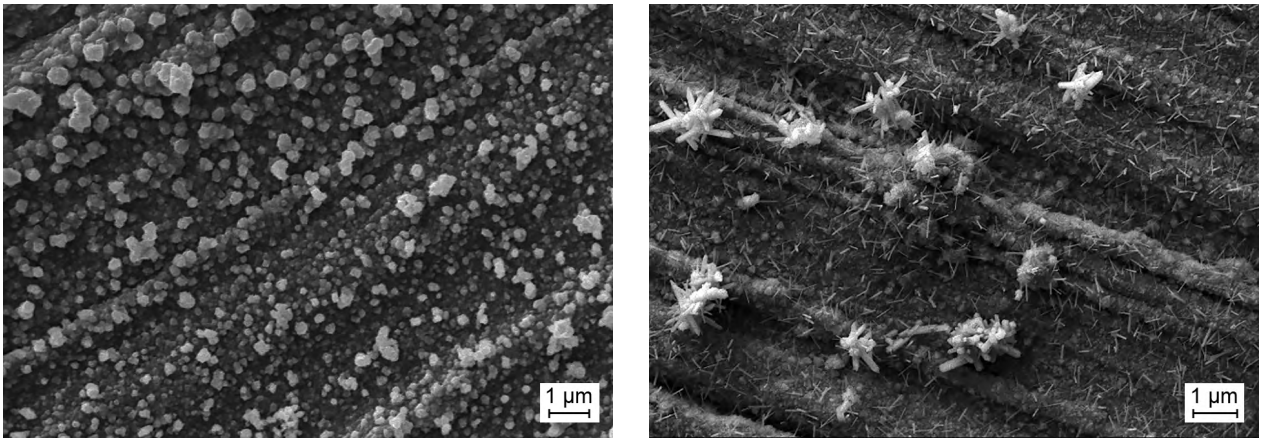
b) 2 h

Fig. 3. Coating prepared in 0.5 M $MnCl_2$ at 120 °C for 1 h (a) and 2 h (b)

Characteristics of coatings

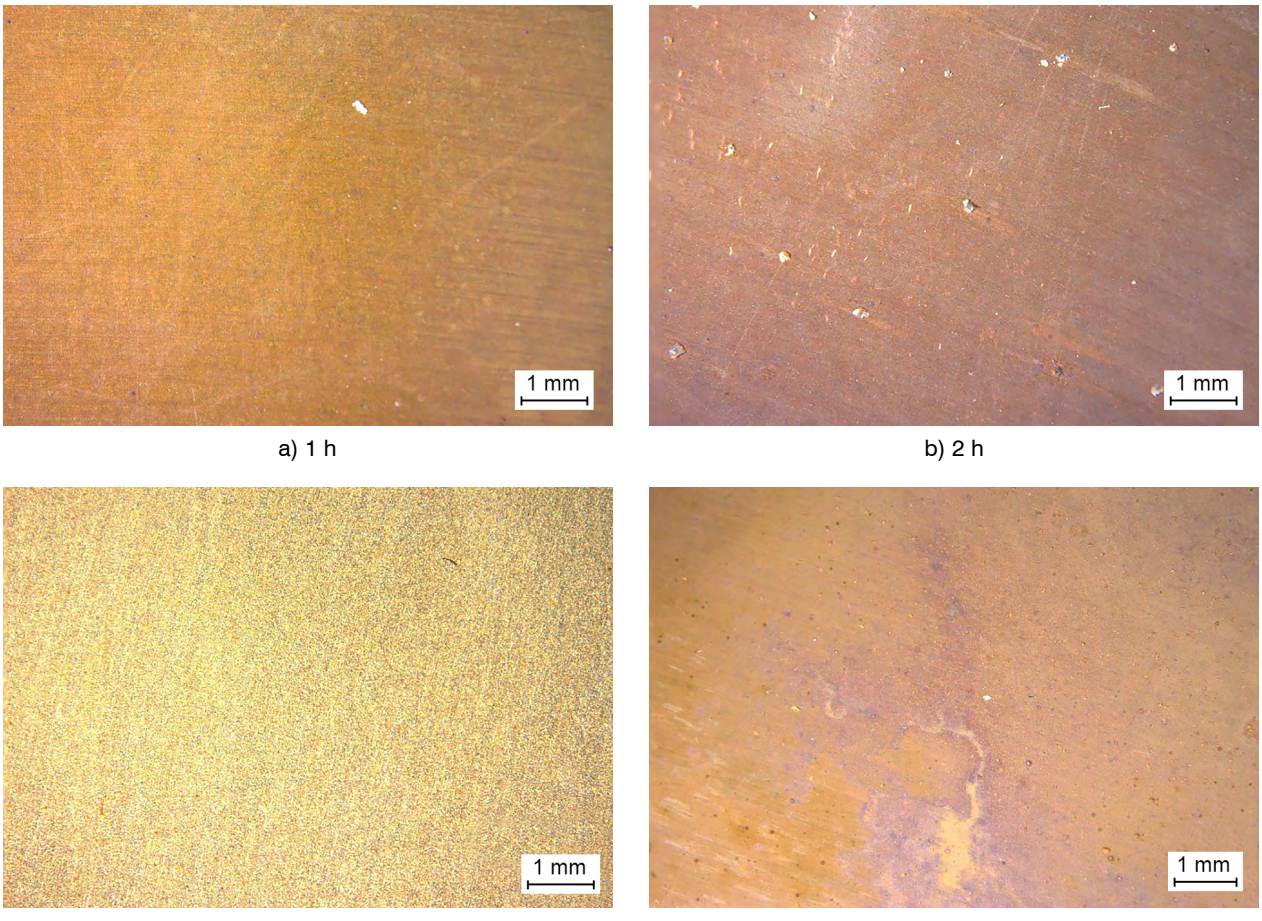
PDP measurements

The samples including bare AZ31 alloy, pre-treated AZ31 alloy, and coatings prepared in 0.25 M $MnCl_2$ at 120 °C for 1, 2, and 4 h were measured in 0.15 M NaCl solution. The values of corrosion potential (E_{cor}) and polarization resistance (R_P) were obtained, which are summarized in Tab. 2. The results clearly show that pre-treatment of AZ31 alloy in NaOH significantly improved the corrosion resistance. The samples prepared by hydrothermal reaction in 0.25 M $MnCl_2$ also showed



a) 1 h b) 2 h

Fig. 4. Coating prepared in 0.5 M $MnCl_2$ at 120 °C for 1 h (a) and 2 h (b)



a) 1 h b) 2 h

c) 3 h d) 4 h

Fig. 5. Coating prepared in 0.25 M $MnCl_2$ at 120 °C for 1 h (a), 2 h (b), 3 h (c) and 4 h (d)

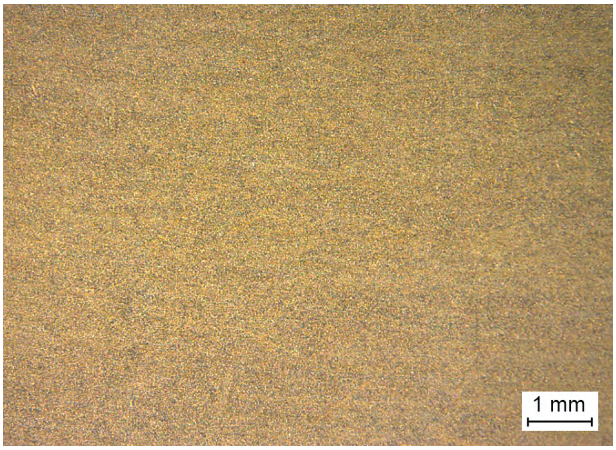
high corrosion resistance. However, as the reaction time of coating formation increased, the R_p decreased and the corrosion potential shifted to more negative values compared to the parameters for the pre-treated sample. The deterioration was negligible for the coating prepared for 1 h, but after increasing the reaction time from 1 h to 2 h, the R_p of the coatings decreased significantly. This fact suggests that not only coating formation but also degradation of the $Mg(OH)_2$ interlayer occurred during the longer reaction time. The deterioration of the corrosion properties from a thermodynamic point of view was also indicated by a shift of the corrosion potential towards negative values. The results show that the corrosion resistance was similar for the coatings prepared for 2 h and 4 h.

SEM-EDS analysis

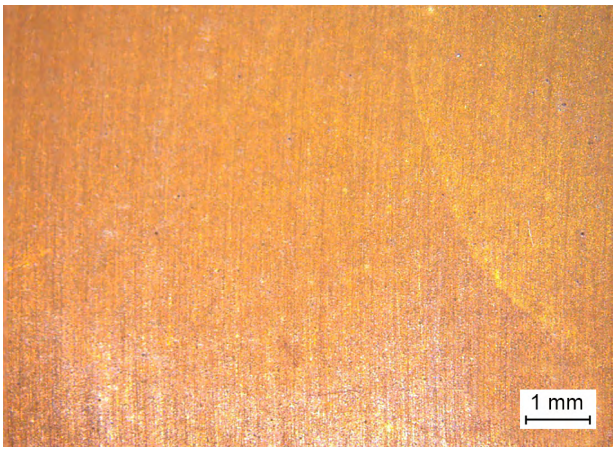
The morphology of the coating that prepared at 120 °C for 1 h in 0.25 M $MnCl_2$ is shown in Fig. 8. The surface was coated with a layer of nanosized crystals, which were non-spherical in shape. The size of the crystals ranged from 80 to 100 nm and appeared as an octahedron. The crystals were not tightly packed, which may have facilitated the penetration of the solution to the $Mg(OH)_2$ interlayer. The lower resolution image also shows the grooves after grinding. Elemental analysis using EDS showed that the chemical composition of the crystals can be attributed to Mn_3O_4 (Mn 42.45 at. %, O 53.61 at. % and C 3.94 at. %). This composition is consistent with the findings of the XRD analysis.

XRD analysis

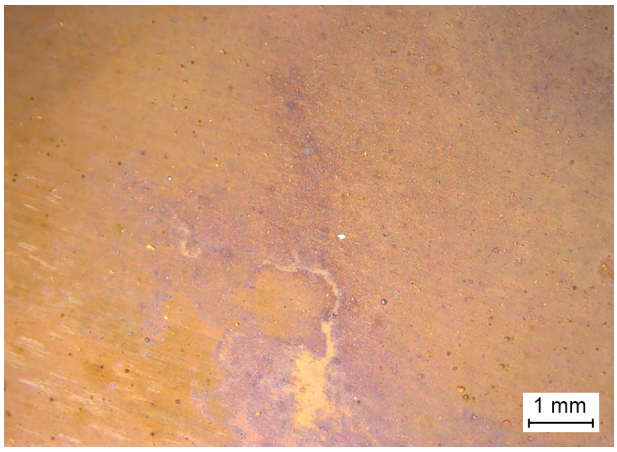
XRD analysis of the coating prepared at 120 °C for 1 h is shown in Fig. 9. The results showed that the surface was mainly covered with Mn_3O_4. Minor $Mn(CO_3)_2$ compounds were also formed, which originated from the reaction with CO_2 dissolved in $MnCl_2$ solution. The reaction probably proceeded via $Mn(OH)_2$, which was also minority identified among the products. The peaks corresponding to $Mg(OH)_2$ originated from the layer of the pre-treated sample.



a) 0.5 h



b) 1 h

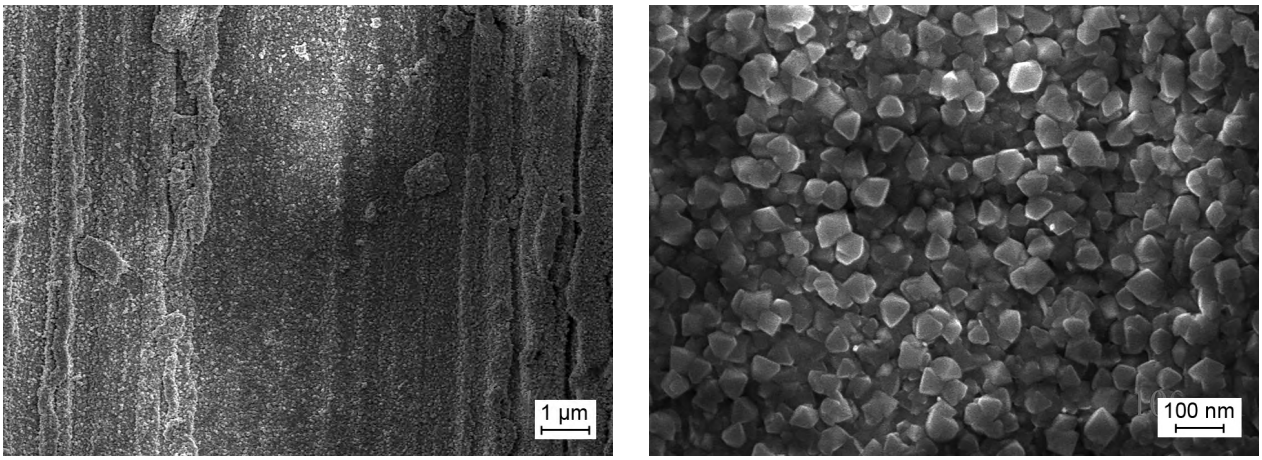


c) 2 h

Fig. 6. Coating prepared in 0.25 M $MnCl_2$ at 90 °C for 0.5 h (a), 1 h (b) a 2 h (c)

Tab. 2. Corrosion parameters obtained from PDP measurements

	AZ31	**$Mg(OH)_2$/AZ31**	**Coatings prepared in 0.25 M $MnCl_2$ at 120 °C**		
			1 h	**2 h**	**4 h**
E_{cor} (mV)	–1.45	–1.26	–1.27	–1.32	–1.33
Rp (kΩ)	0.7	$2.6 \cdot 10^3$	$1.5 \cdot 10^3$	208.1	160.8



a) 1 h b) 2 h

Fig. 8. Low-resolution (a) and high-resolution (b) SEM images for the coating prepared in 0.25 M $MnCl_2$ at 120 °C for 1 h

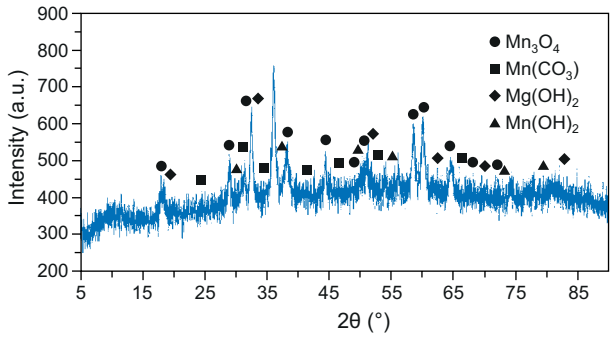


Fig. 9. XRD spectrum of the coating prepared in 0.25 M $MnCl_2$ at 120 °C for 1 h

DISCUSSION

Pre-treatment of AZ31 alloy in NaOH provided a layer that was composed of very fine $Mg(OH)_2$ crystals (Fig. 1). This layer prevented undesirable degradation of the bare AZ31 alloy surface from the attack by $MnCl_2$ during the hydrothermal reaction. Etching of AZ31 alloy with $MnCl_2$ solution was observed in our laboratory (data not presented) and was consistent with the results of other authors [12].

The preparation of the manganese-based coating was dependent on temperature, time, and $MnCl_2$ concentration. If the coating was prepared at high temperature (160 °C) and high $MnCl_2$ concentration (0.5 M) or the reaction time was higher than 2 h and lower temperature (120 °C) and $MnCl_2$ concentration (0.25 M), then local corrosion was observed on the coating surfaces. This indicates that the solution has penetrated through the coating to the substrate and/or the alloy. Milder conditions (90 °C, 0.25 M $MnCl_2$) led to the formation of the coating after 2 h, but the longer reaction time also caused local corrosion to occur. Macroscopic evaluation of the samples showed that promising reaction conditions for coating formation included a temperature of 120 °C, a 0.25 M $MnCl_2$ solution and reaction times of 1 and 2 h, as the rate of coating formation and its stability outweighed its degradation. The experimental results also indicated that increasing the reaction time resulted in the formation of a coating with greater thickness, but at the same time defects appeared in greater numbers.

PDP measurements clearly showed that the corrosion resistance increased on the pre-treated and Mn-coated samples. However, the corrosion resistance of the coatings prepared with longer reaction times (2 h or more) was worse than that for the coating prepared for 1 h. This is attributed to the fact that the increase in reaction time to 2 h or more led to the penetration of the $MnCl_2$ solution to the $Mg(OH)_2$ interlayer and/or the AZ31 alloy and consequently caused local degradation of the coating. The local degradation of the coating allowed the corrosive environment (0.15 M NaCl) to penetrate more easily to the AZ31 alloy, thereby accelerating corrosion. Corrosion environment 0.15 M NaCl was used as an example of the simplest physiological environment. This environment enables monitoring the effect of chlorides on the corrosion behaviour of the coating. The corrosion medium was pilot test and for next test will be used Hank's solution, which is more complex in terms of chemical composition. The corrosion resistance of the coating prepared for 1 h was very similar to the pre-treated sample. However, the observed slight deterioration in corrosion resistance was attributed to the degradation of the $Mg(OH)_2$ interlayer during the hydrothermal reaction. Based on the macroscopic evaluation and PDP measurements, it was decided that the optimum conditions for the preparation of the manganese-based coating were as follows: 0.25 $MnCl_2$, 120 °C, and 1 h. SEM-EDS analysis showed that the coating was composed of polyhedral Mn_3O_4

nanoparticles, which did not form a tightly ordered layer, allowing the corrosive environment to access the $Mg(OH)_2$ interlayer. XRD analysis also showed that the composition of the coating was dominated by Mn_3O_4. Minor $Mn(OH)_2$ and $Mn(CO_3)_2$ were also present, which may have been formed by the reaction of $Mn(OH)_2$ with dissolved CO_2 in $MnCl_2$ solution. The proposed mechanism for the formation of Mn_3O_4 assumed several reaction steps, which can be captured by Equations (1) to (5). Manganese ions released by dissociation (1) could react with OH^- ions (2), which could be released by hydrolysis of the $Mg(OH)_2$ coating (3) or by its dissolution via chlorides (4).

$$3\ MnCl_2 \rightarrow 3\ Mn^{2+} + 6\ Cl^- \quad (1)$$

$$Mn^{2+} + 2\ OH^- \rightarrow Mn(OH)_2 \quad (2)$$

$$Mg(OH)_2 \rightarrow Mg^{2+} + 2\ OH^- \quad (3)$$

$$Mg(OH)_2 + 2\ Cl^- \rightarrow MgCl_2 + 2\ OH^- \quad (4)$$

The formed $Mn(OH)_2$ could be oxidized to Mn_3O_4 under hydrothermal conditions according to the following reaction (5).

$$6\ Mn(OH)_2 + O_2 \rightarrow 2\ Mn_3O_4 + 6\ H_2O \quad (5)$$

The prepared coating has potential applications in the field of medicine, as it is published that Mn_3O_4 nanoparticles have an antibacterial effect against various bacteria and fungi [14]. Furthermore, it is possible to transform this coating into LDH layers, where intercalation of ions and small molecules can take place. This treatment can improve the corrosion properties of the prepared LDH coating and this will be the subject of future research. Further studies will be also devoted to corrosion behaviour in more ionic complex environments such as Hank's solution, which will be more in line with simulated body fluids.

CONCLUSIONS

A manganese-based coating was prepared on AZ31 alloy by hydrothermal reaction. The optimum conditions for the preparation of the coating included a temperature of 120 °C, a reaction time of 1 h, and a $MnCl_2$ solution with a concentration of 0.25 M. The coating consisted of polyhedral nanoparticles consisting of Mn_3O_4. PDP measurements in 0.15 M NaCl showed that the coating prepared under optimum conditions had high corrosion resistance compared to the bare AZ31 alloy and almost identical corrosion resistance to the pre-treated sample. The coating will be further investigated as it may have potential use in biomedical applications due to the antibacterial properties of Mn_3O_4.

Acknowledgement

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