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Comparative Corrosion Resistance of Molybdate Conversion Coatings Containing SiO_2 or TiO_2 Nanoparticles

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Abstract

In this paper, corrosion resistance was compared between molybdate conversion coatings containing SiO_2 or TiO_2 nanoparticles, on five magnesium alloys exposed to a 3.5 wt.% NaCl solution. The surface morphology of the molybdate conversion coatings containing SiO_2 or TiO_2 nanoparticles was examined by scanning electron microscopy (SEM). The corrosion resistance of the nanocoatings was investigated by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and potentiodynamic cyclic anodic polarization measurements. The electrochemical methods showed that the addition of SiO_2 or TiO_2 nanoparticles to the conversion treatment has significantly improved the corrosion resistance property of molybdate conversion coatings for all tested Mg alloys, but revealed that TiO_2 was more effective.

Keywords: magnesium alloy, conversion coating and nano-particles.

Introduction

Magnesium and its alloys have low density and high strength to weight ratio advantages, and can be useful structural materials for automotive, computer, mobile telephone, aerospace and national defense applications [1-3]. However, poor corrosion resistance has significantly limited their development and commercial application. One of the most effective ways to improve the corrosion resistance of magnesium alloys is forming a coating on their surface, to isolate the base material from the environment [4, 5].

As a chromate-free conversion coating, molybdate conversion treatment has been applied on Zn, Al alloy and steel substrates, to improve their corrosion resistance [6]. However, a main problem of molybdate conversion coatings on the magnesium alloy substrate is the presence of pores and cracks that leads to serious protective properties deterioration of conversion coatings [6, 7].

Nanoparticles have many unique physical and chemical properties, because of quantum size, small size and macro quantum tunnel effects [8]. Recently, metal matrix composite coatings containing nanoparticles have been more widely

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studied. In this paper, corrosion resistance was compared between molybdate conversion coatings containing SiO_2 or TiO_2 nanoparticles, and evaluated on different magnesium alloys exposed to a 3.5 wt.% NaCl solution. The surface structures of the coatings were examined by scanning electron microscopy (SEM), and the corrosion resistance was determined by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and potentiodynamic cyclic anodic polarization measurements.

Experimental

Material

To evaluate nanocoating efficiency on a variety of magnesium alloys, five magnesium alloys of dimensions 20 mm x 20 mm x 5 mm, having a chemical composition as shown in Table 1, were used as substrate materials. The specimens were ground to 1000-grit finish on silicon carbide paper, subsequently underwent alkaline cleaning in 40 gL^{-1} of a $Na_3PO_4.12\ H_2O$ solution, at 60 ºC, for 8 min, and then they were submitted to acid pickling in 200 mL of a CH_3COOH and 50 gL^{-1} $NaNO_3$ solution, at room temperature, for 5 s. The specimens were rinsed in flow distilled water after each step, to remove contamination.

Table 1. Chemical composition of the used samples, in % mass.

Samples	Al	Cu	Si	Zn	Ca	Mg
I	0.02	0.004	0.05	0.01	0.016	Bal.
II	0.063	0.001	0.110	0.020	2.040	Bal.
III	3.2	0.05	0.05	1.3	0.04	Bal.
IV	0.063	0 .229	0.103	1.900	0.046	Bal.
V	0.010	0 .003	0.058	1.110	1.202	Bal.

Preparation of molybdate conversion coatings

The molybdate conversion coatings were prepared in a solution containing 25 gL^{-1} $Na_2MoO_4.2H_2O$ and 4 gL^{-1} NaF, with a pH value of 3.0, at a temperature of 65 ºC, for 10 min. To the molybdate conversion coating, 4 gL^{-1} of SiO_2 nanoparticles were added. This specified SiO_2 nanoparticles concentration was recommended by previous weight gain calculations, during the formation process, in a molybdate solution, using AZ31 magnesium alloy as substrate material [9]. For comparison, 4 gL^{-1} of TiO_2 nanoparticles were added to the molybdate conversion coating solution. The molybdate conversion coating solution containing the nanoparticles was stirred with a magnetic stirrer in an ice water bath, for 1 h, to get a uniform suspension. The average size of the SiO_2 and TiO_2 nanoparticles was estimated to be 20 and 28 nm, respectively, from SEM analysis.

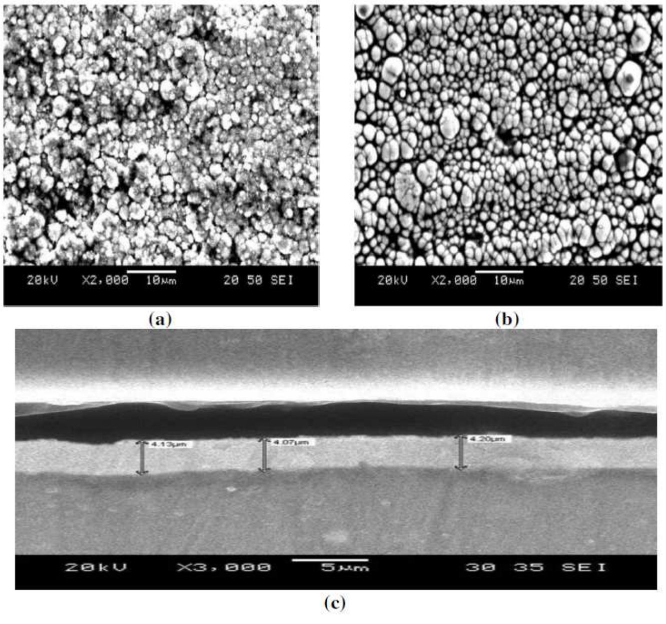
Measurements and instruments

The morphology of molybdate conversion coatings containing SiO_2 or TiO_2 nanoparticles was observed using a JEOL JSM54 10 (Japan) computer controlled scanning electron microscope. The corrosion resistance was estimated by electrochemical measurements, using a Voltalab 40 Potentiostat PGZ301 (Germany) and Volta Master 4 software, to measure and analyze the corrosion rate. EIS, potentiodynamic polarization and potentiodynamic cyclic anodic polarization measurements were carried out in a 3.5% NaCl solution as electrolyte, in a three-electrode system, using the molybdate conversion coatings, without and with SiO_2 or TiO_2 nanoparticles. The five magnesium alloys were the working electrode, saturated calomel electrode (SCE) was the reference electrode, and a platinum sheet was the counter electrode. An area of 1 cm^2 was used for testing, as the remaining working electrodes were masked with epoxy resin. EIS measurements were recorded at open circuit potential, and the frequency ranged from 0.01 to 100.00 Hz, with 10 mV. Polarization curves were at a scan rate of 1 mVs^{-1}. Cyclic anodic polarization measurements were done between -1.9 and +1 V, at a scan rate of 10 mVs^{-1}. All of the measurements were carried out at room temperature.

Results and discussion

Scanning electron microscope (SEM)

The surface of the magnesium substrate samples was highly regular after sanding with #1000 silicon carbide abrasive paper. The surface morphology of the molybdate conversion coatings showed micro-cracks on the coating surface. These cracks appeared due to the hydrogen released from the chemical reaction during the conversion treatment, or to the surface layer dehydration after treatment. Such a structure was often cited in the literature as an example of molybdate conversion coatings [8, 9].



(a) (b) (c)

Figure 1. **(a)** SEM morphology of the sample I with molybdate conversion coatings containing SiO_2 nanoparticles, **(b)** molybdate conversion coatings containing TiO_2 nanoparticles, and **(c)** cross-sectional photomicrographs of molybdate conversion coatings containing TiO_2 nanoparticles.

The molybdate conversion coatings containing SiO_2 or TiO_2 nanoparticles showed superior fineness, uniformity and density, compared to the molybdate conversion coatings, which confirms the uniform distribution of SiO_2 and TiO_2 nanoparticles through the molybdate conversion coatings (Figs. 1a and 1b). The coating cross-sections did not further show any interfacial voids or defects among the coatings and the magnesium substrate, and the molybdate conversion coatings containing TiO_2 nanoparticles (4.33 ± 0.05 μm) were thicker than the molybdate conversion coatings containing SiO_2 nanoparticles (3.13 ± 0.05 μm) (Fig. 1c). Adding nanoparticles to the plating solution increased the thickness of the nanocomposite coatings, thus enhancing the coating deposition rate [8]. TiO_2 performance was superior to that of SiO_2, because the molybdate conversion coatings containing TiO_2 were thicker than the molybdate conversion coatings containing SiO_2.

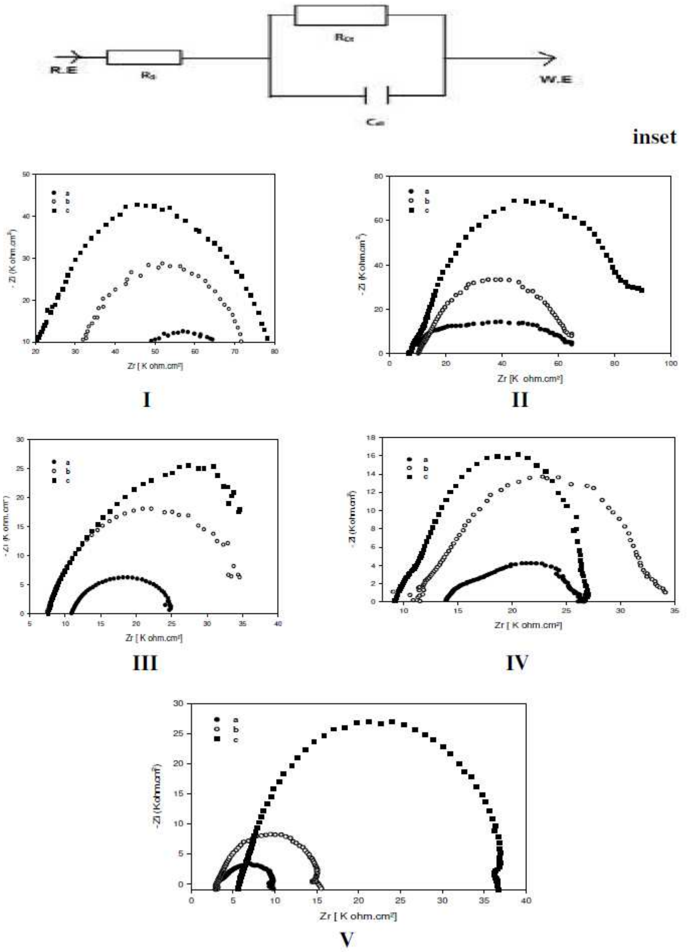


Figure 2. Nyquist plots of the five samples with molybdate conversion coatings. (**a**) molybdate conversion coatings containing SiO_2 nanoparticles, (**b**) molybdate conversion coatings containing TiO_2 nanoparticles and (**c**) 1 cm^2 exposed area in a 3.5 wt% NaCl solution, and electrochemical equivalent circuits used for fitting the experimental data (inset).

Electrochemical Impedance Spectroscopy (EIS)

EIS of the five magnesium samples, after the conversion coating by molybdate, without and with SiO_2 or TiO_2 nanoparticles in 3.5% NaCl solutions, was examined at open circuit potential, after 10 min of immersion, to evaluate their corrosion resistance, as shown in Fig. 2. From Nyquist plot, it can be seen that the molybdate conversion coatings, without and with SiO_2 or TiO_2 nanoparticles, presented single semicircles. From Fig. 2, the semicircle diameter is observed in the following order: molybdate conversion coating < coating with SiO_2 < coating with TiO_2.

Since the diameter of the capacitive semicircle represents the coatings resistance, the latter significantly decreases with the decrease in diameter [10]. This indicates that the samples with molybdate conversion coatings containing TiO_2 nanoparticles exhibited better corrosion resistance, compared to the samples with molybdate conversion coatings containing SiO_2 nanoparticles, and the samples without molybdate conversion coatings.

Table 2. Electrochemical parameters fitted from EIS measurement impedance data.

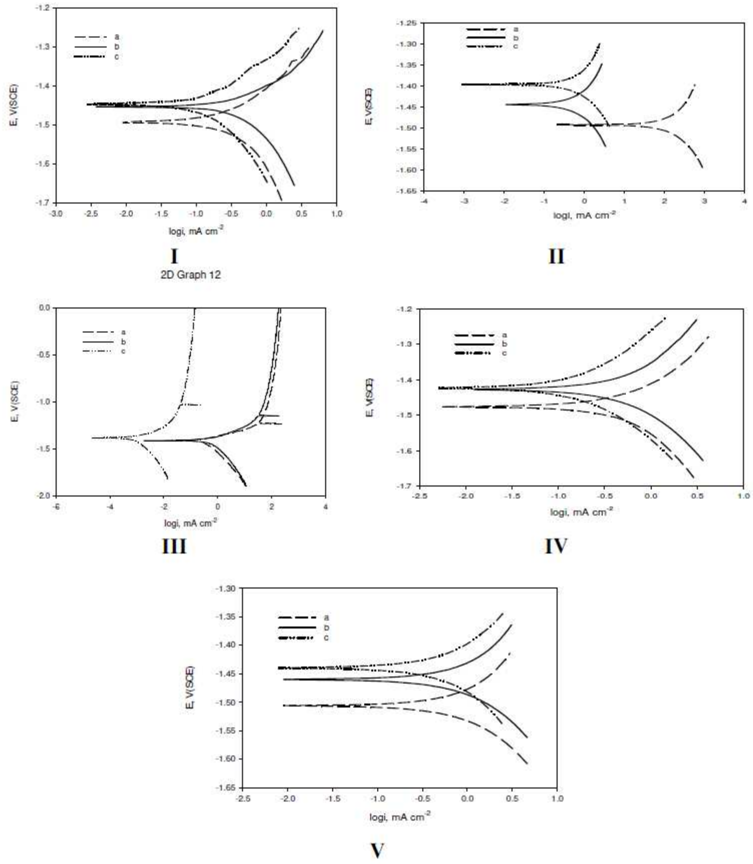
Sample no.		**Molybdate conversion coatings**	**Molybdate conversion coatings containing SiO_2 nanoparticles**	**Molybdate conversion coatings containing TiO_2 nanoparticles**
I	R_{CT} (kohm.cm^2)	17.26	29.19	38.16
	R_s (kohm.cm^2)	34.06	38.93	64.59
	Cdl (μF/cm^2)	21.63	16.83	9.86
II	R_{CT} (kohm.cm^2)	11.40	12.95	33.93
	R_s (kohm.cm^2)	41.59	74.41	75.62
	Cdl (μF/cm^2)	17.10	16.83	10.71
III	R_{CT} (kohm.cm^2)	11.66	11.93	15.45
	R_s (kohm.cm^2)	13.93	24.98	31.61
	Cdl (μF/cm^2)	5.71	5.61	4.96
IV	R_{CT} (kohm.cm^2)	12.07	14.09	15.26
	R_s (kohm.cm^2)	12.69	15.83	21.75
	Cdl (μF/cm^2)	29.25	29.39	20.09
V	R_{CT} (kohm.cm^2)	3.38	5.91	6.54
	R_s (kohm.cm^2)	6.32	11.69	29.77
	Cd (μF/cm^2)	68.02	62.94	38.05

The electrochemical equivalent circuit, as shown from Fig. 2 (inset), was used to model the molybdate conversion coatings, without and with SiO_2 or TiO_2 nanoparticles. The circuit in Fig. 2 (inset) consists of solution resistance (R_s), charge transfer resistance (R_{CT}) and double layer capacitance (C_{dl}). The higher is the charge transfer resistance, the higher is the corrosion resistance of the conversion coatings. The parameters values for the molybdate conversion coatings, without and with SiO_2 or TiO_2 nanoparticles, on the five magnesium samples, are shown in Table 2. From Table 2 we can observe that:

- for the five magnesium samples, R_{CT} reached its maximum values for the molybdate conversion coating containing TiO_2 nanoparticles, while C_{dl} reached its minimum values;
- for the five magnesium samples, R_{CT} values were observed in the following order: sample V < sample IV < sample III < sample II < sample I;
- and, for sample I, R_{CT} value of the molybdate conversion coating containing TiO_2 nanoparticles was 38.16 kohm.cm^2, which was about 2.2 times higher than that of the molybdate conversion coatings, with a R_{CT} of 17.26 kohm.cm^2,

and about 1.3 times higher than that of the molybdate conversion coating with SiO_2 nanoparticles, which was 29.19 kohm.cm^2.

EIS results indicated the nanocoatings high resistance on all tested Mg alloys, and the superior resistance of the coating containing TiO_2 nanoparticles.



I II III IV V

Figure 3. Polarization curves of the five samples with molybdate conversion coatings. **(a)** molybdate conversion coatings containing SiO_2 nanoparticles, **(b)** molybdate conversion coatings containing TiO_2 nanoparticles and **(c)** 1 cm^2 exposed area in a 3.5 wt% NaCl solution.

Potentiodynamic polarization measurements

The stability of the films formed on the five magnesium samples (after the conversion coating by molybdate and molybdate containing SiO_2 or TiO_2 nanoparticles in 3.5% NaCl solutions) was examined by potentiodynamic polarization measurements.

Fig. 3 illustrates that, for the five magnesium samples, the main reaction in the cathodic branch was hydrogen evolution. When the potential increased into the anodic branch, an obvious passivation occurred. It is well known that the corrosion potential (E_{corr}) and the corrosion current density (I_{corr}) are often used to characterize the corrosion protective properties of the oxide layer [11]. In general, it was reported that a low I_{corr} results in a low corrosion rate (C_R) and good polarization resistance (R_p) of the coatings [12]. The electrochemical parameters calculated from the polarization curves are summarized in Table 3.

Table 3 illustrates that, for the five magnesium samples, the resultant molybdate conversion coating containing TiO_2 nanoparticles revealed shifts towards a more passive E_{corr}, when compared to molybdate conversion coated samples having SiO_2 nanoparticles, while molybdate conversion coated samples shifted towards more negative E_{corr} values. In addition, it was clear from Table 3 that the coating containing TiO_2 nanoparticles showed the highest R_p and the lowest I_{corr}, compared to other samples; for the five magnesium samples, I_{corr} values were observed in the following order: sample I < sample II < sample IV <sample III < sample V.

Table 3. Electrochemical parameters of polarization curves.

Sample No.		**Molybdate conversion coatings**	**Molybdate conversion coatings containing SiO_2 nanoparticles**	**Molybdate conversion coatings containingTiO_2 nanoparticles**
I	E_{corr} (V)	-1.49	-1.45	-1.43
	I_{corr} (mA)	0.57	0.43	0.22
	R_p (ohm.cm^2)	63.65	102.18	194.22
	C_R (mm/Y)	7.74	5.08	2.61
II	E_{corr} (V)	-1.49	-1.44	-1.39
	I_{corr} (mA)	0.66	0.72	0. 177
	R_p (ohm.cm^2)	32.43	33.33	142.97
	C_R (mm/Y)	10.28	8.40	2.07
III	E_{corr} (V)	-1.47	-1.42	-1.36
	I_{corr} (mA)	0.90	0.68	0.36
	R_p (ohm.cm^2)	30.02	61.40	71.90
	C_R (mm/Y)	10.57	7.94	4.18
IV	E_{corr} (V)	-1.43	- 1.42	-1.41
	I_{corr} (mA)	0.88	0.36	0.27
	R_p (ohm.cm^2)	56.68	74.02	213.71
	C_R (mm/Y)	6.66	4.26	3.21
V	E_{corr} (V)	-1.49	-1.46	-1.44
	I_{corr} (mA)	1.53	1.09	0.57
	R_p (ohm.cm^2)	21.23	27.84	42.57
	C_R (mm/Y)	14.11	12.75	6.68

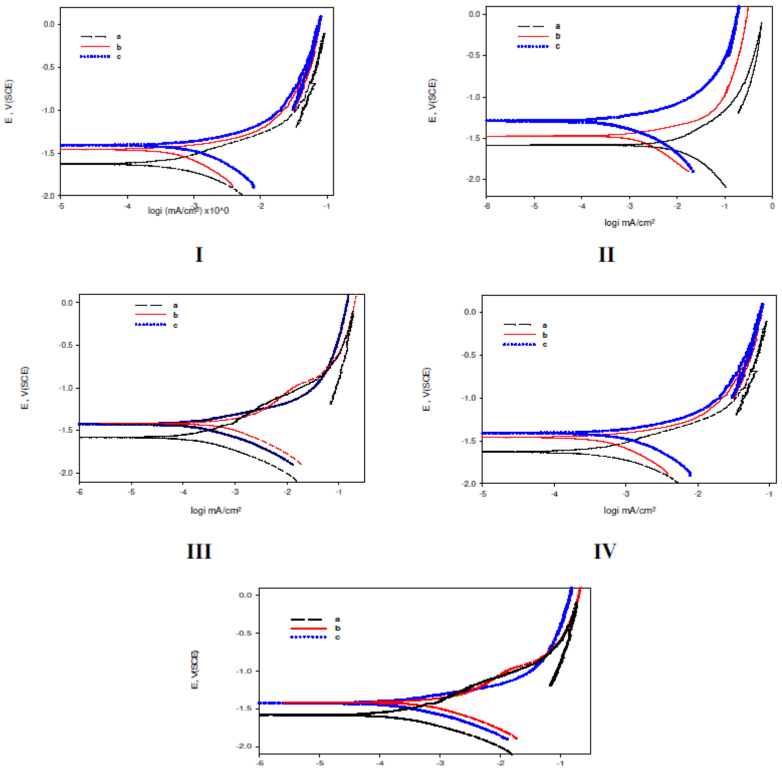
This order was somewhat different from that observed by EIS measurements, which might be attributed to the fact that the surface resistance measured by EIS expresses the total surface resistance, including the pitting, crevice and general corrosion, while the polarization data and EIS measurements provided evidence that molybdate conversion coatings with TiO_2 nanoparticles offered the best corrosion resistance

Potentiodynamic cyclic anodic polarization measurements

In order to further evaluate the corrosion resistance of molybdate conversion coatings containing SiO_2 or TiO_2 nanoparticles in a corrosive 3.5% NaCl solution, potentiodynamic cyclic anodic polarization measurements were performed.

Fig. 4 revealed that, for the five magnesium samples, the potentials of the samples coated with molybdate conversion coatings containing TiO_2

nanoparticles were approximately 50, 50, 180, 90 and 50 mV more positive than those of the samples with molybdate conversion coatings containing SiO_2 nanoparticles, and approximately 230, 210, 290, 130 and 170 mV more positive than those of the samples without molybdate conversion coatings, for samples I, II, III, IV and V, respectively. Accordingly, the highest pitting resistance was obtained from the samples that received coatings containing TiO_2, followed by those containing SiO_2 nanoparticles. Also, the samples that received coatings containing TiO_2 nanoparticles showed better performance where the hysteresis loop was observed during the reverse anodic scan, which indicates that pitting corrosion may have diminished. Moreover, a small shift towards a more passive exchange current was noticed for those samples, compared to the ones containing SiO_2 nanoparticles. Accordingly, the highest protection against pitting corrosion can be sorted in the following order: molybdate conversion coating < coating with SiO_2 < coating with TiO_2.



I

II

III

IV

V

Figure 4. Potentiodynamic cyclic anodic polarization curves of the five samples with molybdate conversion coatings. **(a)** molybdate conversion coatings containing SiO_2 nanoparticles, **(b)** molybdate conversion coatings containing TiO_2 nanoparticles and **(c)** 1 cm^2 exposed area in a 3.5 wt% NaCl solution.

This finding was consistent with EIS and potentiodynamic polarization measurements.

The main experimental results of the present study indicate that, for all tested Mg alloys, the molybdate conversion coatings containing TiO_2 nanoparticles possess higher corrosion resistance than molybdate conversion coatings containing SiO_2

nanoparticles, which, in turn, possess higher corrosion resistance than molybdate without conversion coatings.

Owing to the microgalvanic couple effect, magnesium alloys suffered serious corrosion in a NaCl solution [13]. When the magnesium alloy surface was covered by the molybdate conversion coating, which separated the alloy from the corrosion medium, corrosion was avoided. However, a main problem of molybdate conversion coatings on the magnesium alloy substrate is the presence of pores and cracks that leads to serious protective property deterioration of conversion coatings [6-7].

The incorporation of the high noble potential of TiO_2 and SiO_2 nanoparticles to the molybdate conversion coatings (forming a more homogeneous structure of small grains, as seen in SEM images from Fig. 1) provides an inert physical barrier to the initiation and development of defect corrosion on the conversion coatings, thus preventing electrolytes from penetrating into magnesium alloy substrates. The molybdate conversion coatings containing TiO_2 nanoparticles provided significantly better corrosion protection, compared to the molybdate conversion coatings containing SiO_2 nanoparticles, which might be due to the standard corrosion potential of TiO_2 and SiO_2 [14]. For the coating containing TiO_2 nanoparticles, the higher charge transfer resistance (RCT) (Table 2), the higher $E_{corr.}$ values for all tested Mg alloys that obtained a lower i_{corr} (Table 3), and the higher pitting resistance (Fig. 3) further confirmed that the corrosion protection obtained by TiO_2 incorporation into the molybdate conversion coatings is clearly superior to that obtained by SiO_2 incorporation.

Conclusion

The surface morphology of the molybdate conversion coatings containing SiO_2 or TiO_2 nanoparticles showed superior fineness, uniformity and density, compared to the molybdate conversion coatings. Electrochemical impedance spectroscopy, potentiodynamic polarization and potentiodynamic cyclic anodic polarization measurements were employed to evaluate the corrosion resistance of molybdate conversion coatings containing SiO_2 or TiO_2 nanoparticles, on different Mg alloys in a 3.5 wt.% NaCl solution. The results of the corrosion evaluations showed that the addition of SiO_2 or TiO_2 nanoparticles to the conversion treatment has significantly improved the corrosion resistance property of molybdate conversion coatings for all tested Mg alloys, but revealed that TiO_2 was more effective.

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