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FREQUENCY EFFECT ON ELECTROCHEMICAL CHARACTERISTICS OF MAO COATED MAGNESIUM ALLOY IN SIMULATED BODY FLUID

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ABSTRACT

Dense oxidation coatings have been successfully developed on biocompatible AZ31 magnesium alloy, using microarc oxidation (MAO) technique, to improve the corrosion resistance. Four different deposition frequencies of 300 Hz, 500 Hz, 1000 Hz, and 3000 Hz were employed. The effect of frequency on the coating corrosion resistance has been evaluated through electrochemical experiments in a simulated body fluid (SBF) up to 7 days. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) scans were performed in the SBF solution, followed by optical microscopy surface inspection. The results indicate that the corrosion rates (CRs) of the coatings are in the order of 300 Hz < 500 Hz < 1000 Hz < 3000 Hz after immersion for 7 days, and the charge transfer resistance (Rct) of the four samples has no substantial difference. Both the electrochemical tests and the surface inspection suggest that the 300 Hz coating has the highest corrosion resistance, with lowest corrosion current density, and the best surface quality.

INTRODUCTION

Magnesium and its alloys have gained special interest in medical applications in recent years, as promising biodegradable metallic implant materials [1]. Magnesium is an exceptionally lightweight metal, with a density of 1.74 g/cm^3, which is 1.6 and 4.5 times less dense than aluminum and steel, respectively [2]. The fracture toughness of magnesium is greater than ceramic biomaterials such as hydroxyapatite, while the elastic modulus and compressive yield strength of magnesium are closer to those of natural bone than other commonly used metallic implants [3]. Moreover, magnesium is essential to human metabolism and is naturally found in bone tissue [4-9]. It is the fourth most abundant element in the human body, with an estimated 1 mol of magnesium stored in the body of a 70kg-weight adult, with approximately half of the total physiological magnesium stored in bone tissue [6]. Magnesium and its alloys, therefore, are very attractive materials for implants because of their excellent biocompatibility and mechanical compatibility [10-13].

Although numerous advantages, however, magnesium and its alloys rapidly corrode in human body. The lives of magnesium and its alloy implants exist merely several weeks [11]. To improve the corrosion resistance of metals and alloys, microarc oxidation (MAO) technique has attracted great interest in recent years. MAO coatings can enhance the surface properties of the magnesium substrate, such as hardness, wear resistance, corrosion resistance and adhesion strength by forming a remarkably dense and hard coating [14, 15]. MAO has demonstrated the capability to produce high-quality oxide coatings on the surfaces of light metals such as Ti, Al, Mg and their alloys [16].

The improved corrosion resistance by employing MAO coatings on magnesium alloys has been reported in several studies in the simulated body fluids (SBFs). Zhao et al. showed the corrosion potential (Ecorr) of the sample anodized for 17 minutes shifted towards nobler directions accompanied with a substantial reduction of the corrosion current density (Icorr) compared with that of the bare magnesium [17]. Wang et al. investigated corrosion behavior of coated AZ91 alloy by MAO for biomedical application [18]. The investigation showed that the Ecorr of Mg substrate positively shifted about 300-500 mV and Icorr was reduced more than 100 times after microarc oxidation. However, research concerning the electrochemical corrosion behavior of MAO coatings on AZ31 Mg alloy in the SBF is still very limited compared to AZ91 Mg alloys [18, 19] and pure Mg [17, 20].

In the study, MAO coatings produced at various deposition frequencies on AZ31 magnesium alloy substrates are reported in terms of electrochemical corrosion properties in SBF solution through potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) studies. The effects of applied deposition frequencies on corrosion behavior are discussed. The correlation between the electrochemical performance of the coatings and microstructures is proposed.

EXPERIMENTAL

MAO Coatings Preparation

The commercial AZ31 magnesium alloy, whose chemical nominal composition (wt.%) is 2.5~3.5 wt% Al, 0.7~1.3 wt% Zn, 0.2~1.0 wt% Mn, 0.05 wt% Si, 0.01 wt% Cu, and Mg balance, is employed in this study. Samples from an ingot were cut into a size of 20 mm×10 mm×0.5 mm and are used as the substrate. The surface of the samples was mechanically polished to a roughness of Ra ≈ 1.6 μm, and ultrasonically cleaned in distilled water followed by acetone.

The coatings were prepared on the AZ31 magnesium alloy surfaces with a 50 kW capacity MAO equipment (MAO20, Chengdu PULSETECH Electrical Co., China). The equipment has an adjustable pulsed DC source, a stainless steel container with a sample holder as the electrolyte, and a stirring and cooling system. The magnesium alloy substrates were used as anodes, while the wall of the stainless steel container was used as the cathode in the electrolytic bath. An electrolyte prepared from a solution of 10 g/l Na_3PO_4 in distilled water was kept at room temperature during the entire treatment procedure. A pulsed current was applied at the duty cycle of 0.3. The duty cycle is defined as the ratio between pulse duration and the period of a rectangular waveform. In order to study the effect of the deposition frequency, coatings were produced at four different deposition frequencies, 300 Hz, 500 Hz, 1000 Hz, and 3000 Hz for a constant 5-minute deposition period. The detailed MAO procedure and the microstructures were given in our previous publication [21].

Electrochemical Performance Tests

Electrochemical tests of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were carried out using a computer controlled potentiostat/frequency response analyzer in a corrosion cell (Corrosion Cell Kit, Gamry Instruments, Inc.) to evaluate the corrosion behavior of the MAO coatings. The corrosion cell has three electrodes, with the coated sample as a working electrode, a saturated SCE electrode as reference electrode, and a graphite rod as counter electrode.

The samples with a surface area of 4.18 cm^2 were immersed in 1000 ml SBF solution and soaked for up to 7 days and the SBF was refreshed every 24 h. The SBF had a pH of 7.25 with ion concentrations nearly equal to those found in human blood plasma (Table 1). The corresponding composition of the SBF is listed in Table 2. All the reagents in Table were purchased from Fisher Scientific.

Table 1 Ion concentrations of the simulated body fluid and human blood plasma [22].

Ion	Concentration ($mmol/dm^3$)	
	Simulated body fluid (SBF)	Human blood plasma
Na^+	142.0	142.0
K^+	5.0	5.0
Mg^{2+}	1.5	1.5
Ca^{2+}	2.5	2.5
Cl^-	147.8	103.0
HCO_3^-	4.2	27.0
HPO_4^{2-}	1.0	1.0
SO_4^{2-}	0.5	0.5

Table 2 Reagents for preparation of SBF (pH 7.25, 1 L) [22].

Order	Reagent	Purity (%)	Amount
#1	$NaCl$	99.5	7.996 g
#2	$NaHCO_3$	99.5-100.3	0.350 g
#3	KCl	99.5	0.224 g
#4	$K_2HPO_4 \cdot 3H_2O$	99.0	0.228 g
#5	$MgCl_2 \cdot 6H_2O$	98.0	0.305 g
#6	1 $kmol/m^3$ HCl	—	40 cm^3
#7	$CaCl_2$	95.0	0.278 g
#8	Na_2SO_4	99.0	0.071 g
#9	$(CH_2OH)_3CNH_2$	99.9	6.057 g
#10	1 $kmol/m^3$ HCl	—	Appropriate amount for adjusting pH

Potentiodynamic polarization was used to investigate the corrosion properties of the MAO coating during immersion in SBF solution up to 7 days, with a measurement at end of each day. The scan rate is 3 mV/s. EIS tests were also carried out in a range of 0.2 Hz to 100 kHz on specimens to understand the degradation phenomena. Gamry Instruments Framework software (Version 5.63) was used to collect all the data using a Model Series-G 300 potentiostat. Gamry Echem Analyst software (Version 5.63) was used for the data fitting of the polarization curves and impedance spectra.

All experiments were carried out at open circuit potential (OCP) with an equilibrium time to receive OCP of 3 min. Potentiodynamic polarization curves were thus acquired and the Ecorr and Icorr were determined using the Tafel fit method. The corrosion behaviors of MAO treated specimens were evaluated by immersion in SBF solution at 37±0.5 °C.

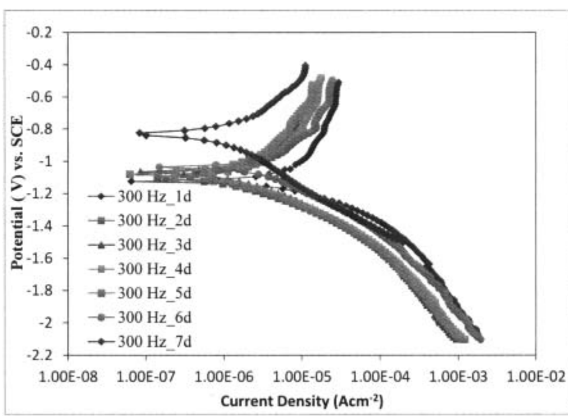
Surface Morphology Observation

The samples were immersed in the SBF solution up to 7 days. At the end of each day, the samples were removed from the SBF, rinsed with distilled water, dried in warm flowing air and then the change of surface micromorphologies were observed by an Olympus BX60 optical microscope. The evolution of surface macromorphologies, caught by a digital camera at each time point, was used to evaluate the degree of corrosion damages.

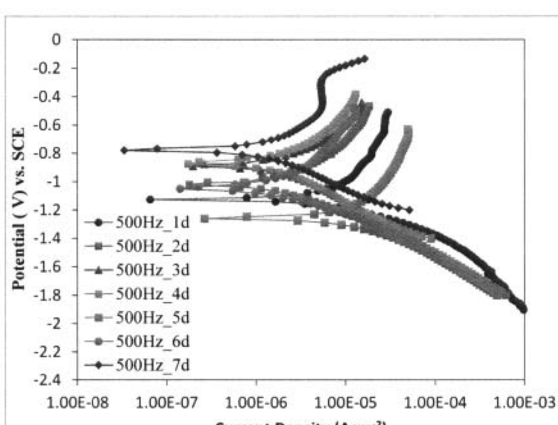
RESULTS AND DISCUSSION

Potentiodynamic Polarization

Fig. 1 shows the corrosion behavior of the MAO coatings coated at different frequencies evaluated by potentiodynamic polarization technique in the SBF at different immersion times, up to 7 days. Ecorr, Icorr and corrosion rate (CR) can be derived from these curves.



(a)



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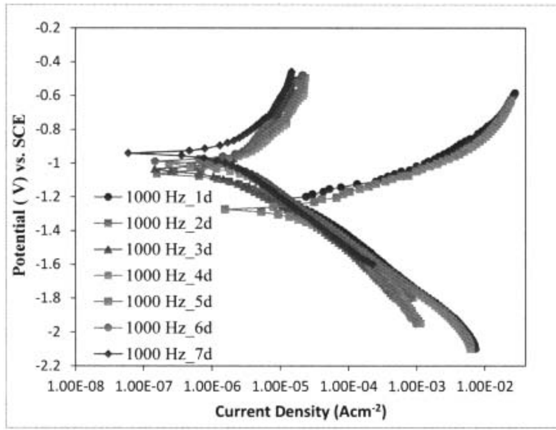

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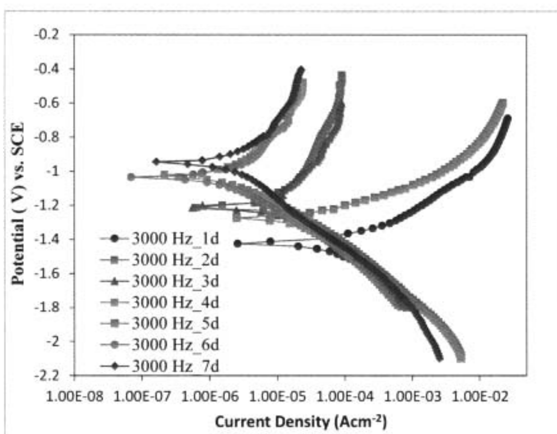


(d)

Fig. 1 The potentiodynamic polarization behavior of MAO coated AZ31 alloy specimens at different frequencies after immersion in the SBF for 7 days. (a) 300 Hz, (b) 500 Hz, (c) 1000 Hz, and (d) 3000 Hz.

From the result in Fig. 1, it could also be observed that Icorr values of four samples were in an order of 300 Hz < 500 Hz < 1000 Hz < 3000 Hz after immersion in the SBF for 7 days, indicating 300 Hz sample has the lowest corrosion rates after the tests. The results also showed that the corrosion rates (CRs) of these MAO coatings on AZ31 alloy were close to the order of magnitude of the MAO coatings on AZ91D alloy in phosphate electrolyte [19], but were two orders of magnitude lower than that of 22-min MAO coatings on pure Mg in SBF [17], and were in three orders of magnitude lower than that of MAO coatings on AM50 alloy after immersion for 50 h [23]. The above results suggest that MAO coatings on AZ31 alloys are more corrosion resistant than pure Mg and AM50 alloy.

Fig. 2 shows the CR curves of four samples after immersion in the SBF for different times up to 7 days. Overall, the CRs decreased with test time for all four samples. For the 300 Hz sample, the CRs were consistently low. While other samples decreased continuously with immersion time till 4 days. The CRs of the 500 Hz, 1000 Hz and 3000 Hz samples were not as stable as the 300 Hz sample. They initially decreased with immersion time from 1 to 4 days and then increased to a high value at 5 days, then decreased again. After 6 days immersion, the CRs decreased gradually and tended to be stable. Compared with the other samples, the 300 Hz sample had the most stable and the lowest CR after immersion for 7 days with the value of 0.025 mm/yr. Consequently, the CRs of four samples were in the order of 300 Hz < 500 Hz < 1000 Hz < 3000 Hz after 7 days of immersion.

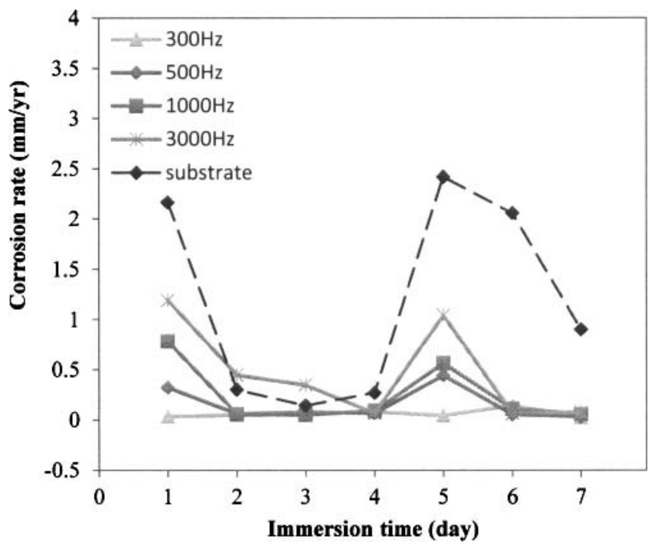
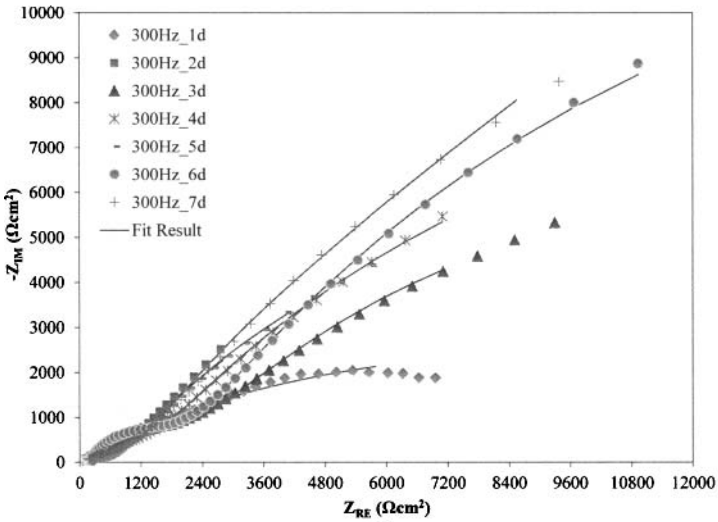


Fig. 2 CRs of four samples deposited various frequencies and substrate in immersion test for different times up to 7 days.

EIS Characteristics

Fig. 3 shows the Nyquist plots of MAO coatings coated at four frequencies after immersion in the SBF for 1 to 7 days. The Nyquist plots consisted of one capacitive loop in the high frequency range (one time constant) and one capacitive loop in low frequency range (one time constant). The diameter of the capacitive loop in the high frequency range represented the charge transfer resistance (Rct). The Rct value reflected the difficulty of the electrochemical corrosion reaction.


300Hz_1d
300Hz_2d
300Hz_3d
300Hz_4d
300Hz_5d
300Hz_6d
300Hz_7d
Fit Result
$-Z_{IM}$ (Ωcm^2)
Z_{RE} (Ωcm^2)
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
10000
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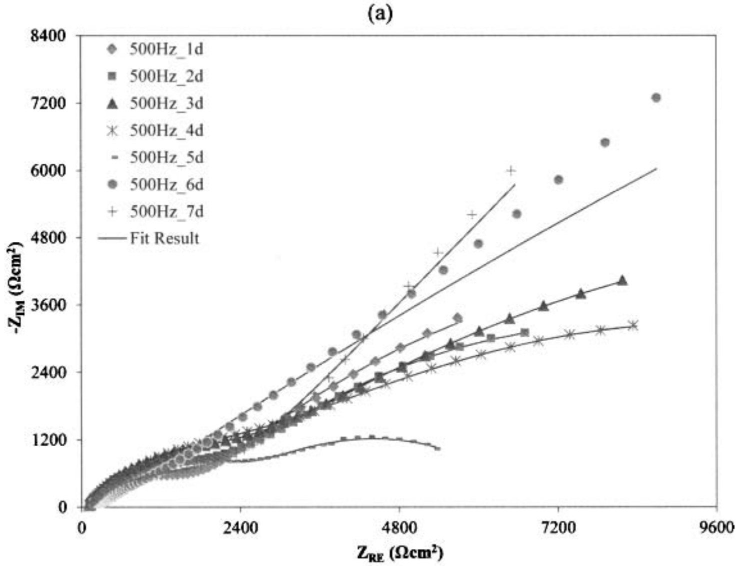
2400
3600
4800
6000
7200
8400
9600
10800
12000

(a)


500Hz_1d
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500Hz_7d
Fit Result
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Z_{RE} (Ωcm^2)
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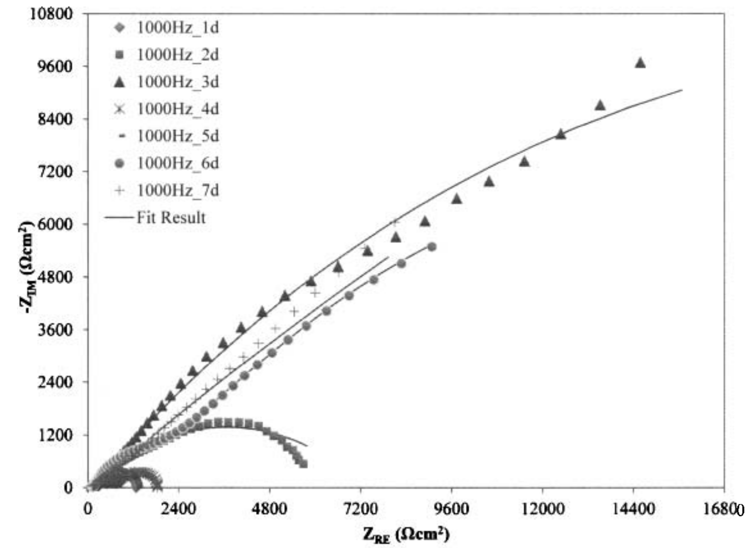
(b)



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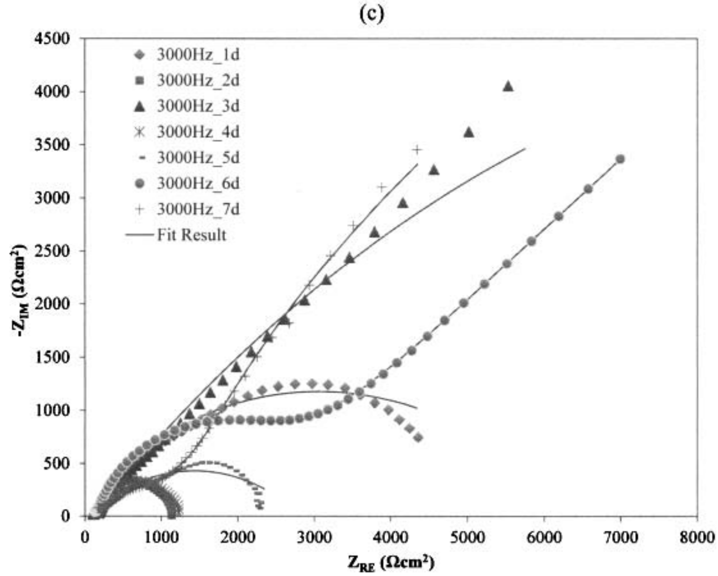


(d)

Fig. 3 The Nyquist plots of MAO coatings coated at different frequencies after immersion in the SBF for different times. (a) 300 Hz, (b) 500 Hz, (c) 1000 Hz, and (d) 3000 Hz.

The measured Rct values and Rct vs. time curves of four samples and the substrate, after immersion in the SBF for 1 to 7 days extracted from Fig.3, are given in Fig. 4. It was observed that Rct values of all samples were similar, oscillating till 5 days and increasing dramatically afterwards. The variation of Rct is related to the dynamic process of the growth, crack or stripping of the corrosion film [24], as the phenomenon observed in Fig. 5. The corrosion films on the sample became thicker as the SBF immersion test proceeded. With the growth continued, the stripping and the pits increased rapidly from 5 to 7 days. The stripping and pits of the samples can also be observed in Fig. 6. It could be deduced that a vigorous corrosion occurred after 5 days of immersion.

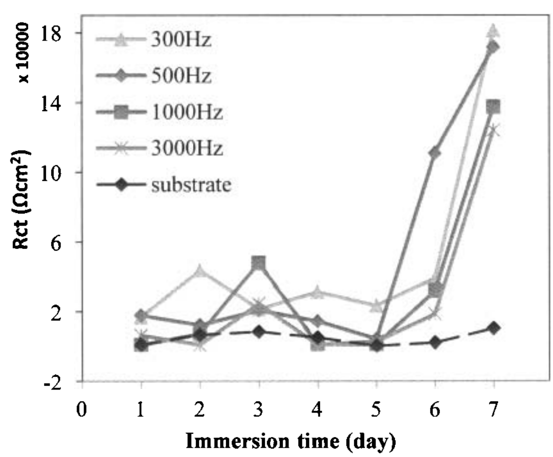
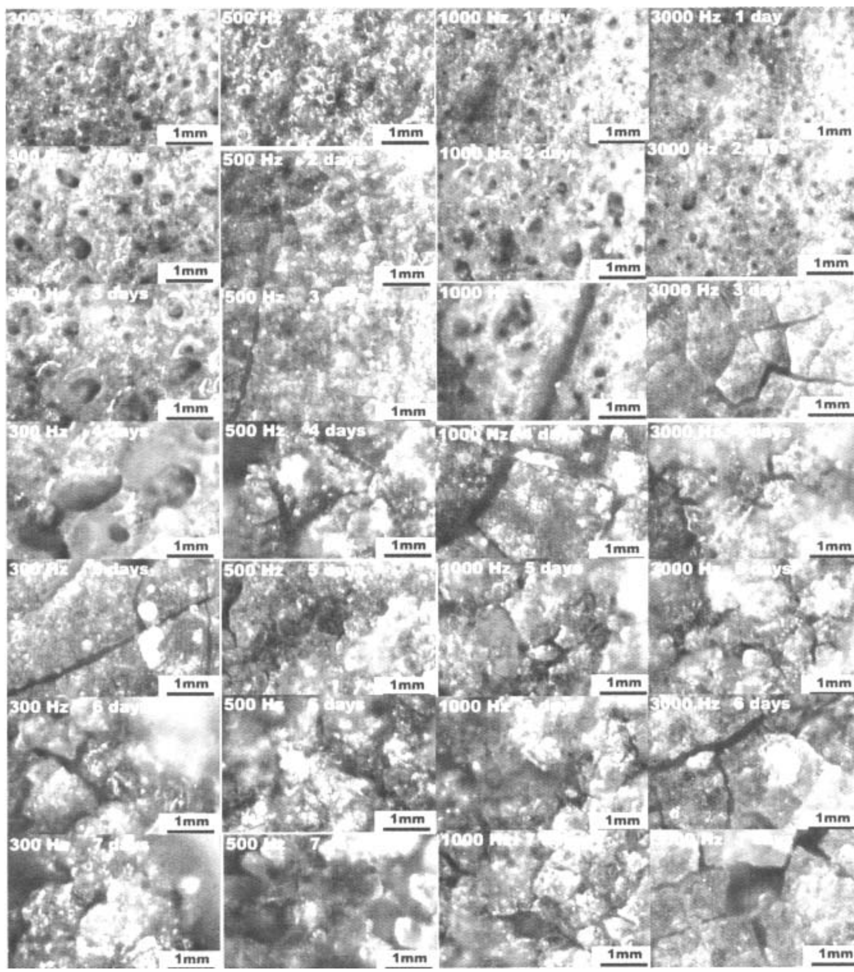


Fig. 4 The Rct of MAO coatings coated at different frequencies and substrate after immersion in the SBF for different times, up to 7 days.

Surface Micromorphology

The surface micrographs of four samples in Fig.5 were taken after immersion in the SBF at the end of each day. The examination of the corroded surfaces after electrochemical tests in the SBF solution revealed the corrosion evolutions of the coatings. It was observed that the surfaces of the four samples were first covered by a thin corrosion layer. The layer became thicker as the test proceeded. After 4 days of immersion, the appearances of the coatings began to form multiple cracks and pits. These results are consistent with their corrosion rates shown in Fig. 2. The potentiodynamic polarization data for the 7 days specimen clearly demonstrated the corrosion rate of the 3000 Hz is the highest, and this phenomenon was also reflected in the EIS measurement.



(a) 300 Hz (b) 500 Hz (c) 1000 Hz (d) 3000 Hz

Fig. 5: Surface micrographs of four samples after immersion in the SBF for different times: (a) 300 Hz, (b) 500 Hz, (c) 1000 Hz, and (d) 3000 Hz.

Surface Macromorphology

Fig. 6 shows the macroscopic appearance of the samples after immersing in the SBF for 7 days. It can be observed that 300 Hz sample surface was smooth with few corrosion pits, and the 3000 Hz sample had the most pits among the four samples. Therefore, the coatings produced at 300 Hz are more corrosion resistant than other frequencies.

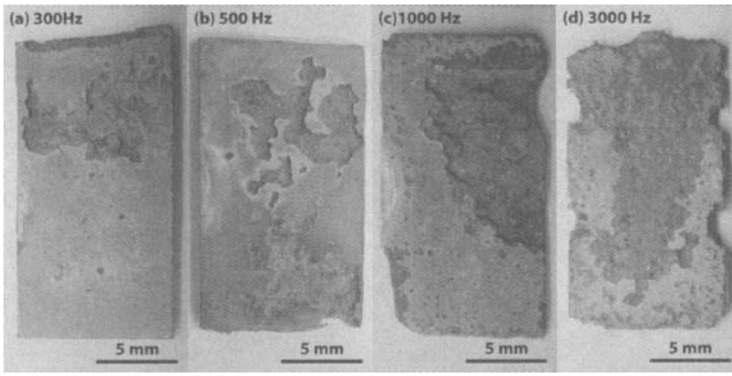


Fig. 6. The appearance of the samples after the total immersion test in the SBF for 7 days.(a) 300 Hz, (b) 500 Hz, (c) 1000 Hz, and (d) 3000 Hz.

CONCLUSIONS

1) The applied MAO deposition frequency significantly affects the coating's electrochemical properties in the SBF. The potentiodynamic polarization tests showed that the CRs of the samples were in the order of 300 Hz < 500 Hz < 1000 Hz < 3000 Hz after immersion for 7 days, which was consistent with the EIS results.
2) Surface morphology studies showed that the 300 Hz sample had the least corrosion damages with the smoothest surface and least pitting. The result is consistent with the data from potentiodynamic polarization and the EIS experiments.
3) Both the electrochemical tests and the surface inspection suggest that the 300 Hz coating has the highest corrosion resistance, with lowest corrosion current density, and the best surface quality.

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