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Effects of surface laser treating on structure and corrosion resistance of MAO coating on magnesium alloy

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ABSTRACT

AZ91 biomedical magnesium alloy was first treated by Micro arc oxidation (MAO) process and then samples with MAO coating on the surface were subjected by surface laser treating. Effects of laser treating on surface characteristics and corrosion resistance of the coated sample were studied. The results indicated that after surface laser treating, The surface structure of coated sample was improved showing fewer and smaller holes. The AFM photos revealed that the surface roughness of MAO coating was dramatically decreased. The whole surface became more unique and compact. Electrochemical polarization curves tests revealed that the corrosion resistance of MAO coating in SBF was further increased by laser treating, with the corrosion current density decreasing by 10 times and the corrosion potential increasing by 0.06V. Electrochemical impedance spectra (EIS) revealed that the polarization resistance of the MAO coating on AZ91 alloy was also increased by 10 times after surface laser treating.

KEYWORDS

Laser treating; MAO coating; Corrosion resistance; Biomedical magnesium alloy.

INTRODUCTION

Biomedical materials have been one of the research focus in recently years and biomedical magnesium alloy materials which are considered as the revolutionary biodegradable implant material, have been widely studied[1-3]. They possess several advantages including eliminating the effects of stress shielding, improving biocompatibility and degradation properties, high specific strength and good castability [1,4-5]. However, biomedical magnesium alloy is easy to suffer corrosion resistance in vivo environment which leads to implant failure[1,5]. Therefore, it is necessary to improve the corrosion resistance of biomedical magnesium alloy.

Many methods and techniques have been used to improve the corrosion resistance biomedical magnesium alloy, among which, the surface modification technique have been thought to be an effective one. The surface modification technique of micro arc oxidation (MAO) has been widely used recently to improve corrosion resistance of the biomedical magnesium alloys and desirable results were obtained [1,6-7]. However, MAO coating on magnesium surface are always porous which is inherent from the technique itself and hence limits the further improved of corrosion resistance[8]. So some post treatments are usually needed to further improve the corrosion resistance of the MAO coating on metals surface[9-10]. This paper develops a method of surface laser treating to further enhance the corrosion resistance of MAO coating on biomedical magnesium alloys. Effects of laser treating on surface structure and corrosion resistance of MAO coating on AZ91 in simulated body fluids (SBF) were studied.

EXPERIMENTAL PROCEDURE

MAO and laser treatment AZ91 alloy whose chemical composition are listed in TABLE 1, was cut into pie shape of 15 mm in diameter and 0.5 mm thick. The polished AZ91 alloy substrate was first subject to MAO treatment and then followed by surface laser treating. The electrolyte was a mixture solution of Na_3PO_4, Na_2SiO_3, NaOH and glycerinum. A bi-pole power source was used during MAO and the whole treating time was 10 min. The anodic and cathodic current densities were 10A/dm^2 and 4 A/dm^2, respectively; the pulse frequency was 3000 Hz; duty ratio was 50%. A Nd:YAG Nanosecond pulse laser (Precision Ⅱ 8010, USA) with wavelength of 532 nm was used to treat the MAO coating surface. The pulse duration was about 6ns. The pulse frequency was 10Hz.

TABLE 1 : Chemical compositions of AZ91 alloy

Elements	Al	Zn	Mn	Si	Cu	Ni	Fe
contents	8.5-.9.5	0.35-1.0	0.15-0.50	<0.01	<0.03	<0.002	<0.005

Surface structure characterization and corrosion resistance tests The morphology of the MAO coatings before and after surface laser treating were investigated by scanning electron microscopy (SEM, S-3400N, Hitachi, Japan) and Atomic Force Microscopy) (AFM asylum research MPF-3D,USA). The corrosion behavior of samples were tested by polarization curve which was carried out on CHI760D electrochemical analyzer (Shanghai, China) in simulated body fluid (SBF) solution at 37℃. The electrochemical impedance spectra (EIS) were performaned on the same electrochemical analyzer in a frequency range of 0.01 Hz to 100 kHz at an a.c. signal amplitude of 10 mV. During electrochemical, the conventional three electrodes system was used here. A SCE was used as the reference electrode; a Pt foil electrode was used as the auxiliary electrode; coated or uncoated AZ91 sample (with the exposed area of 1 cm^2) was used as the working electrode.

RESULTS AND DISCUSSION

SEM tests SEM images of MAO coating on AZ91 with and without laser treating are show in Figure 1. Figure 1 (a) and (b) are photos of MAO coating on AZ91 without laser treating and the latter is magnified photo. Figure 1 (c) and (d) are photos of MAO coating treated with laser and the latter is also the magnified photo. Figure 1 (a) reveals that MAO coating on AZ91 alloy exhibits typical porous and coarse surface, which are formed during the plasma discharges the MAO. Figure 1 (c) shows that as a whole, after surface laser treating the coating surface becomes more unique and compact. Figure 1 (d) further indicates that the pores on the surface became few and the number of pores became less. So, it can be concluded that laser treating of MAO coating can improve the surface quality of MAO coating.

AFM tests AFM images of MAO coating before and after surface laser treating are showed in Figure 2. From the three-dimensional photo, it can be seen that before surface laser treating, the coating surface is more asperous, and after laser treating, the surface become more uniform. According to the SEM images and the analyses, the reason was that the pores on the surface became smaller and the number of pores became fewer. It can also be deduced that surface roughness of the laser treated sample was also dramatically decreased. This reveals that the pores on the surface also become less deep. Thus, combing the SEM and AFM test, a conclusion can be draw that through surface laser treating, many pores on the coating surface become disappeared and some pores become small and shallow. This results in a more unique and compact surface of MAO coating.

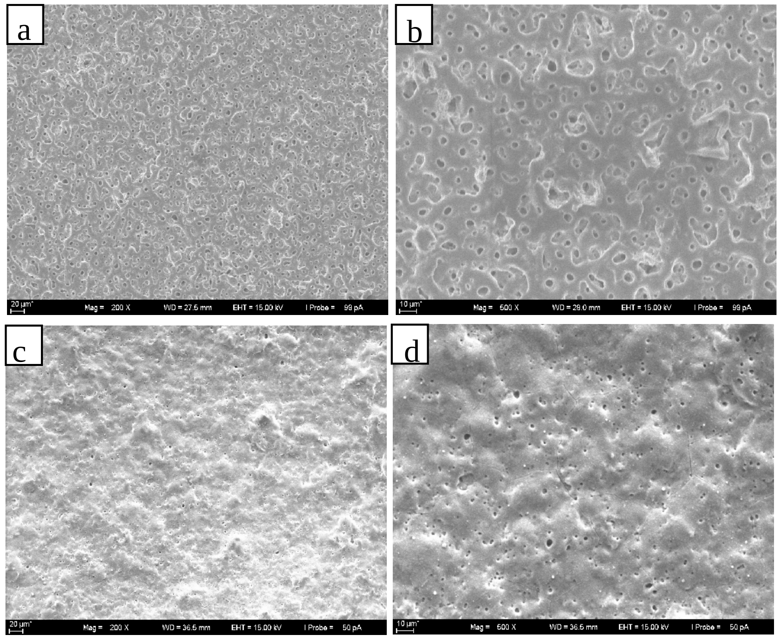

Figure 1 : SEM images of coatings on AZ91 alloy before (a, b) and after laser treating (c, d)

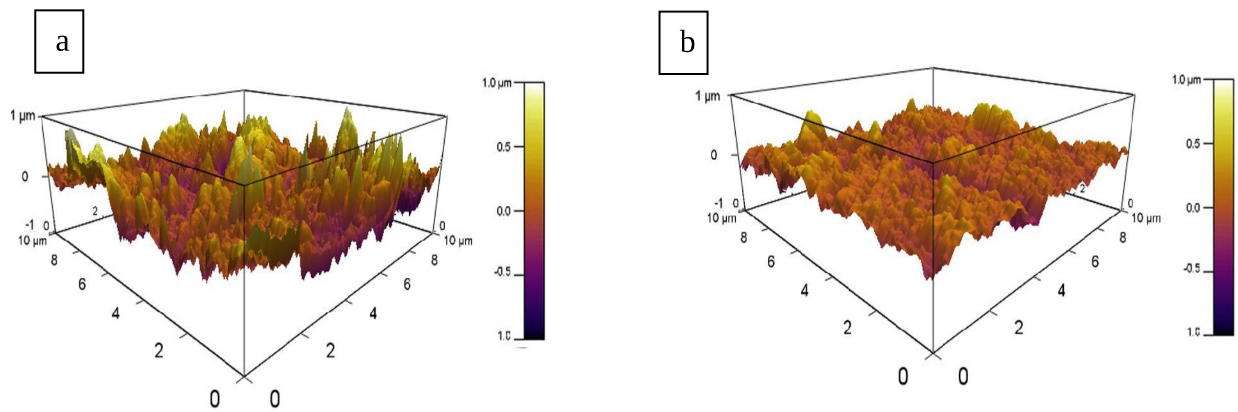

Figure 2 : AFM photos of MAO coatings on AZ91 alloy before (a) and after (b) laser treating

Corrosion resistance tests

Potentiodynamic polarization tests The corrosion resistance of AZ91 substrate sample AZ91 with MAO coating on its surface without laser treating and AZ91 with MAO coating on treated with laser are all subjected to potentiodynamic polarization tests and the polarization curves are plotted in Figure 3. The relevant results are listed in TABLE 2. It can be seen from both Figure 3 and TABLE 2 that the corrosion current density (I_{corrr}) of the three samples decrease gradually in the order of AZ91 substrate, AZ91 with MAO coating and laser treated MAO coating, and the corrosion potential (E_{corr}) increase gradually in the opposite order. This result indicated that the corrosion resistance of AZ91 sample was significantly improved with MAO on the surface, and after subjected to laser treating, the corrosion resistance of MAO coating could be further increased.

EIS tests Electrochemical impedance spectra tests of the three samples are plotted in Figure 4. The fitting equivalent circuit of the three samples are shown in Figure 5, and the fitting results are listed in TABLE 3. In equivalent circuit, the capacitances used are usually replaced with the constant phase elements (CPE, with the symbol of *Q*). The impedance for the constant phase element is

$$Z_Q = 1/[Y_0(j\omega)^n]$$

where, Y_0 and n are frequency-independent fit parameters, ω ($=2\pi f$) is the angular frequency and j equals to $\sqrt{-1}$. The factor n, defined as a power, is an adjustable parameter that lies between 0 and 1. If n = 0, CPE is an ideal resistance; if

n=1, CPE describes an ideal capacitor with Y_0 equal to the capacitance C. The physical meaning of n is not yet clear. In the equivalents, circuit R_s represents the resistance of the solution between the working electrode and the reference electrode; R_p is resistance of the outer porous layer paralleled with constant phase element Q_p; R_b is resistance of the inner compact layer paralleled with Q_b.

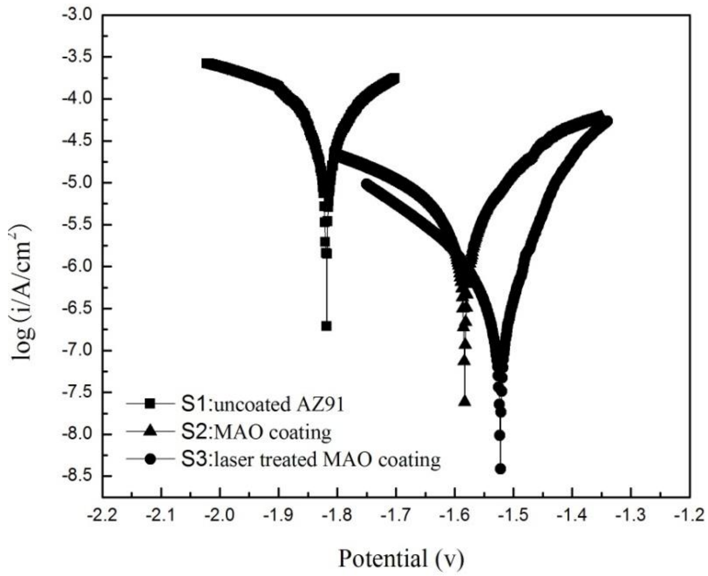

Figure 3 : Potentiodynamic polarization of samples

TABLE 2 : Corrosion current density (I_{corrr}) and corrosion potential (E_{corr})

Samples	E_{corr} (V)	I_{corr} (A/dm^2)
Uncoated substrate	-1.82	9.09×10^{-5}
As-treated MAO sample	-1.59	8.63×10^{-7}
Laser treated sample	-1.53	8.74×10^{-8}

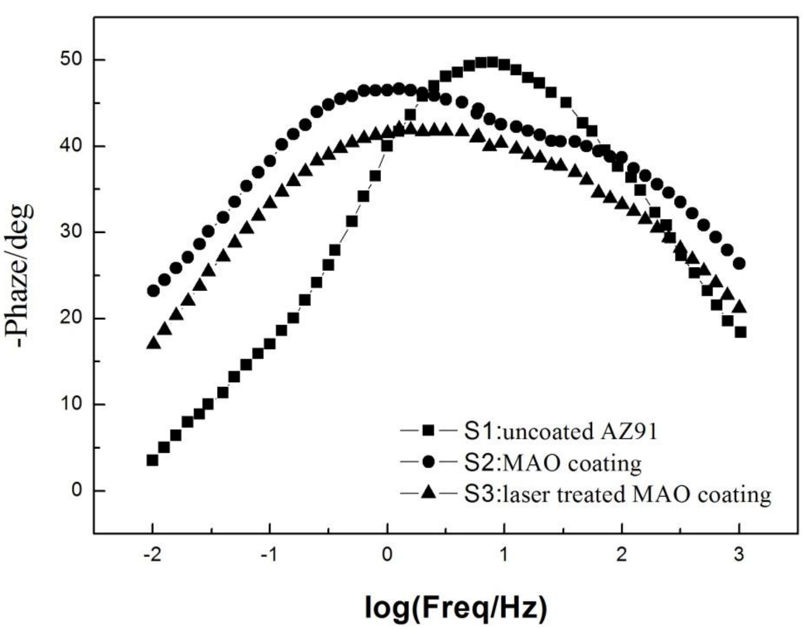

Figure 4 : Bode plots of samples

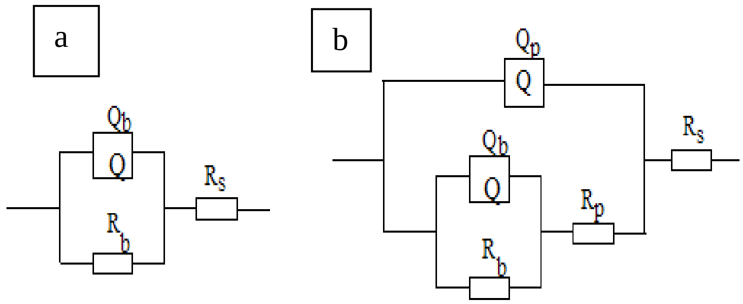

Figure 5 : Equivalent circuit models used for fitting the impedance spectra a: substrate and laser treated sample, b: MAO coated sample without laser treating

TABLE 3 : Fitting values of samples

Samples	R_s (Ω cm^2)	Q_p–Y_0 ($\Omega^{-1}s^{-n}/cm^2$)	n_p	R_p (Ω cm^2)	Q_b–Y_0 ($\Omega^{-1}s^{-n}/cm^2$)	n_b	R_b (Ω cm^2)
Uncoated	18.25	_	_	_	4.832×10^{-6}	0.6813	1.149×10^{4}
Coated	22.48	4.601×10^{-8}	0.7962	1.892×10^{5}	6.443×10^{-8}	0.8166	7.836×10^{6}
Laser treated	25.43	3.483×10^{-8}	0.7348	2.478×10^{6}	3.274×10^{-9}	0.8831	8.662×10^{7}

CONCLUSION

Micro arc oxidation coating on was first prepared on AZ91 biomedical magnesium alloy and then the coating surface was subjected to laser treating. By surface laser treating, the micro pores on the MAO coating surface became fewer and smaller. The micro cracks were also decreased. The whole surface became more unique and compact. The corrosion resistance of MAO coating in SBF was increased by laser treating. The corrosion current density of MAO coating on AZ91 was further decreased by 10 times by surface laser treating and the corrosion potential was also increased by 0.06V. The EIS fitting exhibited that the polarization resistance of MAO coating on AZ91 was also increased by 10 times after surface laser treating. The study indicated that by laser treating, the surface defects of MAO coating on AZ91 could be decreased and the corrosion resistance in SBF could be increased.

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