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Study on Micro-arc Oxidation-Silica-Berberine Composite Bio-coating of Magnesium Alloy

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Abstract. The berberine drug-loading coating was prepared on the surface of micro-arc oxidation magnesium alloy, and the corrosion resistance and bone growth of composite coating was investigated. Surface morphology of each sample was observed by scanning electron microscopy. The drug loading was studied by the infrared spectroscopy. Phase analysis of composite coating was performed by X-ray diffraction. The corrosion of the coating was studied by electrochemical corrosion tester. The coating adhesion was tested by the scratch tester. Friction and wear are detected by pin-disc friction wear meter, the change of the wetting angle is detected by a wetting angle meter, the weight loss rate, and composition analysis change of the composite coating were studied by simulated body fluid test. The results show that the composite coating improves corrosion resistance and promotes bone growth.

1. Introduction

Surface modification of medical biomaterials has always been a hot topic in the study of materials science workers. Surface modification of metal materials can accelerate bone healing stages of implantation in vivo in the early. Magnesium alloys are considered to be the most promising biomaterials due to their excellent biocompatibility and load carrying capacity. Despite the excellent performance of magnesium alloys, the degradation rate and postoperative infections limit the clinical medical treatment after the implantation in the in vivo environment[1-3]. For the implantation of magnesium alloys, biocompatible protective coatings are the best choice[4]. The corrosion resistance of the magnesium alloy is improved by a surface modification method, such as chemical deposition[5], ion implantation[6], micro-arc oxidation[7-10]. Micro-arc oxidation technology is the simple operation, green environmental protection, high efficiency and strong applicability. It has always been the concern of material scholars. However, the micro-arc oxidation of the magnesium alloy has a microporous structure, which reduces the barrier effect of the erosive liquid and does not promote bone growth. The research group prepared magnesium micro-arc oxidation-silane-berberine composite coating to study the protective effect of different content of berberine medicinal coating.

2. Experimental materials and methods

The specimens was pure magnesium with a size of 10 mm × 10 mm. The pure magnesium sample using silicon carbide abrasive paper from 150 to 1200 grit was prepared, and then placed in 95 % absolute ethanol to prevent oxidation. The sample is placed in an acid treatment solution of oxalic acid, acetic acid, nitric acid and distilled water at a volume ratio of 1: 1: 1: 150 for 10 s. Micro-arc oxidation treatment process: ultrasonic frequency 50 kHz, pulse width 500 Hz, voltage 300 V, oxidation time 10 min, micro-arc oxidation electrolyte is distilled water silicate system electrolyte. 120 g/L NaOH solution was placed in a constant temperature water bath for alkali treatment for 1 h after micro-arc oxidation. A silane solution is prepared by water, alcohol, and a silane coupling agent in a volume ratio of 1:9:1. Add berberine to obtain a drug-loading solution at concentrations of 0g/L, 2g/L, 4g/L, 6g/L. The micro-arc oxidation sample was impregnated into berberine to obtain drug-loaded coatings of 0g/L, 2g/L, 4g/L, 6g/L. The surface morphology of the sample was observed by JSM-6360LV SEM. The element content of the coating was analyzed by FALCON60S spectrum, and the phase composition of the coating was analyzed by XRD. The corrosion equilibrium potential, corrosion current and linear polarization resistance of magnesium alloy were measured by CHI660C potentiometer in simulated body fluid at 37 °C. The potential scanning rate was 0.01 mv/s and the scanning range was -2.5~1V. The brooke VECTOR33 fourier transform infrared spectrometer was used to determine the composition of functional groups in the coating. The resolution is $4cm^{-1}$ and the scanning wavelength is $400\sim4000cm^{-1}$. The friction and wear properties of magnesium alloy micro-arc oxidation-silane-berberine composite coating were studied by the pin-disk friction and wear tester.

3. Experimental results and analysis

3.1. Surface morphology and elemental analysis of the coating

The surface coating of berberine is not added with pores of different sizes. Different concentrations of berberine, and the surface of the coating is covered with a uniform film layer. The pores are filled, the pores become smaller, and the number of pores decreases. After the silane treatment, the silane molec-

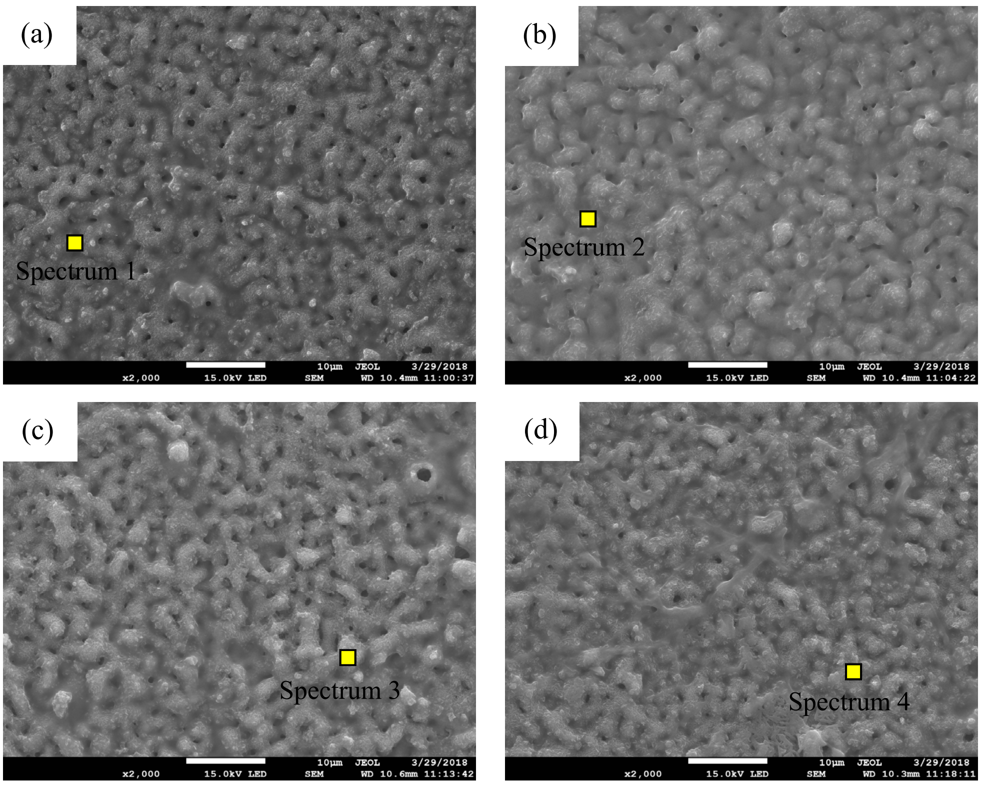

Figure 1. Surface morphology of coatings treated with different concentrations of berberine of (a) 0g/L (b) 2g/L (c) 4g/L (d) 6g/L.

ules are hydrolyzed to form silanol, which reacts with the hydroxyl groups on the surface of the sample and the metal oxides of the pores after the alkali treatment, and the silane molecules themselves condense to form a film, so that the surface of the test piece has a concave and convex surface smooth[11]. The pores of the surface coating layer become smaller after the silane-loading treatment. With the increase of the drug loading, the pores are filled with small pores and the surface of the coating is uniform. When the concentration of berberine is 6g/L, the pore is the least, the film layer is the most dense and uniform, as shown in figure 1.

Figure 2 shows that the distribution of EDAX elements on the surface of different concentrations of berberine. It can be seen from in figure 2, when the concentration of berberine is 0g/L, the surface of the coating mainly contains O, Mg, C, Si and a small amount of N, P and Na elements. The content of Si element is significantly increased, but the content of Mg element is gradually reduced. With the increase of the concentration of berberine, the elements of C, N and O increased significantly. This is because Mg reacts with the hydroxyl groups remaining on the surface of the sample to form $Mg(OH)_2$. Due to the presence of N element in berberine, as the concentration of berberine increased, the content of N increased, which improved the biological activity of the coating.

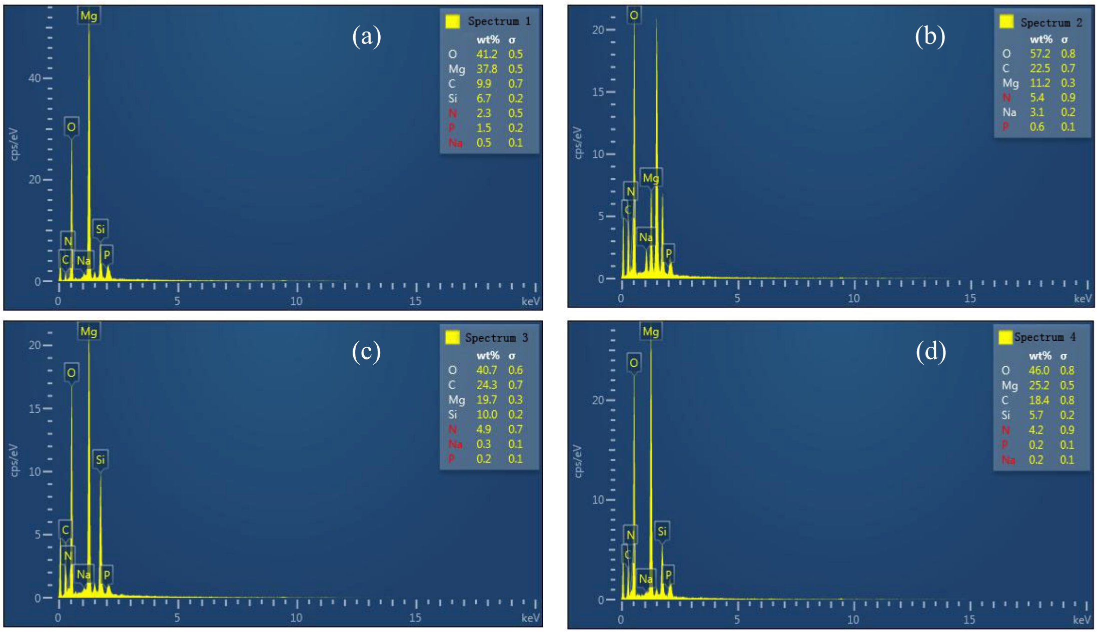

Figure 2. Distribution of surface elements after treatment with different concentrations of berberine of (a) 0g/L (b) 2g/L (c) 4g/L (d) 6g/L.

3.2. Infrared spectroscopy

Figure 3 shows that the infrared spectrum of the coating after treatment with different concentrations of berberine. There is a Mg-O characteristic peak at a wave number of 557 cm^{-1}, which is a MgO phase in a ceramic coating. The wave number is 1311cm^{-1} with a characteristic peak of -SiO_3-, which is the $MgSiO_3$ phase in the ceramic film. There are hydroxyl characteristic peaks at wave numbers of 2360 cm^{-1} and 3442 cm^{-1}, which may be caused by alkali-treated hydroxyl groups, as shown in figure 3. The infrared spectrum of the coating treated with berberine is shifted downwards compared with the spectrum after only silane treatment, because the alkali treatment leaves the hydroxyl groups on the surface of the sample and the metal oxides exposed through the pores. The reaction causes a change in the surface material of the coating, which affects the frequency of the characteristic band.

3.3. Bond strength

Figure 4 shows that the binding force curves of the coatings treated with different concentrations of berberine. It can be seen from figure 4 that as the concentration of berberine increases, the critical binding force of the coating increases. Since the silane molecule itself condenses to form a film after the silane-loading treatment, the surface coating pores become smaller, and the pore filling pores are smaller as the drug loading is increased, and the film is more tightly bonded to the matrix, improving the bonding strength of the coating. The adhesion of the silane-treated coating was 1 N, when the concentration of berberine was 2 g/L, the coating adhesion was 1.9 N, and when the concentration of berberine was 6 g/L, the coating adhesion was 2.9 N.

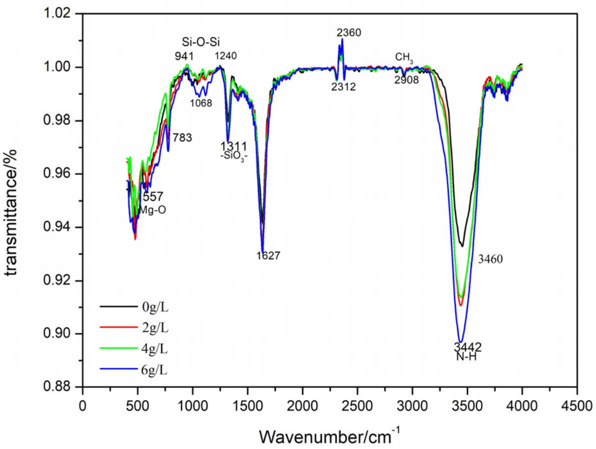

Figure 3. Infrared spectra of coatings treated with different concentrations of berberine.

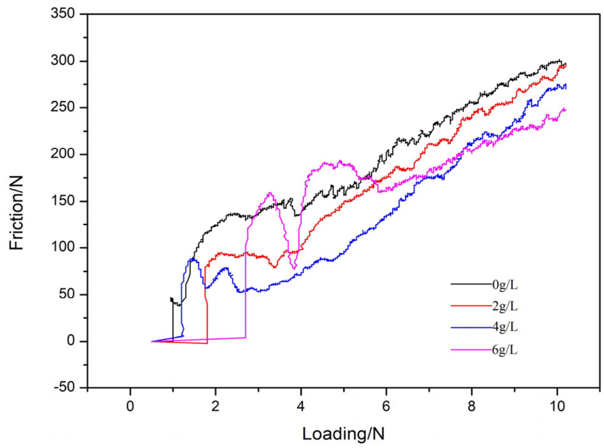

Figure 4. Curve of binding force.

3.4. *Wetting angle*

Figure 5 shows that the contact angles of different concentrations of berberine treated coatings. As shown in figure 5, the silane-treated coating is more hydrophobic, and the hydrophobicity of the coating is significantly weakened after silane-citrin treatment. As the drug loading increases, the wetting angle of the coating surface decreases, enhanced hydrophilicity. J G Liu[12] found that lipoteichoic acid contained in the bacterial cell wall, bacteria was more likely to adsorb to hydrophobic materials. The surface of the coating treated with silane-berberine reduces the ability of bacteria to ad-

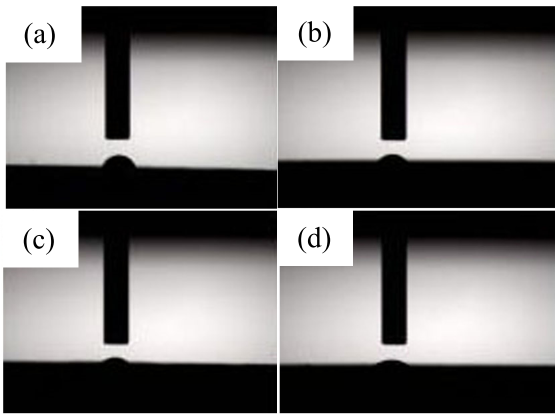

Figure 5. Contact angle after treatment with different concentrations of berberine of (a) 0g/L (b) 2g/L (c) 4g/L (d) 6g/L.

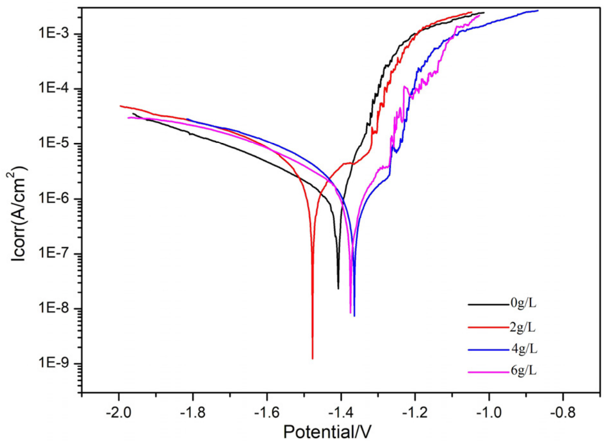

Figure 6. Tafel curve of different concentrations of berberine treated coatings.

sorb, lead to improve coating bone binding capacity. The wetting angle of the surface of pure magnesium micro-arc oxidation-silane-berberine coating is gradually reduced. With the increase of drug loading, the surface wetting angle of the coating tends to decrease, and the hydrophobicity of the surface of the composite membrane decreases, and conversion to hydrophilicity.

3.5. Electrochemical corrosion
Figure 6 shows that the tafel curve of different concentrations of berberine treated coatings. The UMAO-silane-berberine composite coating gradually increased from the corrosion potential with the increase of berberine concentration, and the self-corrosion current gradually became smaller. It is known from the relationship between the self-corrosion current density and the metal corrosion rate that the smaller the icorr, the slower the corrosion rate and the better the corrosion resistance of the coating. It can be seen that the UMAO-silane coating can effectively inhibit the polarization process after the treatment with berberine, slow down the corrosion rate of the material, and better protect the magnesium matrix.

3.6. Composite coating simulating body fluid soaking
Figure 7 shows that the surface morphology of the coatings treated with different concentrations of berberine after 7 days of simulated body fluid soaking. It can be seen from figure 7 that white crystallites appear on the surface of the test piece, and distribute irregularly on the surface of the coating in the form of dispersion.

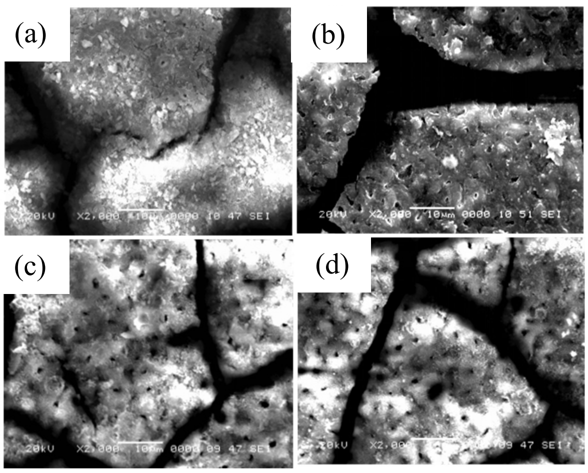

Figure 7. SEM surface of simulated body fluid immersion of (a) 0g/L (b) 2g/L (c) 4g/L (d) 6g/L.

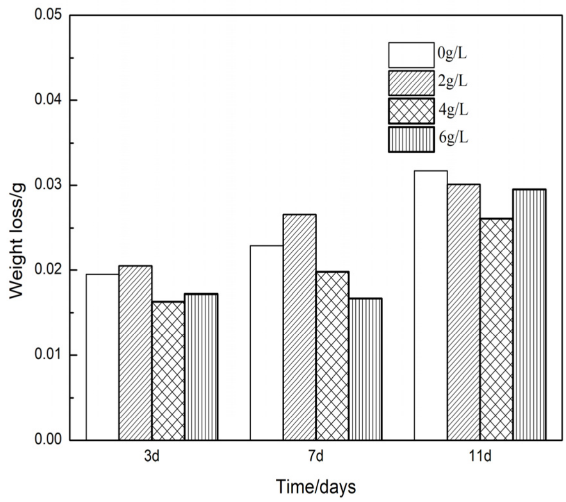

Figure 8. The weight loss of the coating.

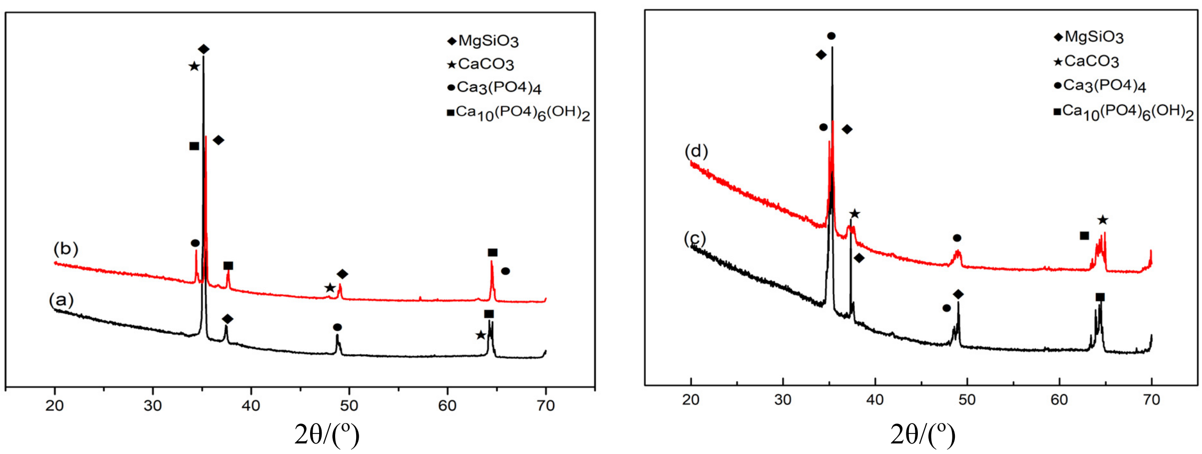

Figure 9. Phase analysis after 7 days simulated body fluid of (a) 0g/L (b) 2g/L (c) 4g/L (d) 6g/L.

With the higher the concentration of berberine, the more white crystallites. With the higher the concentration of berberine, the less weight loss from the 7-day simulated body fluid weight change in figure 8. It is speculated from figure 9 that hydroxyapatite is formed, and the solubility of hydroxyapatite is very low, easy to nucleate and grow on the surface of the sample. In addition to this, some insoluble phosphate containing Mg/Ca is formed and deposited on the sample. It can be seen from figure 8 that the immersion in the simulated solution for 3 days, 7 days and 11 days, the lower the weight loss with the higher concentration of berberine. Due to the corrosion of MgO in the coating, $Mg(OH)_2$ and H_2 are formed by reaction with OH^- in water. As the immersion time is prolonged, $Mg(OH)_2$ continues to react with a large amount of ions and elements in the solution to form calcium carbonate. Magnesium salt and sodium magnesium phosphate salt, is bone-like apatite. From the XRD phase analysis in figure 9, it can be seen that the metal oxide in the coating reacts with a large amount of ions in the body fluid to form a new substance. With the concentration of berberine increases, the bone-like phosphorous formed on the surface of the coating.

4. Conclusion

With the increase of the drug loading of berberine, the surface pores of the coating became smaller and uniform. The berberine-treated coating binds well to the substrate. The coating strength of 6g/L berberine treatment reached 2.9N, and the wear resistance was improved. The surface contact angle of the pure magnesium UMAO-silane-berberine composite coating was reduced from 70° to 41°, and the corrosion resistance was superior to that of the pure magnesium UMAO-silane coating. New material-like bone apatite was formed on the surface of the coating after simulating body fluid.

Acknowledgments

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