Studies on degradation performance of Mg-4.0Zn-1.5Sr alloy with coated of the laser surface processing combining alkaline treatment

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Abstract. The surface modification of biomaterial Mg-4.0Zn-1.5Sr alloy has been done by means of laser surface processing combining alkaline treatment process, as well as the degradation performance of Mg-4.0Zn-1.5Sr alloy with and without coatings in Hank's solution has been analyzed comparatively. The results indicate that the optimal parameters of laser surface processing are that the power is 3 kW, the current 200 A, the width 1mm, the defocus amount 135 mm and the scanning speed 1mm/s. The optimal parameters of alkaline treatment are that the solution is NaOH, the concentration 0.5 mol/L, the temperature 80 ℃ and the time 12 h. There are only two phases of $Mg(OH)_2$ and magnesium matrix, and the surface generated most of $Mg(OH)_2$ which can improve the corrosion resistance of the alloy after laser combining alkaline treatment, as well as the corrosion rate is almost the stable, which is much smaller than both of uncoated and laser surface processing. The study of the electrochemical corrosion behavior shows that the corrosion potential of the alloy with coated of laser combining alkaline treatment is improved 0.1277 V than that of laser treatment, and the corrosion current is decreased 470.2 muA than laser treatment. The corrosion resistant ability of Mg-4.0Zn-1.5Sr alloy is greatly improved by means of laser combining alkaline treatment.

1. Introduction

In recent decades, as a novel biomedical planting material, the study of magnesium alloys is paid more attentions [1-3]. It is well known that magnesium (Mg) and magnesium alloys possess many properties superior to other metallic biomaterials. However, magnesium alloys studied at present are mostly focused on industrial area, usually containing some elements that are harmful to human healthy such as aluminium, manganese or rare earth elements. In addition, the rapid degradation rate and relatively low biological activity restrict its widespread use in clinical applications. Therefore, the research on magnesium-based implant materials which are consisted with all of the nourishment elements and with the lower degradation rate has become an important subject with growing interests [4-6].

The surface modification is one of the most effective ways to improve the alloy corrosion resistance, including the laser surface treatment can greatly improve the fatigue corrosion resistance, and alkali heat treatment can significantly improve the corrosion resistance. In this paper, In order to improve the corrosion resistance of the alloy, the Mg-4.0Zn-1.5Sr alloy alloys is designed, and laser surface processing combining alkaline treatment process is optimized to improve the corrosion resistant properties of the alloy, and the degradation performance of the alloy with and without coating has been studied.

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2. Materials and experimental

In the experiment, pure magnesium with a purity of 99.9 % was adopted. The Mg-4.0Zn-1.5Sr (wt.%) alloy ingots was produced by melting with Ar gas protection. The magnesium and its alloy ingots were rolled into sheets in three sequential steps at 350 ℃. The final sheet size was 13×13×1 mm. By means of YAG laser device to make laser surface treatment, and hot type magnetic stirrer to make alkaline treatment. the optimal parameters of laser surface processing are that the power is 3 kW, the current 200 A, the width 1 mm, the defocus amount 135 mm and the scanning speed 1 mm/s. The optimal parameters of alkaline treatment are that the solution is NaOH, the concentration 0.5 mol/L, the temperature 80 ℃ and the time 12 h. The alloy samples with and without coating were immersed in SBF. To make the SBF, 700 mL of deionized water was poured into a 1L beaker in which the temperature was held at (36.5±1.5) ℃. 8.035 g NaCl, 0.355 g $NaHCO_3$, 0.225 g KCl, 0.231g K_2HPO_4 $3H_2O$, 0.311 g $MgCl_2$ $6H_2O$, 0.292 g $CaCl_2$, 0.072 g Na_2SO_4, 6.118 g $(HOCH_2)_3CNH_2$ and 5 ml of 1 mol/L HCl were added into the beaker sequentially. Deionized water was added until reaching a final volume of 1000 ml and pH was finally adjusted to 7.4. For degradation studies, the specimens were hung vertically by a fine line and fully immersed in SBF. The study of electrochemical behavior of the alloy by means of electrochemical equipment CHI600B at 37 ℃ in SBF. The surface morphology and composition of corrosion products were observed and analyzed by means of Scanning electron microscopy (SEM) and X-ray diffraction (XRD).

3. Results and discussion

3.1 The surface morphology and microstructure of Mg-4.0Zn-1.5Sr alloy, Mg-4.0Zn-1.5Sr alloy with coating of laser surface processing and with coating of laser surface processing combining alkaline treatment

The metallographical image of the cast structures of Mg-4.0Zn-1.5Sr alloy is shown in Figure 1. It can be seen that the alloy which grain is uniform and fine is mainly composed of a gray α-Mg matrix and a black second phase and the second phase is mainly concentrated near the grain boundaries.

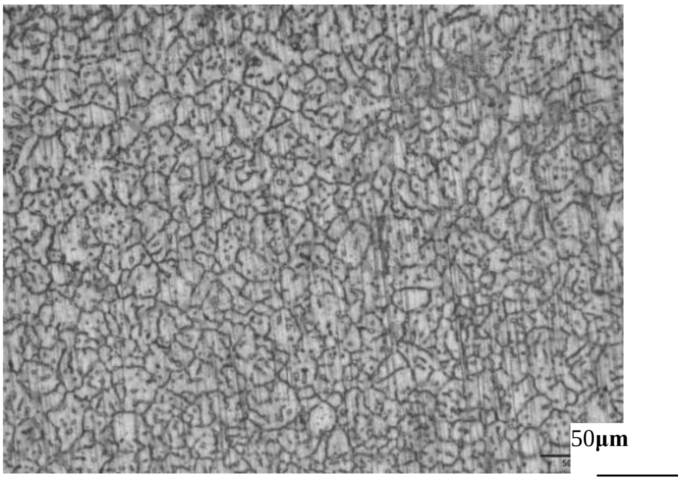

Figure 1. The metallographical image of the cast structures of Mg-4.0Zn-1.5Sr alloy

The SEM image of sample after laser surface processing is shown in Figure 2(a). It can be seen that there are many molten pools after laser scanning, and the surface composition is very close to the cast alloy. The metallographical image of Mg-4.0Zn-1.5Sr alloy after laser surface processing combining alkaline treatment is shown in Figure 2(b). It can be seen that after alkaline treatment the surface is changed smooth and compact compared with only laser surface processing. The SEM image and EDS analysis of sample after laser surface processing and alkaline treatment is shown in Figure 3 and Table 1. It can be seen that after alkali heat treatment, there are only two elements of Mg and O. It can be explained that the main composition is Mg $(OH)_2$, and the coating is uniform and density, which is

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separated with the matrix. The XRD analysis result of Mg-4.0Zn-1.5Sr after laser surface processing and alkaline treatment is shown in Figure 4. It can be seen that after alkaline treatment, there are only two phases of Mg $(OH)_2$ and magnesium matrix. In addition, the large amount of Mg $(OH)_2$ generated the surface can improve the corrosion resistance of the alloy.

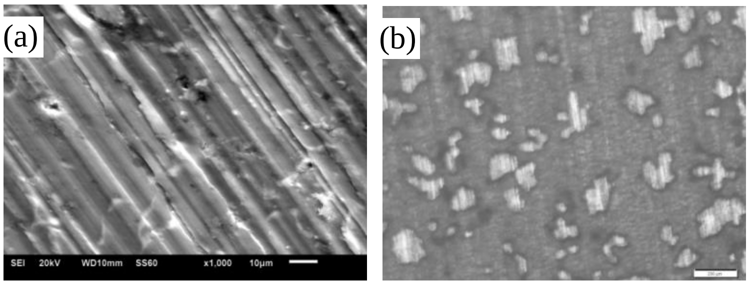

Figure 2. The metallographical image of Mg-4.0Zn-1.5Sr alloy after (a) laser surface processing ; (b) laser surface processing combining alkaline treatment

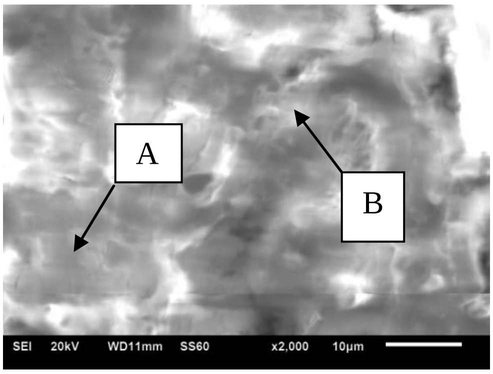

Figure 3. The SEM image and EDS analysis of sample after laser surface processing and alkaline treatment

Table 1. The percentage elements of place A to B by EDS analysis

The elements	Position A		Position B	
	Wt%	At%	Wt%	At%
O	54.02	64.41	50.54	59.75
Mg	45.98	35.59	49.47	40.25

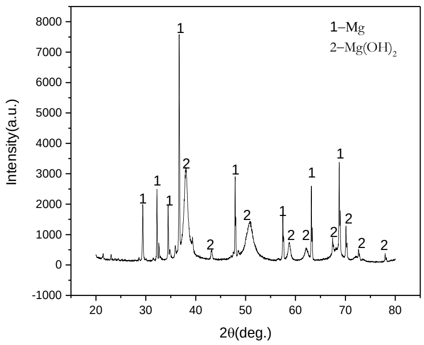

Figure 4. XRD analysis result of Mg-4.0Zn-1.5Sr alloy after laser surface processing and alkaline treatment

3.2 The test of Mg-4.0Zn-1.5Sr alloy with coating of laser surface processing combining alkaline treatment after immersed in SBF

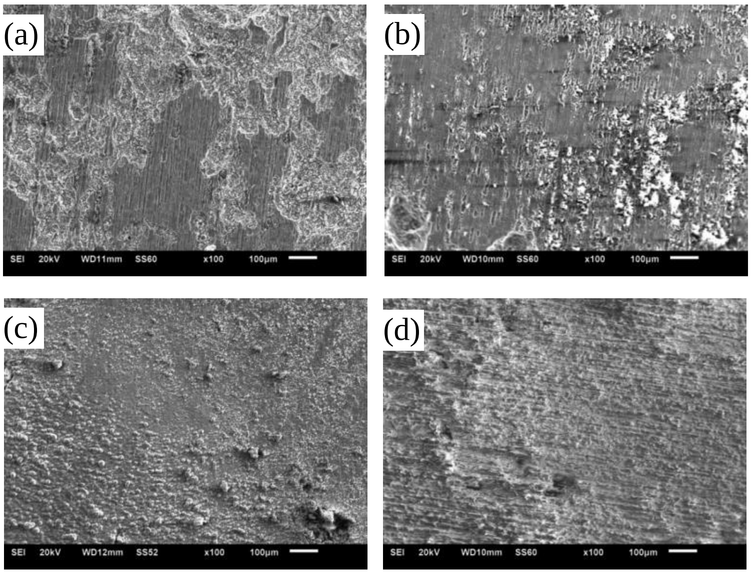

Figure 5. The surface metallographs of Mg-4.0Zn-1.5Sr with laser surface processing and alkaline treatment after immersion in SBF for (a) 1 d; (b) 7 ds; (c) 12ds (a) and (d): 15ds

The surface metallographs of Mg-4.0Zn-1.5Sr with laser surface processing and alkaline treatment after immersion in SBF for the different times is shown in Figure 5. It can be seen that only a small area is very slight damage happened in the surface after the sample immersed in SBF for 1 day shown in Figure 5(a). In Figure 5(b) immersed in SBF for 7 days, only local area is slight damage with shallow corrosion depth, and does not have the phenomenon of continuous, pitting corrosion and no lateral extension. In Figure 5(c) and Figure 5(d) immersed in SBF for 12 and 15 days, respectively. It can be seen that only local area is slightly destroyed with a shallow corrosion depth expressing that the corrosion is very slight. And corrosion coating remained very good adhesion with matrix, there is no large area falls off phenomenon happened for 15 days. The sample surface has a lot of small particles bump for 12 days, which is gone for 15 days. It is possible that corrosion products or coating fall off. The loss mass change compared of Mg-4.0Zn-1.5Sr alloy, Mg-4.0Zn-1.5Sr alloy with coating of laser surface processing and with coating of laser surface processing combining alkaline treatment immersed in SBF is shown Figure 6. The change trend of loss mass of uncoated alloy is similar with the laser surface treatment, which is increased gradually, but the loss mass ratio is different. As well as the both values of loss mass are closed. While, for the laser surface processing combining alkaline treatment, the loss mass ratio is almost stable during the immersed times with the slower increased at immersed times in SBF. As well as the value of loss mass is much lower than the alloy with uncoated and laser surface processing. The corrosion rate of Mg-4.0Zn-1.5Sr alloy with coated of laser surface processing and alkaline treatment in SBF is shown in Figure 7. For the alloy with uncoated and laser surface processing, the corrosion rate is increased before 7 days, then declined during 7 days to 15 days, but for the laser surface processing combining alkaline treatment, the corrosion rate is almost the stable, which is much smaller than both of uncoated and laser surface processing.

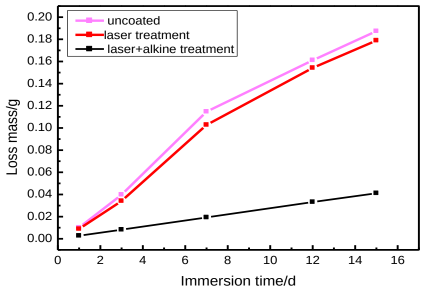

Figure 6. The loss mass change Mg-4.0Zn-1.5Sr alloy with coated of laser aalkaline treatment in SBF

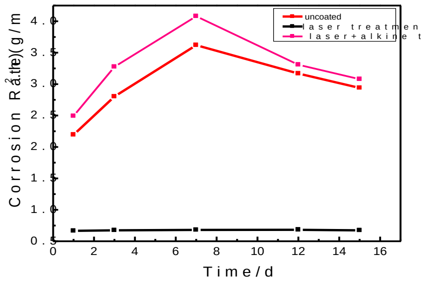

Figure 7. The corrosion rate of Mg-4.0Zn-1.5Sr alloy with coated of laser surface processing and alkaline treatment in SBF

3.3 The electrochemical corrosion behavior of Mg-4.0Zn-1.5Sr alloy with coated of laser combining alkaline treatment

Dynamic polarization test is used on Mg-4.0Zn-1.5Sr alloy with coated of laser combining alkaline treatment. The sample effective area is 1 cm^2, scanning speed is 0.01 V/s. Corrosive medium pH is 7.35. In general, the higher the corrosion potential, corrosion current density is smaller, the material of the corrosion rate is smaller, and the material has stronger corrosion resistance ability. Dynamic polarization test result on Mg-4.0Zn-1.5Sr alloy with coated of laser + alkaline treatment is shown in Figure 8, and the results are shown in table2. For Mg-4.0Zn-1.5Sr alloy with coated of laser combining alkaline treatment, the corrosion potential is improved 0.1277 V than that of laser treatment, and the corrosion current is decreased 470.2 muA than laser treatment. The result is consistent with the weight-loss method which the corrosion resistant is greatly improved by means of laser and alkaline treatment.

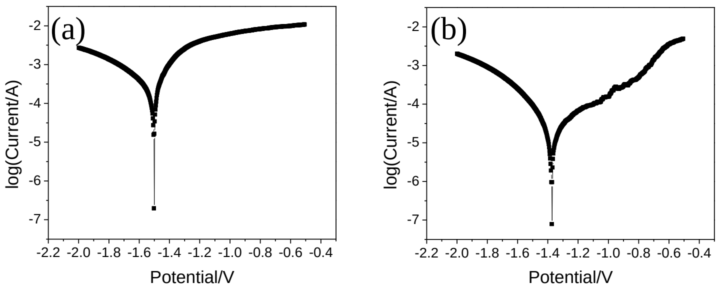

Figure 8 The dynamic polarization curves of Mg-4.0Zn-1.5Sr alloy after alkaline treatment (a): Laser surface treatment; (b): Laser combining alkaline treatment

Table 2. The electrochemical corrosion results of Mg-4.0Zn-1.5Sr alloy with coated of laser and alkaline treatment

The process	Effective area/cm^2	Corrosion potential /V	Corrosion current/uA	Corrosion current density /uA/cm^2
Uncoated	1	-1.5062	566	566
Laser treatment	1	-1.4995	479	479
Laser + alkaline treatment	1	-1.3718	8.8	8.8

4. Conclusion

The optimal parameters of laser surface processing are that the power is 3 kW, the current 200 A, the width 1mm, the defocus amount 135 mm and the scanning speed 1mm/s. The optimal parameters of alkaline treatment are that the solution is NaOH, the concentration 0.5 mol/L, the temperature 80 ℃

and the time 12 h. There are only two phases of Mg $(OH)_2$ and magnesium matrix, and the surface generated most of Mg $(OH)_2$ which can improve the corrosion resistance of the alloy after laser combining alkaline treatment, as well as the corrosion rate is almost the stable, which is much smaller than both of uncoated and laser surface processing. The study of the electrochemical corrosion behavior shows that the corrosion potential of the alloy with coated of laser combining alkaline treatment is improved 0.1277 V than that of laser treatment, and the corrosion current is decreased 470.2 muA than laser treatment. The corrosion resistant ability of Mg-4.0Zn-1.5Sr alloy is greatly improved by means of laser combining alkaline treatment.

5. References

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