J Mater Sci (2007) 42:8523–8528
DOI 10.1007/s10853-007-1738-z

Corrosion and wear resistance of AZ91D magnesium alloy with and without microarc oxidation coating in Hank's solution

X. P. Zhang · Z. P. Zhao · F. M. Wu · Y. L. Wang · J. Wu

Received: 9 January 2007 / Accepted: 2 April 2007 / Published online: 23 June 2007

Abstract Immersion test, electrochemistry test and block-on-cylinder type wear test have been applied to study the corrosion and wear resistance of AZ91D Mg alloy with and without microarc oxidation (MAO) treatment in Hank's solution. Through MAO, a ceramic coating is directly formed on the surface of AZ91D Mg alloy, by which its corrosion and wear resistances are greatly improved. The immersion test results show the mass loss of untreated AZ91D Mg is 15 times of that of MAO ones after 21 days immersion test. The electrochemical corrosion experiments show that the corrosion potential of Mg alloy is improved from –1.5786 V to –0.43019 V through MAO surface treatment, the corrosion current is reduced from 0.028703 A/cm^2 to 2.0456×10^{-7} A/cm^2, and the polarization resistance is improved from 1.2753×10^{-5} Ω/cm^2 to 0.90886 Ω/cm^2. The lubricate sliding wear test results show the mass loss of untreated AZ91D Mg is 1.5 times of that of MAO ones.

Introduction

Magnesium alloys exhibit an attractive combination of low density and high strength/weight ratio. Owing to easily removed impurity, recycling property of magnesium is superior to Fe, Ni, etc. Therefore, magnesium alloy parts are used in a variety of applications, such as in automotive, materials handling and aerospace equipment [1–13].

Currently approved and commonly used metallic biomaterials include stainless steels, cobalt–chromium-based alloys and titanium alloys. Compared with these conventional metallic biomaterials, magnesium and its alloys have many obvious advantages. The oceans contain approximately 1.3 Mt/km^3 magnesium and magnesium is relatively abundant. The density of magnesium, which is very similar to that of human calvarium bone, is 35% lower than that of aluminum and only two-fifths of Ti6Al4V or two-ninths of stainless steels. The elastic modulus of pure magnesium is 45 GPa, which is very similar to that of human bone (40–57 GPa), only a half of that of Ti6Al4V(109–112GPa), and it can greatly reduce the stress shielding effects in bone tissue initiated by the presence of the implants. In addition, magnesium is one of the most important bivalent ions associated with the formation of biological apatite [2–6]. The two major drawbacks of magnesium in many applications are low corrosion resistance and poor wear resistance. For example, the first attempt of applying magnesium to biomaterial, which was reported by Lambotte in 1907, was failed as the magnesium metal corroded too rapidly in vivo, disintegrating only 8 days after surgery and producing a large amount of gas beneath the skin [5]. Therefore, many surface treatment techniques, such as electroplating, chemical plating, anodic oxidation, chemical conversion coatings, physical vapor deposition and laser surface treatment, have been developed for preventing the corrosion and increasing the anti-wear behavior of Mg alloys [7, 12]. Microarc oxidation (MAO) is a recently developed surface treatment technology under anodic oxidation. Through MAO, in-situ-grown

X. P. Zhang (✉) · Z. P. Zhao · Y. L. Wang
Department of Materials Science and Engineering,
Nanjing University of Science and Technology,
Nanjing 210094, P.R. China
e-mail: zxp_0517@163.com

F. M. Wu · J. Wu
Stomatological College, Nanjing Medical University,
Nanjing 210094, P.R. China

Y. L. Wang
General Research Institute for Nonferrous Metals,
Beijing 100088, P.R. China

ceramic coating is directly formed on the surface of magnesium alloy, titanium alloy and aluminum alloy, by which its corrosion resistance, wear resistance are greatly improved in industrial environment [12, 14]. Little has been report on the Corrosion and wear resistance of AZ91D magnesium alloy with and without MAO coating in simulation body fluid. In this paper, the corrosion and wear resistance of AZ91D magnesium alloy in Hank's solutions with and without MAO treatment were preliminarily investigated.

Materials and methods

Materials

Samples for corrosion tests and wear tests were cut to a size of $25 \times 25 \times 2$ mm^3. All of these samples were prepared from an ingot of AZ91D magnesium alloy, whose chemical nominal composition (wt.%) was 8.73%Al, 0.70%Zn, 0.15% Mn and balance Mg. All of the specimens were prepared from one die casting in order to minimize the differences resulting from variations in composition and microstructure. The MAO surface treatment was processed by Metallic Corrosion & Protection Center, Shanghai Institute of Microsystem an Information technology, Chinese Academy of Sciences.

Immersion test

The sample surfaces were cleaned with acetone and demineralized water. After atmosphere drying, the specimens were weighed for the original weight $w0$, which was measured by electric balance with 0.1 mg accuracy, and then the specimens were then submerged in Hank's solution by hanging the specimens in beakers. The tests were conducted at 37.5 °C. After immersion tests, the corroded specimens were cleaned with distilled water and dried. They were then immersed in a chromate acid (200 g/L CrO_3 + 10 g/L $AgNO_3$) at ambient temperature for 5–10 min to remove the corrosion products. It has been repeatedly demonstrated in the laboratory by using not corroded specimens in the acid under the same conditions that the chromate acid can cause almost no weight loss to a not corroded AZ alloy specimen, i.e., the chromate acid can remove the corrosion products on AZ91D alloy without etching its metallic substrate or non-corrosion areas. The specimens were then quickly washed with distilled water and dried again. In the end, the specimens were weighed for the final weight $w1$. The difference between $w0$ and $w1$ was the corrosion weight loss $\Delta w = w1 - w0$. After 1, 2, 3 up to 21 days, specimens for different intervals were taken out of the electrolyte, cleaned and weighed according to the above methods. All of these tests were repeated six times. For comparison purpose, the corrosion tests were also performed on the untreated AZ91D Magnesium specimens.

Electrochemistry test

Electrochemistry tests were carried out using a Solatron 1255B electrochemical measurement system controlled by an IBM computer using the CorrWare software package (Scribner and Associates, Charlottesvile, VA). The electrochemical cell for corrosion test was a three-electrode setup. The reference electrode was a saturated Hg-Hg_2Cl_2 electrode. The counter electrode was a platinum electrode and a specimen, connected to a copper wire, as the working electrode. Before each polarization curve measurement, the sample was immersed in the test solution for 30 min to allow the open circuit potential to become stable. After the electrochemical testing system was stable, the polarization curves were measured from a cathodic potential of about –300 mV relative to the corrosion potential and stopped at an anodic potential 300 mV positive to the corrosion potential. The scanning rate was 10 mV/min. The corrosion current densities, corrosion potential and polarization resistance were measured by the Tafel extension [15]. For comparison purpose, the electrochemistry tests were performed on the untreated AZ91D Magnesium specimens. The crystallographic characteristics of the MAO coating were investigated using a powder X-ray diffraction (XRD) using CuK_ radiation.

Wear test

Lubricate sliding wear tests were performed using a block-on-cylinder type wear test machine in room temperature, and the lubricant is a Hank's solution. Block specimen was the MAO sample or the untreated sample, and it was fixed. The material of the cylinder was Cr12# die steel with a hardness of HV700 and its outer and inner diameter was 30 and 20 mm, respectively. The surface of the cylinder was polished to a roughness of $Ra = 0.25$ μm and the rotation speed is 200 rpm. The loads used in the test include 10, 20 and 40 N. The sliding distances were 125, 250 and 375 m, respectively. The wear loss and normalized wear rate were evaluated by the mass loss, which was measured by an electric balance with 0.1 mg accuracy. The worn surfaces were analysed using a scanning electron microscope (SEM, Philips Quanta 200). The hardness of the samples was measured using microhardness tester, the applied load was 200 g and the loading time was 20 s.

Results

Immersion test

Just one minute after the samples immerged in Hank's solution, all of the untreated samples exhibited visible dense gas bubbles. About 10 min, the solution with the untreated samples was became turbidity, and after 1 day there were some white flocculent deposits in the bottles for all untreated samples. After 2 days, there were many pores appear on surface of these samples. In addition, the numerical and area of the pores were increased with time. There were no gas bubbles for the MAO samples during the first day. On second day, there were few gas bubbles appear. The solutions keep limpid after an observation time of 21 day. As can be seen from Fig. 1, the mass losses of all samples were increasing during the observation time. After an observation time of 21 days, the untreated samples loss in weight an average of 18.83 ± 2.35 mg while the MAO samples was only 1.24 ± 0.18 mg.

Electrochemistry test

Figure 2 demonstrated polarization curves of the untreated and MAO samples. The results of electrochemistry corrosion were shown in Table 1. Corrosion potential of the MAO sample was –0.4309 V more positive than that of the untreated one, corrosion current of the MAO samples (2.0456×10^{-7} A/cm^2) was lower than that of untreated ones (0.028703 A/cm^2), and polarization resistance of the MAO ones (0.90886 Ω/cm^2) was higher than the untreated ones (1.2753×10^{-5} Ω/cm^2).

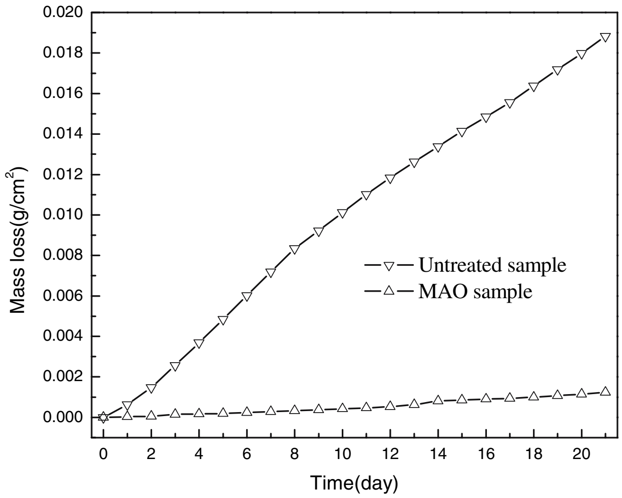

Fig. 1 Mass loss of MAO and untreated samples over immersion test time

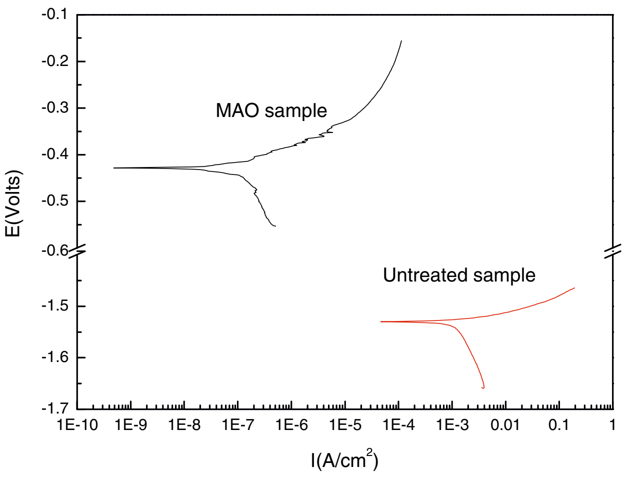

Fig. 2 Polarization curves for MAO sample and untreated one

Table 1 The results of electrochemistry corrosion

Sample	Open circuit potential (V)	Corrosion current density (A/cm^2)	Polarization resistance (Ω/cm^2)
Untreated	–1.5786	0.028703	1.2753×10^{-5}
MAO	–0.43019	2.0456×10^{-7}	0.90886

Wear test

Figure 3 illustrated the mass wear rate suffered by the MAO and untreated sample as a function of normal load. Both of mass loss of the MAO samples and that of the untreated ones were increased continuously with normal load. The difference was that mass loss of the untreated samples was increased greatly with normal load while that of the MAO ones increased slight. The ratio of mass loss of the untreated samples and that of MAO was rise from 1.5 to 2.42 when normal load was increased from 10 N to 40 N in the case of sliding distance was 125 m. On the other hand, when sliding distance extended to 375 m, the ratio of the untreated samples to MAO ones reduced from 3.14 to 1.5 when normal load was increased from 10 N to 40 N. Figure 4 shown the mass wear rate suffered by the MAO and untreated samples as a function of sliding distance. Both of mass loss of the MAO samples and the untreated ones increased continuously with sliding distance, too. The mass loss of the untreated sample increases greatly and that of the MAO ones increases slight with sliding distance. The ratio of mass loss of the untreated samples to that of MAO was rise from 1.5 to 3.14 with sliding distance increases from 125 m to 375 m when normal load was 10 N. When normal load rose to 40 N, the ratio of the untreated samples to MAO ones reduced from 2.42 to 1.5.

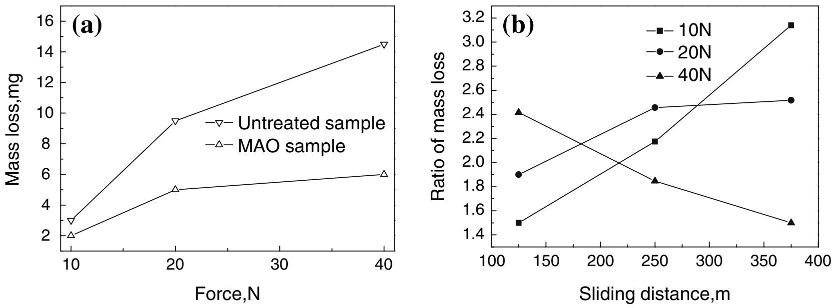

Fig. 3 Influence of normal load on untreated and MAO samples. (**a**) The mass losses of untreated samples and MAO ones for difference loads and 125 m sliding distance; (**b**) the ratios of mass losses of untreated samples and that of MAO ones for difference loads

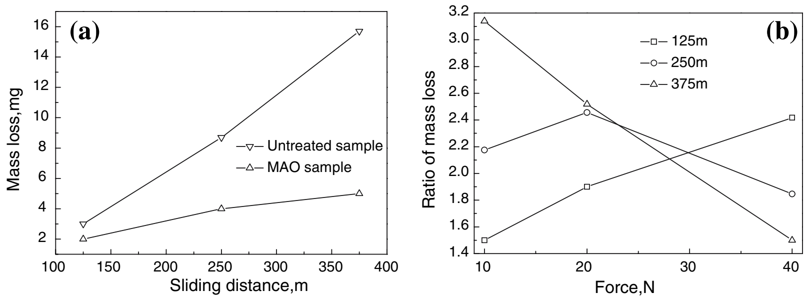

Fig. 4 Influence of sliding distance on untreated and MAO samples. (**a**) The mass losses of untreated samples and MAO ones for difference sliding distance; (**b**) the ratios of mass losses of untreated samples and that of MAO ones for difference sliding distance

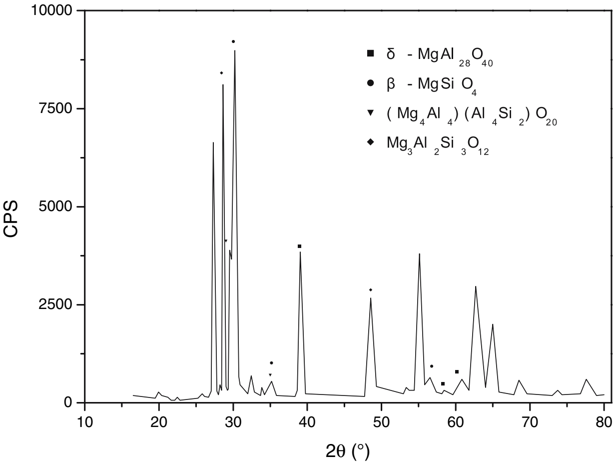

Fig. 5 The XRD pattern of ceramic coating formed by microarc oxidation on AZ91D magnesium alloy surface

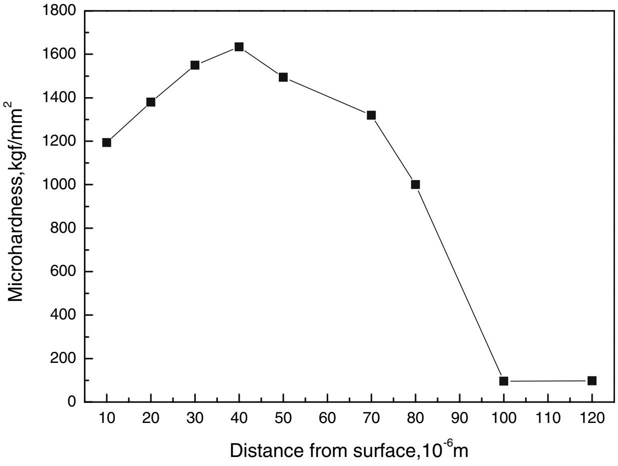

Fig. 6 Cross-sectional hardness profile of MAO sample

Discussions

The purpose of this study was to investigate the corrosion and wear resistance of AZ91D magnesium alloy with and without MAO coating in Hank's solution. From our results, we conclude, that the corrosion and wear resistances of AZ91D alloy in Hank's solution can be improved by MAO surface treatment. Figure 5 displays the diagram of XRD of MAO coating. The coating is mainly composed of δ-$MgAl_{28}O_{40}$, β-$MgSiO_4$, $(Mg_4Al_4)(Al_4Si_2)O_{20}$, $Mg_3Al_2Si_3O_{12}$ sharp spinels. Such structure can increase the hardness and corrosion resistance of AZ91D alloy.

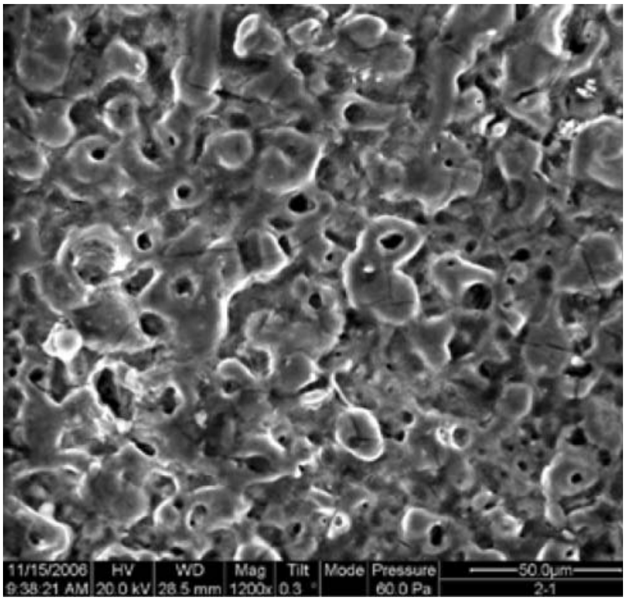

Fig. 7 SEM micrograph of surface of MAO sample

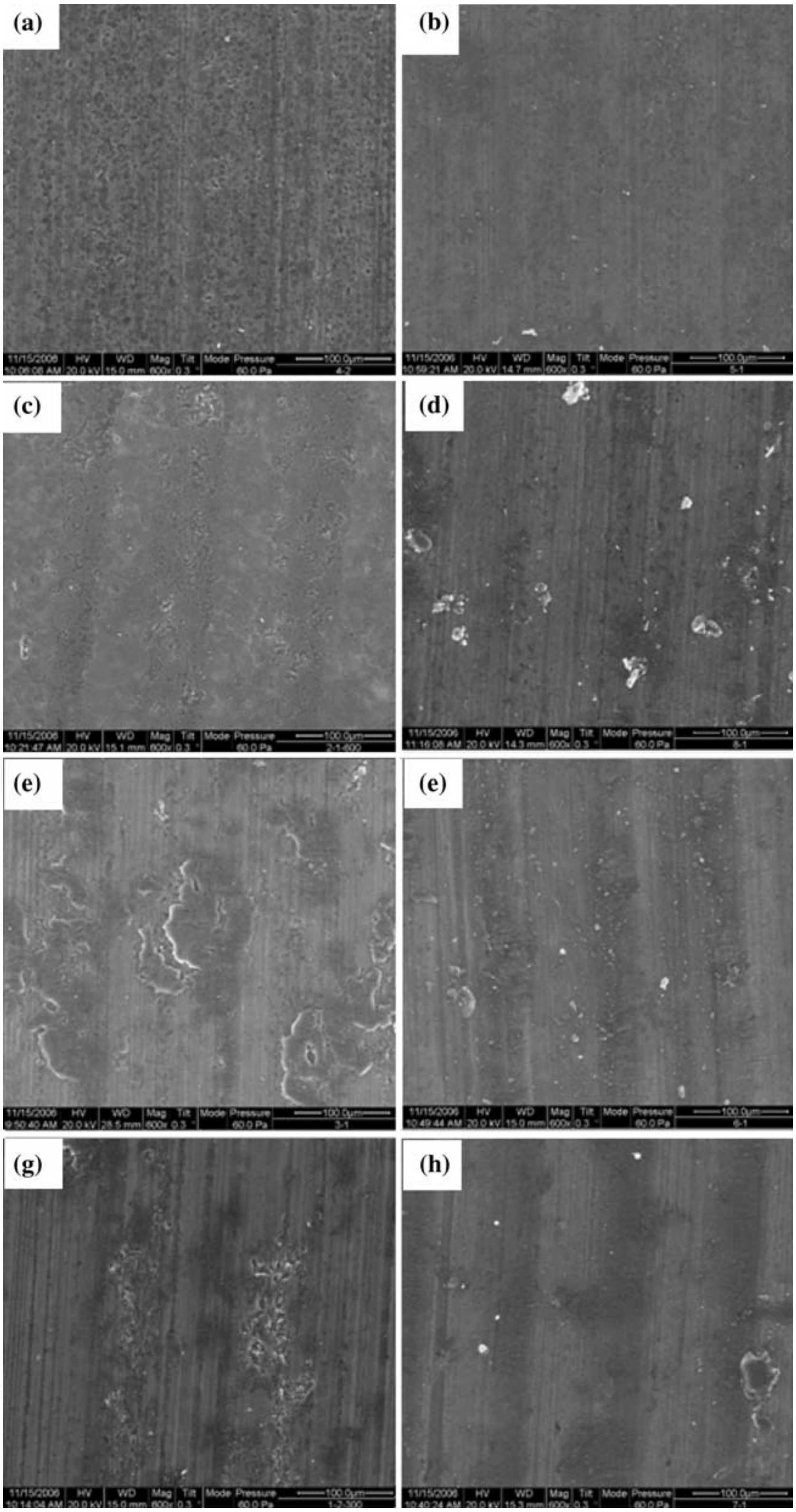

Fig. 8 SEM micrographs of worn tests of MAO samples and untreated ones. (**a**) MAO sample, load is 10 N and sliding distance is 125 m; (**b**) untreated sample, load is 10 N and sliding distance is 125 m; (**c**) MAO sample, load is 10 N and sliding distance is 375 m; (**d**) untreated , load is 10 N and sliding distance is 375 m; (**e**) MAO sample, load is 40 N and sliding distance is 125 m; (**f**) untreated sample, load is 40 N and sliding distance is 125 m; (**g**) MAO sample, load is 40 N and sliding distance is 375 m; (**h**) untreated sample, load is 40 N and sliding distance is 475 m

Figure 6 displays microhardness profile of MAO coating on AZ91D Mg alloy. From the outer layer to the interior of the coating, the microhardness gradually increases. Its maximum valus is about 1634 kgf/mm^2 at about 40 μm distance away from outer layer. The microhardness of AZ91D Mg is about 100 kgf/mm^2. It is clear that the microhardness of MAO coating is higher than that of AZ91D Mg alloy, which can improve wear resistance of the samples. In additional, many chimbs and holes can be seen on the surface of MAO coating, as shown in Fig. 7, these chimbs and holes may hold lubricant during wear test, which can improve wear resistance to a certain extent, too. A clearly phenomenon is that the mass loss of early stage of MAO samples is larger than that of steady stage, as shown in Figs. 3 and 4. There are many chimbs and holes on the surface of MAO coating, at early wear stage, the contact is the projecting points of the surface of MAO sample and that of Cr12# die steel cylinder. Compared the plane, the projecting points can easily be rubbed out. With the process of wear, the projecting points are abrading and the contact area is increasing, the mass loss is decreasing, accordingly. In Fig. 8 SEM micrographs of the wear tracks developed on the untreated and MAO samples surfaces after a wear test. The wear tracks produced on these samples exhibited different topography. A typical feature of rough wear track produced on untreated surface was extensive shear deformation (Fig. 8b, d, f, and h). The wear tracks on MAO samples were smooth (Fig. 8a, c, e, and g) and contained microcracks with traces of local material removal (Fig. 8d, f, and h). Thus, for MAO samples wear was initiated by disruption of ceramic layer and followed by the wear of base metal at extended testing times.

Conclusions

(1) Through MAO, a ceramic coating is directly formed on the surface of AZ91D Mg alloy, by which its surface properties are greatly improved.

(2) The corrosion resistance of AZ91D Mg alloy in the Hank's solution is obviously improved after MAO in comparison with that of untreated AZ91D Mg alloy. The immersion test results show the mass loss of untreated AZ91D Mg is 15 times of that of MAO ones. And the electrochemical corrosion experiments show that the corrosion potential of Mg alloy is improved from –1.5786 V to –0.43019 V through MAO surface treatment, the corrosion current is reduced from 0.028703 A/cm^2 to 2.0456×10^{-7} A/cm^2, and the polarization resistance is improved from 1.2753×10^{-5} Ω/cm^2 to 0.90886 Ω/cm^2.

(3) The wear resistance of AZ91D Mg alloy in the Hank's solution is also improved after MAO. The lubricate sliding wear test results show the mass loss of untreated AZ91D Mg is 1.5 times of that of MAO ones.

References

1. Yo K (2001) Mater Tans 42(7):115
2. Liang J, Guo BG, Tian J et al (2005) Appl Surface Sci 252:345
3. Witte F, Fischer J, Nellesen J, Crostack HA et al (2006) Biomaterials 27:1013
4. Witte F, Fischer J, Nellesen J et al (2005) Biomaterials 26:3557
5. Staiger MP, Pietaka AM, Huadmai J et al (2006) Biomaterials 27:1728
6. Li LC, Gao JC, Wan Y (2004) Surface Coatings Technol 185: 92
7. Zozulin AJ, Bartak DE (1994) Metal Finish 4:39
8. Wen CE, Yamada Y, Shimojima K et al (2004) Mater Lett 58:357
9. Heublein B, Rohde R, Kaese V (2003) Heart 89:651
10. Inoue H, Sugahara K, Yamamoto A et al (2002) Corros Sci 44(3):603
11. Wimmer MA, Loos J, Nassutt R et al (2001) Wear 250:129
12. Gray JE, Luan B (2002) J Alloys Compd 336:88
13. Zhang XP, Chen G (2005) Surface Rev Lett 12(2):279
14. Xue WB, Wu XL, Li XJ et al (2006) J Alloys Compd 425:302
15. Zhou WF (1985) Electrochemistry measure. Shanghai Science Technology Book Concern, Shanghai