One step synthesis of HA composite bio-coating on AZ91 magnesium alloy by a single method of MAO

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Abstract

Hydroxyapatite (HA) composite bio-coating was synthesized on AZ91 medical magnesium by one step of a single micro-arc oxidation（MAO）technique. The microstructure and corrosion resistance of the coating were investigated. The results showed that the coating obtained with HA powders in electrolyte were composed of HA, MgO and Mg2SiO4 crystals phases. Without HA powders in electrolyte, The coating only consisted MgO, and some Mg3(PO4)2 and Mg2SiO4. The HA coating showed microporous surface and the average pore diameter was 2-3µm.

Keywords

HA composite bio-coating; corrosion resistance; medical magnesium alloy; MAO.

1. Introduction

Recently, biomedical magnesium are widely studied in biomedical materials fields, owing to its excellent characters [1-2]. However, due to its chemical nature, biomedical magnesium is liable to suffer corrosion and hence exhibits fast degradation rate [2]. Therefore, many methods are developed to overcome this drawback and surface modification is found to be an effective method. Among the various surface modification techniques, micro-arc oxidation (MAO) is gaining increasing attention and is widely used, especially for surface modification of biomedical materials including titanium alloy and magnesium alloy [3-4]. MAO is an electrolysis process that takes place in liquid and the chemical composition of MAO coating can be controlled by adjusting the ingredients in electrolyte. Various bio-coating on biomedical metal materials surface were obtained by researchers [5-6]. However, HA coating, which is the one of most biocompatible specie, is found to be difficult to be synthesized on these biomedical metals by a single MAO technique. For a long time, duplex methods combining MAO and other techniques were used to synthesize HA coating on these alloys [3-4, 7-8]. Recently, this was realized on Ti alloy by further controlling the electrolyte ingredients and electric parameters [4, 9]. However, synthesis of bio-coating on Mg alloy containing HA by a single technique of MAO is still rarely reported.

In this paper, we made a further step of synthesizing HA composite bio-coating on AZ91 alloy by a single technique of MAO, which was realized by optimizing the basic electrolyte system ingredients and additives. The microstructure and corrosion resistance of the obtained coating were primarily studied. As expected, desirable results were obtained finally.

2. Experimental details

2.1 Synthesis of coating

AZ91 alloy, whose chemical compositions is listed in table 1, was cut into dimension of 15 mm pie with a thickness of 0.5 mm. The sample was grounded and polished and served as anode; a stainless steel plate served as the cathode. The basic electrolyte system was an optimized Na_3PO_4-Na_2SiO_3-NaOH (8-15g/L Na_2SiO_3, 1-3 g/L Na_3PO_4,1-2 g/L NaOH) electrolyte system containing proper concentration of HA powders. For comparison, electrolytes with and without HA powders were both used to studied the microstructure of the coatings. A little glycerinum and surfactant OP-10 were also used to moderate the MAO process and electrolyte. During MAO treatment, the current density was kept constant at 10A/dm^2; the pulse frequency was kept 3000 Hz; duty ratio was 50% and the treating time was 10 min.

2.2 Characterization and corrosion resistance tests

The phase composition of the coating was detected by XRD （D8 ADVANCE, Germany). The surface morphologies of the coating were observed by SEM（S-3400N, Hitachi, Japan).

Table 1 chemical compositions of AZ91 alloy

Element	Al	Zn	Mn	Si	Cu	Ni	Fe
content	8.3-9.7	0.35-1.0	0.15-0.50	<0.01	<0.03	<0.002	<0.005

3. Results and discussion

3.1 Chemical composition

Fig. 1 is the XRD spectra of the coating. The XRD spectra reveal that without adding HA powders in the electrolyte, the coating mainly contains MgO, and some $Mg_3(PO4)_2$ and Mg_2SiO_4. It seems that slight peaks of Mg are also found. The electrolyte used here is Na_3PO_4-Na_2SiO_3 system, so $Mg_3(PO_4)_2$ and $MgSiO_4$ are easily be formed during MAO treating. Similar results are also found by other researchers [10], but the phases also show difference when the parameters are not completely the same. When HA powders are added into the electrolyte, HA is obtained, which is the dominate phase. Some MgO and Mg_2SiO_4 are also found, but $Mg_3(PO_4)_2$ nearly disappears.

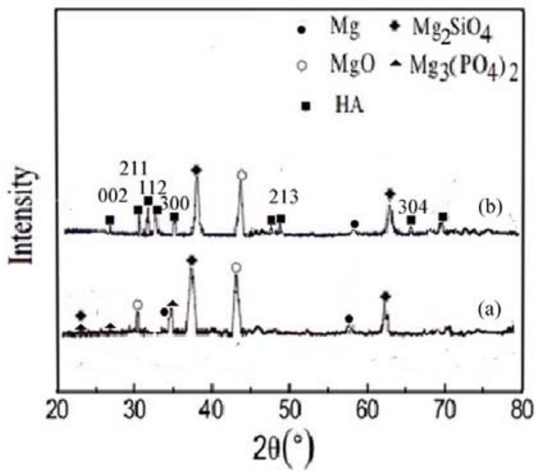

Fig. 1. XRD spectra HA coating (a) and non-HA composite coating (b)

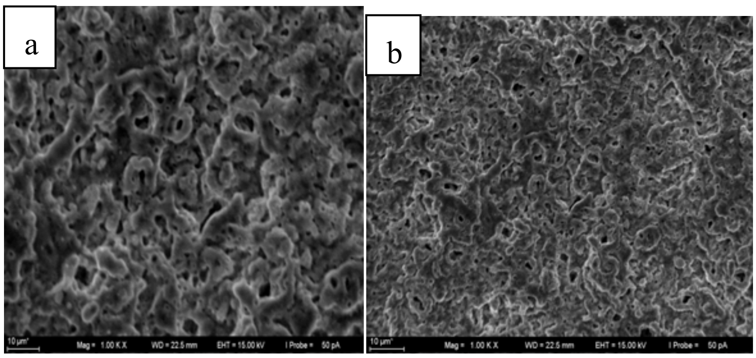

Fig 2. SEM photo of non-HA coating (a) and HA composite coating (b)

3.2 Surface morphologies

Fig. 2 is the SEM image of samples, which reveals that both the coating surface is porous and coarse. This is the typical morphology of MAO coating. The pores are the residual discharge channels formed during the discharge reaction in MAO. But there are also some differences. The pores on non-HA coating surface are a little bigger. The average diameters are about 5-6μm, and 2-3μm on non-HA coating and HA coating, respectively. For implantation metal materials, porous surface in this scale will be helpful for adsorption and growth of cells. In addition, it can also been from SEM photos that there are fewer micro cracks on HA coating surface than non-HA coating surface. As a whole, The HA coating is more uniform and even with smaller pores on the surface.

4. Conclusion

HA composite bio-coating was synthesized on AZ91 medical magnesium by one step of a single MAO technique. The dominated phase of the coating was HA accompanying with some MgO and $MgSiO_4$ crystals phases. The coating showed typical porous morphologies surface of MAO with average pore diameter 2-3μm.

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