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Effect of Adding SiO_2-Al_2O_3 Sol into Anodizing Bath on Corrosion Resistance of Oxidation Film on Magnesium Alloy

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Abstract

Due to the widely use in automobile and construction field, AZ91D magnesium alloy need to be protected more effectively for its high chemical activity. In this paper, three kinds of films were formed on magnesium alloy. The first kind of film, named as anodic oxidation film, was prepared by anodic oxidation in the alkaline solution. The processes for preparing the second kind of film, named as multiple film, involved coating sol-gel on the samples and heat-treating before anodic oxidation. The third kind of film was prepared by anodic oxidation in the alkaline oxidation solution containning 5% (vol) SiO_2-Al_2O_3 sol, named as modified oxidation film. The corrosion resistance of the three different films was investigated. The results showed that the modified oxidation film had the highest corrosion resistance due to the largest thickness and most dense surface morphology. Sol was discussed to react during the film forming process, which leaded to the difference between modified oxidation film and anodic oxidation film.

Introduction

Magnesium alloy has been widely used due to its advantages such as low density, high strength-to-density ratio, nice electromagnetic shielding, etc[1-2]. However, magnesium alloy is very active and its oxidation film formed in air is very loose and porous[3], therefore, magnesium alloy is very apt to be corroded in corrosive environment.

In order to protect magnesium alloy, many methods have been used, such as chemical conversion[4-6], anodic oxidation[7-11], micro-arc oxidation[12-13], electroless plating[14], plating[15-16] and so on. Among these methods, anodic oxidation has been studied by many researchers and has made some progress. However, the forming oxidation film on magnesium alloy has many pores[17-18], which will lead to the film easy to be corroded after some certain time.

In recent years, sol-gel dip coating method has been used to increase corrosion resistance of magnesium alloy, aluminum alloy and nickel plating on carbon steel[18-20], and sol plays a role in sealing holes on surface coating.

Generally speaking, sol-gel film is very thin and several dip coating cycles are needed to obain expected thickness. In order to get excellent film through more simple process, sol was added into anodizing bath and was expected to plays a positive role in anodizing process.

In our previous study, electrochemical oxidation characteristic and growth characterization of anodic film on AZ91D magnesium alloy under the effect of silica sol[8,9,17] were investigated, and the effect of sol composition on anodic oxidation film on magnesium alloys[21] was studied. The results showed that the addition of silica sol in Na_2SiO_3 solution could decrease the surface energy and the conductivity of the solution, and could increase the anodic film thickness and improve the uniformity of the anodic film on AZ91D magnesium alloy.

In this paper, modified oxidation film was prepared by adding sol into alkaline oxidation solution, and its corrosion resistance was investigated in comparison with multiple film and anodic oxidation film. The purpose is to form a more protective film on magnesium alloy surface using more simple process.

Experimental Procedure

(1) Materials

The raw material was AZ91D molten magnesium alloy, and samples were cut into the size of 40mmx25mmx2mm. The chemical composition(mass percentage) includes: 8.5 ~ 9.5 % Al, 0.17 ~ 0.4% Mn, 0.45 ~ 1.90% Zn, 0.05 % Si, 0.25% Cu, 0.001 % Ni, 0.004% Fe and Mg is the balance.

(2) Preparation of films on magnesium alloy

Before the films were prepared, the magnesium alloy samples were polished using sand paper and then degreased in acetone in an ultrasonic device.

The prepared sol was SiO_2-Al_2O_3 composite product (volume rate is 70:30). The reactant used to prepare sol was methyltriethoxysilane and aluminum iso-propoxide. The solvent was absolute ethanol and acetone. The reaction time was 6~8 hours, and the temperature was 60~90°C. The power supply for anodic oxidation process was an autotransformer (voltage and current output are 0~250V and 0~4.0A, respectively).

Three kinds of films were made in this paper.

The process for preparing the first kind of film was anodic oxidation in the solution containing 150g/L NaOH, 35 g/L Na_3PO_4 and 35 g/L NaF. The anodic oxidation voltage was 65V and the duration was 30 min. This kind of film is named as "anodic oxidation film".

The second kind of film was made by coating sol on the samples and heat-treating before anodic oxidation. The parameters for anodic oxidation process were the same to that of anodic oxidation film. This kind of film is named as "multiple film".

The third kind of film was prepared by anodic oxidation, the oxidation solution was prepared by adding 5%(vol) SiO_2-Al_2O_3 sol into the anodic oxidation solution. The anodic oxidation voltage and duration were the same to that of anodic oxidation film. And this kind of film is named as "modified oxidation film".

(3) The device and methods for measurement

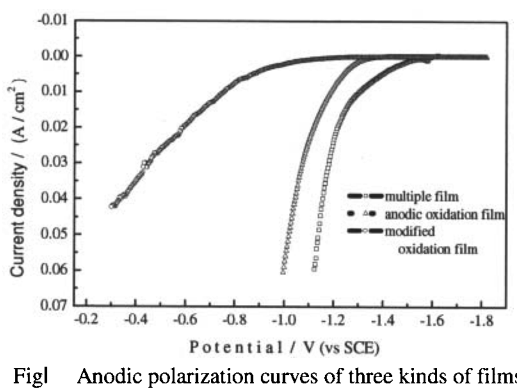
The thickness of the films was measured by E110B whirlpool testing instrument made by FISCHER company in west Germany. The surface morphology was analyzed by S-530 scanning electron microscope and Hirox KH-3000 digital microscope. The composition of films was examined by Link ISIS instrument made in Japan.

The corrosion resistance was studied in 5 wt% sodium chloride solution, and the techniques used included salt-solution dipping, anodic polarization curve measurement and galvanic corrosion test. The anodic polarization curves were recorded on a CHI604A electrochemical analyzer. In salt-solution dipping test, the anti-corrosion time was defined as the time of the first corrosion spot to be found. The galvanic corrosion test was done on ZRA-1 galvanic corrosion instrument. Galvanic corrosion current was examined relative to LY12CZ aluminum alloy.

Results and discussion

(1) Corrosion resistance of modified oxidation film

As shown in figureⅠ, the modified oxidation film has much higher corrosion resistance than that of anodic oxidation film and multiple film. FigureⅠ shows that the potential of the samples coated with modified oxidation film is more positive than those of anodic oxidation film and multiple film at the same current value, and the largest potential difference for the examined value is about 850mV, which indicates that the samples treated with modified oxidation film have small tendency to be corroded than the other two kinds of films in the same condition.



FigⅠ Anodic polarization curves of three kinds of films

The result of salt-solution dipping test is presented in tableⅠ, which shows the corrosion resistance comparison of the three kinds of films. It can be seen that compared with anodic oxidation film and multiple film, modified oxidation film has the lest corrosion pit number after dipped in the 5wt% NaCl solution for 12h in the same area, and can stand the longest time before being corroded. In other word, it owns the highest corrosion resistance.

TableⅠ Corrosion Resistance of the Three Kinds of Films

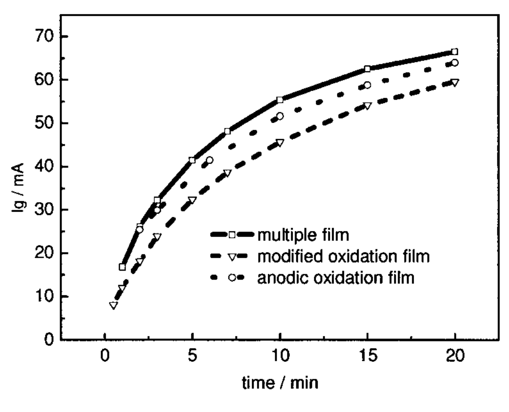
Films	Anodic oxidation film	Multiple film	Modified oxidation film
Corrosion pit number (/10cm^2)	8~10	9~11	1~2
Time for pit emerging (h)	4~6	3~5	12~14

FigureⅡ is the result of galvanic corrosion test for three kinds of films. It can be seen that in the same corrosive condition, modified oxidation film has the lowest current value in comparision with the other two kinds of films. From figureⅢ, there are fewer corrosion pits on the surface of modified oxidation film than that of anodic oxidation film, which further comfirms the results in figureⅠ and Ⅱ.

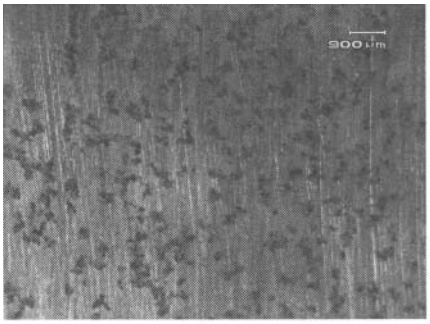
From the three kinds of corrosion test, the same conclusion can be achieved that the modified oxidation film has the highest corrosion resistance.

(2) Discussion

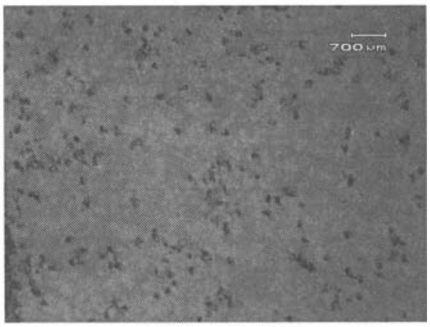
As shown in tableⅡ, the modified oxidation film has the largest thickness in comparision with anodic oxidation film and multiple film. And the thickness of multiple film is a little smaller than that of anodic oxidation film. FigureⅣ shows the cross section morphology of modified oxidation film, which matches well with the thickness of this film in tableⅡ.



FigⅡ Corrosion current trends for three kinds of films



a Anodic oxidation film

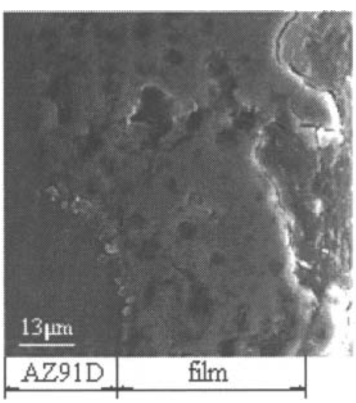


b Modified oxidation film

FigIII Micro morphologies of magnesium alloys samples after galvanic corrosion test with aluminum alloy for 15min

TableII Thickness of the Three Kinds of Films

Film	Anodic oxidation film	Multiple film	Modified oxidation film
Thickness(μm)	4.0~4.9	3.4~4.0	29.8~36.2



FigIV Cross section morphology of modified oxidation film

The multiple film is thinner, perhaps because there is a breaking and solving effect on the formed sol-gel film on the surface during the anodic oxidation process. Because the sol film is rather thin, it can be equally broken down when the applied voltage is high enough for the following anodic oxidation process, then sol would go into the oxidation solution. As a result, the composition of the multiple film has little difference with that of anodic oxidation film, as shown in tableII . Due to the breaking and solving effect, the anodic oxidation process would be affected, which leads to a slightly thinner film.

After adding 5% (vol) SiO_2-Al_2O_3 sol into anodic oxidation solution, the thickness of oxidation film increased greatly and is much larger than those of anodic oxidation film or multiple film. This may be due to that the sol in the anodic oxidation solution greatly affected the oxidation process, and increased the growing rate of oxidation film. This can be verified in tableIII. It can be seen that Si and Al elements were found in the modified oxidation film, while the Al element content is lower than that of anodic oxidation film or multiple film. The reason is not very clear yet, and will be studied in detail in future work.

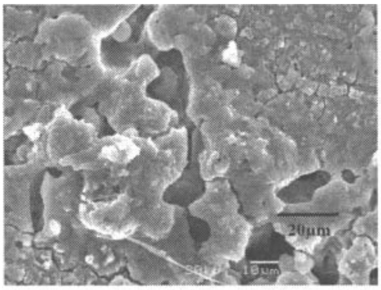
TableIII Element Composition Comparison of the Films (Atom%)

Films	O	Mg	Al	Si
anodic oxidation film	27.1~29.2	65.5~68.5	4.1~5.7	___
multiple film modified	26.8~27.7	65.9~68.3	5.0~6.3	___
oxidation film	29.8~33.6	63.5~64.9	2.3~3.2	1.8~2.4

In the process of anodic oxidation in the solution containing sol, sol transfers to magnesium alloy surface. Thanks to the exothermic action of sparks discharging, the sol network is destroyed. The electriferous groups such as $:\dot{Si}:$, $:\dot{Al}\cdot$, $:Si-R$(alkyl), $:Al-R$(alkyl), $:\dot{Si}-O$, $:Al-O$ will form and adsorb on the surface, which participate in the oxidation reaction and forming film, and hence SiO_2 and Al_2O_3 formed. These reactions will increase the growth rate of oxidation film on magnesium alloy, so there is an obvious increase in film thickness. So the film can act as barrier effect and increase corrosion resistance of modified oxidation film. Although the comparision experiments have not been done with the addition of inorganic salt, the effect of sol on forming modified oxidation film is obvious.

Comparing the morphology of modified oxidation film(figureV c) with those of anodic oxidation film(figureV a) and multiple film(figureV b), it can be seen that there are some relatively big holes and some holes connect with each other on the anodic oxidation film and multiple film. These holes will obviously reduce the corrosion resistance of magnesium alloy. In comparision with the anodic oxidation film and multiple film, the modified oxidation film is uniform and dense and no big holes on the film are observed, which can effectively increase the corrosion resistance of oxidation film.

With respect to anodic oxidation process, a common viewpoint is that at the initial stage of oxidation, when voltage is higher than the broken voltage of the oxidation film formed in air, sparkle discharging phenomenon would appear. Since the instantaneous temperature induced from sparkle discharging is very high, magnesium and other alloy composition would be partially melted and then oxidation film would be formed under the cooling effect of solution. As oxidation duration prolongs, voltage to break the sample surface film persistently increased, and the repeating break of formed film would lead to the increase in film thickness, and thus oxidation process could go on. A great deal of heat from sparkle discharging was absorbed by solution, and metal oxide formed on sample surface was cooled, which leads to the shrinkage of formed film and hence porous morphology of anodic oxidation film was obtained.



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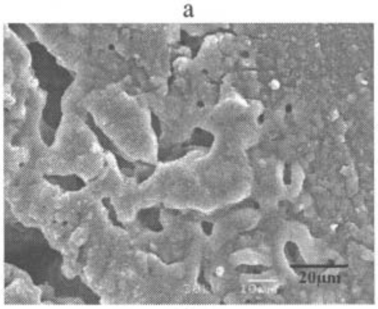

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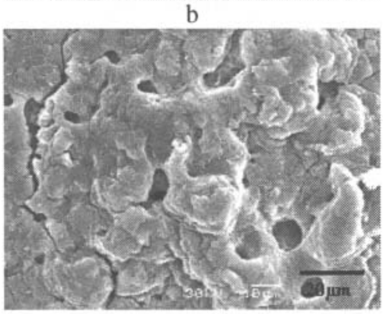

c

FigV Micro morphologies of the three kinds of films

The effect of sol on the thickness and density of the oxidation film may be explained as follows. The sol in anodic oxidation solution will decrease the conductivity of solution, as reported in reference 17. At the early stage of anodic oxidation, the spark discharging voltage increased, higher than that in anodic oxidation solution, then the growth rate of oxidation film increased and the rate of holes in the film also increased. When anodic oxidation went on, SiO_2-Al_2O_3 sol in the anodizing solution reacted on the interface of anodic oxidation film, and some SiO_2-Al_2O_3 sol composition entered into the film. So the film was more dense and there were fewer big holes. With oxidation duration increasing, the anodic oxidation process continued, and due to sol composition act on the interface of the film or sealed some defaults, the film growed gradually and the thickness of the film increased. The more dense and uniform modified oxidation film will get the better corrosion resistance than anodic oxidation film and multiple film. And from figureIV, there are no penetrable holes in the film, this denser and thicker film would increase the corrosion resistance of magnesium alloy.

Conclusion

(1) After adding SiO_2-Al_2O_3 sol into anodizing bath, modified oxidation film has the largest thickness of about 34μm and the highest corrosion resistance relative to anodic oxidation film and multiple film. In the 5wt% NaCl solution, time for pits emerging of modified oxidation film was about three times longer than that of anodic oxidation film.

(2) The modified oxidation film had the largest thickness, was the most dense and had the least pinholes on the surface among the three kinds of films, and no penetrable holes were observed from the cross section morphology. These were the reasons for the highest corrosion resistance.

(3) Sol played an important role in film forming process, some electriferous groups were formed under the condition of high temperature and electric intensity. These groups adsorbed on the sample surface and reacted to form film. This process leaded to a more thick and dense modified oxidation film in comparision with anodic oxidation film.

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