Surface & Coatings Technology 283 (2015) 281–285

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Characterization and formation mechanism of grey micro-arc oxidation coatings on magnesium alloy

Wei Yang [a,*], Jianli Wang [a], Dapeng Xu [a], Jinhua Li [a], Tao Chen [b,*]

[a] School of Materials Science and Chemical Engineering, Xi'an Technological University, Xi'an 710032, China
[b] Jiangsu Provincial Key Laboratory of Advanced Robotics & Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou 215123, China

ARTICLE INFO

Article history:
Received 21 July 2015
Revised 25 October 2015
Accepted in revised form 27 October 2015
Available online 29 October 2015

Keywords:
Magnesium alloy
Grey micro-arc oxidation coating
Mechanism
Properties

ABSTRACT

Grey micro-arc oxidation (MAO) coatings were prepared on AZ80 Mg alloy using DC electrical source in the electrolytes with different addition of K_2TiF_6. Microstructure and properties of the coatings were comparatively studied by SEM, XPS, Nano-indentation and electrochemical experiment. The results showed that with the increase of K_2TiF_6 into the developing electrolyte, the size and distribution of micropores on the grey coatings were obviously improved. The roughness decreased and the density of coating surface increased. The grey MAO coatings mainly contained MgO and MgF_2 phases. Ti element was only found on the coating after surface etching. The grey colour of MAO coatings was caused by the interaction of MgF_2 phase and Ti element on the coating surface, which was different from the traditional preparation of MAO coatings. The nano-hardness and corrosion resistance of these grey MAO coatings could be enhanced as adding 10 g/L K_2TiF_6 into the base solution. Furthermore, the reason of corrosion resistance variance of this grey MAO coating was discussed.

1. Introduction

Magnesium has great application potential in computer, communication and consumer electronic (3C products), such as mobile phone shell, laptop shell and so on. However, it is severely limited in the wide application in the field of 3C products due to its active chemical characteristics and low hardness [1]. Surface modification technology is an effective way to improve the performance of magnesium alloy and micro-arc oxidation (MAO) has shown great potentials. Currently, a large number of institutions have carried out the research in this area [2–5]. However, only the preparation of white MAO coating has been successfully developed on magnesium alloy. It is far to meet the colour diversity expectation in the market of 3C products [6]. Therefore, to develop MAO coatings with various colours and reveal the formation mechanism could be helpful to expand its colour system.

It has been found that the MAO coatings have different colours in different electrolytes and the colour of MAO coating depends on their compositions. For example, adding Cu^{2+}, Co^{2+}, Ni^{2+} or Cr^{3+} into the solutions is beneficial for the formation of coatings with different chemical compositions in red, green, blue or grey colours due to their colourful ions and compounds [7–8]. Some literature have reported that, the blue MAO coating on Mg alloy has been prepared due to the formation of cobalt oxide by adding a certain Co salt into the base electrolyte containing NaOH and Na_2SiO_3. The formation mechanism of this blue coating is similar with the back coating reported by Li [9–10].

In this paper, we added different amount of K_2TiF_6 into the KOH and Na_2SiO_3 base solution for the preparation of grey MAO coatings. The theoretical basis for this grey MAO coating preparation was that, as adding K_2TiF_6 into the base electrolyte, MgF_2 phase could be formed in the MAO coating. It is known that the solid powder of MgF_2 is white, but the MgF_2 film may display different colours. Furthermore, the colour could be also affected by the existence of Ti transition element in the MAO coating. Thus, the grey MAO coating might be prepared by interacting of MgF_2 phase and Ti element in the coatings. The properties were characterized and the formation mechanism was illustrated afterwards. It was found that the formation mechanism of this grey MAO coating was different with the traditional preparation of colouring MAO coatings depending on the colour of metal oxide. So, this work could provide a new method of forming MAO coating in colours independent of the oxide colour in solute elements from the electrolyte.

2. Experimental

MAO60 micro-arc oxidation equipment (made by Xi'an University of Technology, China) was used to prepare the MAO coatings on magnesium surface. The magnesium alloy specimen and the stainless steel plate were used as anode and cathode, respectively. The AZ80 Mg alloy substrate (mass fraction: Al 7.6–8.4%, Mn 0.15–0.4%, Zn 0.35–0.65%, Si <0.01, Cu < 0.005, Ni < 0.003, Fe < 0.01, Mg balance) discs (Φ20 mm × 5 mm) were mechanically polished with 600 #, 1000 #, and 1500 # abrasive papers, respectively. The constant voltage mode

---

* Corresponding authors.
E-mail addresses: yangwei_smx@163.com (W. Yang), cht22@sina.com (T. Chen).

http://dx.doi.org/10.1016/j.surfcoat.2015.10.065
0257-8972/

was selected for MAO treatment and 350 V was predefined. The MAO parameters were as follows: frequency 400 Hz, duty cycle 10% and time 15 min. The solution used for MAO was composed of an aqueous solution of potassium hydroxide (KOH, 8 g/L) and sodium silicate ($Na_2SiO_3 \cdot 9H_2O$, 15 g/L). Fluoride potassium titanate (K_2TiF_6) with different concentration of 0 g/L (instead of KF), 3.5 g/L, 5.0 g/L and 10 g/L was added into the solutions for the grey MAO coating preparation. The solution temperature was kept below 30 °C. As a result, the four MAO coatings with the thickness of about 10 μm were prepared. As shown in Fig. 1, it was found that the MAO coating was white without K_2TiF_6, and the grey coatings were prepared with the increase of K_2TiF_6. Also the coating colours were characterized by a colourimetry test, using the CM-700d spectrocolourimeter, shown in Table 1. It was obtained that the average L values were 88.86, 60.54, 54.50 and 44.25 with the different addition of K_2TiF_6 0 g/L, 3.5 g/L, 5 g/L and 10 g/L, respectively. It is known that the average L values are used to characterize the degree of the grey MAO colour and the low L values always come with dark colour. Interestingly, it was found that the average b value was −8.62 with the addition of K_2TiF_6 10 g/L, which indicated that this coating tended to become blue with the increase of K_2TiF_6.

The thickness of the coating was measured using the TT230 eddy-current coating-thickness measurement gauge. The surface morphologies was observed using atomic force microscopy (AFM), S-4800 field emission scanning electron microscope (SEM). An energy dispersive spectroscope (EDS) attachment operated at an acceleration potential of 20 kV was used for the chemical analysis. An AXIS UTLTRADLD X-ray photoelectron spectroscopy (XPS) with Al (mono) Kα irradiation at pass energy of 160 eV was used to characterize the chemical bonds of the coatings. The binding energies were referenced to the C 1s line at 285.0 eV. Microhardness measurements were conducted by G200 Nano-indentation using the nano-indentation technique in a continuous stiffness measurement (CSM) mode. The hardness of the coatings on the AZ80 magnesium alloy substrates was chosen in the depth around 1/10th of the coating thickness to minimize the substrate contribution. The corrosion resistance of the MAO coatings formed in the electrolytes with different concentrations of K_2TiF_6 was tested by Zahner IM6e electrochemical system in 3.5% NaCl solution under room temperature using electrochemical potentiodynamic polarization. During the process of test, the specimen with the surface area of 0.785 cm^2 exposed in the solution was the working electrode, the platinum sheet was auxiliary electrode, and the saturated calomel electrode was the reference electrode. The scanning speed was 1 mV/s.

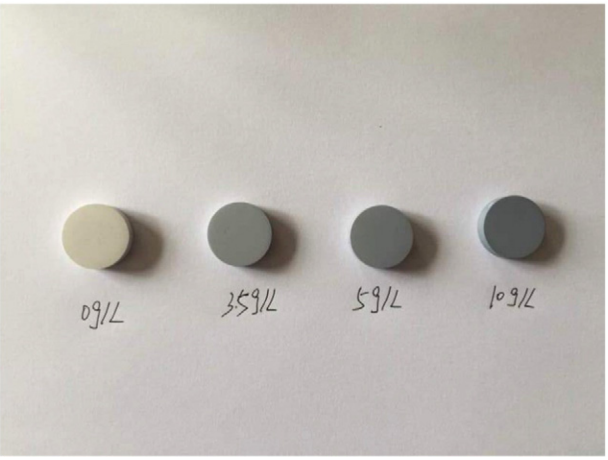

Fig. 1. Macrograph of AZ 80 Mg alloy treated by MAO in the electrolytes with different K_2TiF_6 addition.

Table 1
L, a and b values of four MAO coatings prepared in the electrolytes with different K_2TiF_6 addition.

Coating	L value	a value	b value
MAO − 0 g/L	88.86	0.08	0.12
MAO − 3.5 g/L	60.54	−0.88	1.50
MAO − 5 g/L	54.50	−0.35	−2.76
MAO − 10 g/L	44.25	−0.15	−8.62

3. Results and discussion

Fig. 2 shows the surface morphologies of the MAO coatings with different addition of K_2TiF_6. It was noted that some islands (region I) and many micropores (diameter ranging from 1 μm to 6 μm) were found on the surface of oxide coating (Fig. 2(a)), which showed the highest roughness value of about 350 nm. With the increase of K_2TiF_6 into the electrolytes, the surface roughness value decreased linear, shown in Fig. 3. When the concentration of K_2TiF_6 was increased to 3.5 g/L, the islands became almost invisible on the surface of oxide coating and the pore distribution became uniform with smaller size (diameter ranging from 1 μm to 4 μm) (Fig. 2(b)). When the concentration of K_2TiF_6 was increased to 5.0 g/L, the islands became visible on the coating surface with significantly decreased pores in number and size (Fig. 2(c)). As a result, the surface roughness was further reduced to about 250 nm. The surface of the MAO coating formed with 10 g/L K_2TiF_6 showed smooth. The distribution of pores became uniform and the size of the pores was further decreased (Fig. 2(d)). The surface roughness value was only about 225 nm, which was beneficial for improved mechanical property and corrosion resistance.

The EDS analysis of the MAO coatings with different K_2TiF_6 addition into the electrolytes was shown in Table 2. It was obtained that the four MAO coatings all mainly contained the elements of Mg and O. Comparing with the MAO coating without the addition of K_2TiF_6, Ti element was found with more F element in the grey MAO coatings with addition of K_2TiF_6. So it could be preliminarily deduced that the reason of obtaining the grey coatings was strongly affected by the F and Ti elements in the coatings and the formation mechanism would be further elaborated by the XPS analysis. It was also found that with the increase of K_2TiF_6 into the electrolytes, the grey colour of the MAO coatings became obvious although the contents of F and Ti elements in the grey MAO coatings changed slightly. From Fig. 2, it was seen that the surface morphologies of the grey coatings dramatically changed. Since the colour of the coatings was mainly affected by the light scattering, it could be speculated that, K_2TiF_6 in the solutions resulted in the surface microstructure change, which made the MAO coating show the grey colour.

In order to further reveal the formation mechanism of the grey MAO coatings, the XPS analysis has been employed. XPS survey spectra of the coatings formed without or with the addition of K_2TiF_6 is shown in Fig. 4. The Mg and O elements were found in the two coatings. Comparing with the MAO coating formed without the addition of K_2TiF_6, the F1s peak of the grey coating with the addition of K_2TiF_6 had been found and the atomic percentage of the F element in this coating was 8.94%, which was approximately consistent with the EDS results. However, the Ti2p peak was not found in the grey MAO coating and the atomic percentage of the Ti element in this coating was only 0.68 at.%, which did not accord with the EDS results (2.29 at.%). It is known that XPS is a more sophisticated characterization tool than EDS. The reason might be that the XPS results were obtained after surface etching, which indicated that the Ti element was mainly adsorbed on the grey coating surface and F element was involved in the formation process of the grey MAO coating.

Typical O1s and F1s high-resolution XPS spectrum of the MAO coatings with or without addition of K_2TiF_6 after Ar sputtering was shown in Fig. 5. The O1s peak of 529.8 eV indicated the existence of MgO, shown in Fig. 5(a) and (b). So it could be obtained that the titanium oxide was not formed. The F1s peak was not found in the MAO coating formed