

*Short Communication*

## **Improving the Anti-Corrosion Ability of Anodization Film of AZ31B Magnesium Alloy by Addition of $\text{NH}_4\text{VO}_3$ in the Electrolyte**

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AZ31B magnesium alloy was anodized in an alkaline electrolyte containing sodium borate, sodium silicate and sodium citrate. Ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) was used as an additive to improve the anti-corrosion ability of anodization film. The anodization film was characterized by X-ray diffraction and scanning electron microscopy. The anti-corrosion ability of the film was evaluated by electrochemical impedance spectrum. The results show that  $\text{VO}_3^-$  ions react with  $\text{Mg}^{2+}$  to form yellow magnesium vandate. Magnesium oxide in anodization film is restrained by  $\text{VO}_3^-$ . The pores on the film decreases and the cracks can be filled by the addition of  $\text{NH}_4\text{VO}_3$ . The film also becomes smoother and compacter which increase the resistance of film and charge transfer resistance of the corrosion process of the AZ31B magnesium alloy. The anti-corrosion ability of the anodization film is obviously enhanced.

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**Keywords:** Magnesium alloy; anodization film; anti-corrosion; ammonium metavanadate

### **1. INTRODUCTION**

Magnesium alloys are promising structure materials because of its special properties, such as small density, great strength, great stability in size, good casting property, etc. These properties are important in the manufacture of aircraft and automotive industries. Reducing the consumption of fuel and emission of waste gas to protect the environment are urgent in transportation industry. It is recognized as a better choice to reduce the mass of transportation tools by using light structure materials. Magnesium alloys can meet this requirement [1-4]. However, magnesium alloys are active and prone to be corroded, which limits their usage as structure materials [5-7]. So it is necessary to

enhance the anti-corrosion ability of magnesium alloys for their actual applications. Among different methods, surface treatments are commonly employed to deal with this limitation. Electrochemical anodization is an effective surface treatment technique for magnesium alloys [8-12]. The most successful anodization process of magnesium alloys is HAE [13] and DOW17 [14]. The two methods are all superior in both corrosion and abrasion resistance. The shortcoming of the two technologies is that they contain chromate or fluoride and are harmful to environment. So developing a process of chromium-free or/and fluoride-free electrolyte is necessary to the anodization of magnesium alloys. Among these anodization electrolytes, environmental friendly silicate and borate containing system have absorbed researchers' attentions [15-17].

In this study, AZ31B magnesium alloy was anodized in an environmental friendly alkaline electrolyte containing sodium borate ( $\text{Na}_2\text{B}_4\text{O}_7$ ), sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) and sodium citrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ ). The ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) was also added into the electrolyte to investigate its influence on the anodization film.

## 2. EXPERIMENTAL

AZ31B magnesium alloy was used as the test material, which contains 3 wt% Al and 1 wt% Zn. A disk-shaped specimen with a diameter of 20 mm and a thickness of 8 mm was cut from an alloy rod. The specimen was connected with a copper conductive wire on one side and mounded in epoxy resin with another side exposed as working surface. Prior to anodization, the working surface was orderly polished with SiC emery paper from #200, #400, #600, #800, #1000 to #1200, and rinsed with de-ioned water and acetone. The basic electrolyte consists of 50 g/L of NaOH, 40 g/L of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , 60 g/L of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , 20g /L of  $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ . Different concentration of  $\text{NH}_4\text{VO}_3$  was added into the electrolyte to investigate its effect on the anodization film. The anodization was carried out at a current density of  $10 \text{ mA} \cdot \text{cm}^{-2}$  for 15 minutes at 298 K with continuous stirring. A 40 mm×100 mm stainless steel was used as cathode in the anodization.

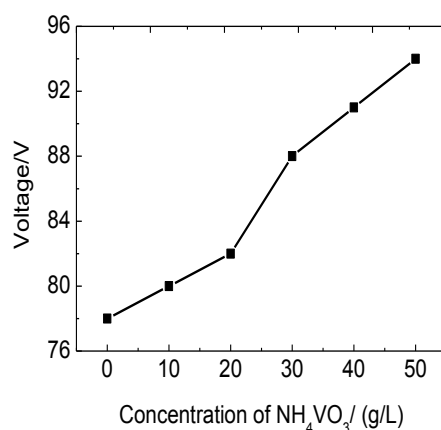
The surface morphology of the anodization film was examined by scanning electron microscopy (SEM) (VEGA 3 EasyProbe, TESCAN). X-ray diffraction (XRD) pattern was acquired on a DX-2600 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda=0.15418 \text{ nm}$ ) at 40 kV and 25 mA.

The anti-corrosion performance of the anodization film was characterized by electrochemical impedance spectrum (EIS). EIS was measured using a CHI760E workstation (CH Instruments) at 298 K in 3.5 wt% NaCl solution. The measurement was carried out at the open circuit potential from  $10^5$  Hz to 0.1 Hz with a perturbation voltage of 5 mV. A three-electrode cell was used with a saturated calomel electrode (SCE) as the reference electrode, and a platinum sheet as the counter electrode. The AZ31B magnesium alloy electrode was immersed in NaCl solution for 10 minutes before EIS measurement.

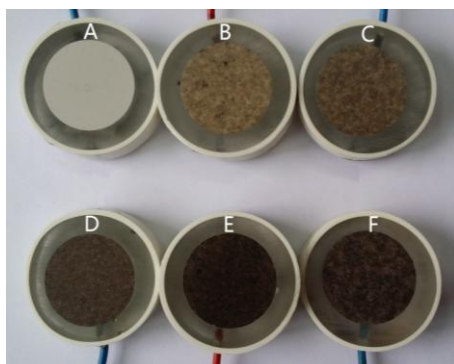
## 3. RESULTS AND DISCUSSION

The concentration of  $\text{NH}_4\text{VO}_3$  in the basic electrolyte is 0 g/L, 10 g/L, 20 g/L, 30 g/L, 40 g/L and 50 g/L, respectively. Upon the electrolyzer was imposed with  $10 \text{ mA} \cdot \text{cm}^{-2}$  current, the anodization

film was immediately formed on the working surface of AZ31B alloy and the resistance of film increased. About initial 30 seconds later, white spark was observed on the working surface, moving over the entire surface. Fig. 1 shows the relation between the spark starting voltage and concentration of  $\text{NH}_4\text{VO}_3$ . The spark starting voltage increases from 78V to 94V by increasing the concentration of  $\text{NH}_4\text{VO}_3$  from 0 g/L to 50 g/L. The result indicates that the  $\text{VO}_3^-$  ions move to the anodic working surface and take part in the formation of film in the anodization process, which can increase the resistance of the film. The participation of  $\text{VO}_3^-$  ions in the anodization process can also be confirmed by the color of anodization film as shown in Fig. 2. The film obtained in the electrolyte without  $\text{NH}_4\text{VO}_3$  is gray. With the addition of  $\text{NH}_4\text{VO}_3$ , the color of film changes to yellow and becomes darker and deeper with increasing the concentration of  $\text{NH}_4\text{VO}_3$ . The changing color is the result that the  $\text{VO}_3^-$  ions react with  $\text{Mg}^{2+}$  ions to form the yellow magnesium vandate ( $\text{Mg}_2\text{V}_2\text{O}_7$ ).



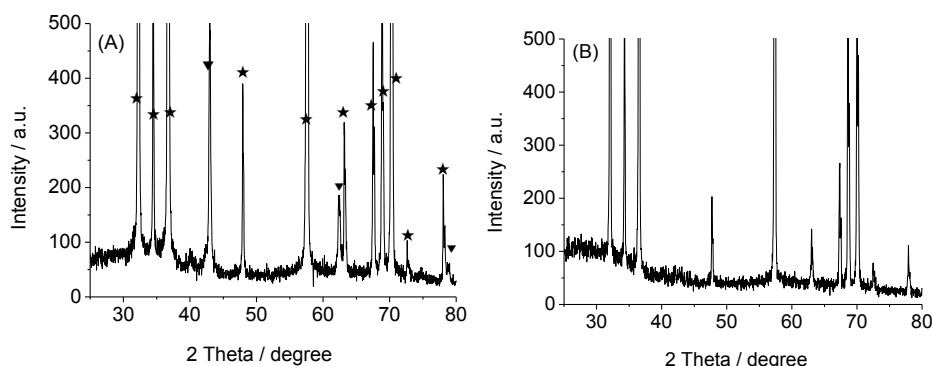
**Figure 1.** Relation between the spark starting voltage and concentration of  $\text{NH}_4\text{VO}_3$



**Figure 2.** Optical images of anodization films obtained in electrolytes containing different concentration of  $\text{NH}_4\text{VO}_3$ , (A) 0 g/L, (B) 10 g/L, (C) 20 g/L, (D) 30 g/L, (E) 40 g/L, (F) 50 g/L.

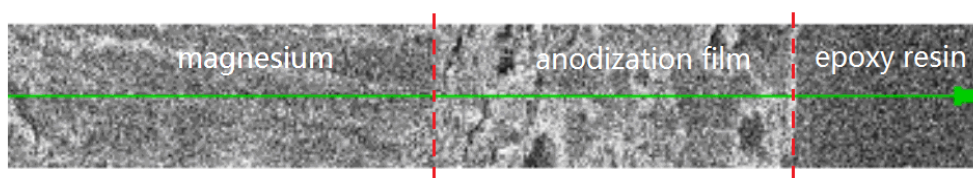
The XRD patterns of anodization films obtained in electrolytes containing 0 g/L and 40 g/L of  $\text{NH}_4\text{VO}_3$  are shown in Fig. 3. Besides the diffraction peaks of metallic magnesium, strong diffraction peaks of  $\text{MgO}$  can be found in the anodization film obtained in the basic electrolyte without  $\text{NH}_4\text{VO}_3$ .

By adding  $\text{NH}_4\text{VO}_3$  into the electrolyte, just the diffraction peaks of metallic magnesium can be found, and the diffraction peak of  $\text{MgO}$  disappears. The result further indicates the  $\text{VO}_3^-$  ions react with  $\text{Mg}^{2+}$  ions to form a part of anodization film and restrain the formation of  $\text{MgO}$ . However, the diffraction peaks of the product, yellow  $\text{Mg}_2\text{V}_2\text{O}_7$ , of  $\text{VO}_3^-$  ions with  $\text{Mg}^{2+}$  ions can not be found in the XRD pattern, too. The possible reason is that the  $\text{Mg}_2\text{V}_2\text{O}_7$  exists as amorphous state in the anodization film.



**Figure 3.** XRD patterns of anodization films obtained in electrolytes containing (A) 0 g/L, (B) 40 g/L of  $\text{NH}_4\text{VO}_3$  (★: Mg, ▼:  $\text{MgO}$ ).

SEM image of cross-section of specimen anodized in the electrolyte containing 40 g/L of  $\text{NH}_4\text{VO}_3$  was shown in Fig. 4. The anodization film closed to the magnesium substrate is loose and porous, and then the film become compact which can well protect the magnesium substrate from corrosion. Table 1 lists content of elements in the anodization film by line analysis on the cross-sections of different specimens. It can be found that the boron atom can not be detected in the film. So the  $\text{B}_4\text{O}_7^{2-}$  ion may not take part in the formation of the anodization film. On the other hand, the  $\text{SiO}_3^{2-}$ ,  $\text{C}_6\text{H}_5\text{O}_7^{3-}$  and  $\text{VO}_3^-$  ions all move to the surface of magnesium alloy substrate and take part in the formation of the anodization film.



**Figure 4.** SEM image of cross-sections of specimen anodized in the electrolyte containing 40 g/L of  $\text{NH}_4\text{VO}_3$

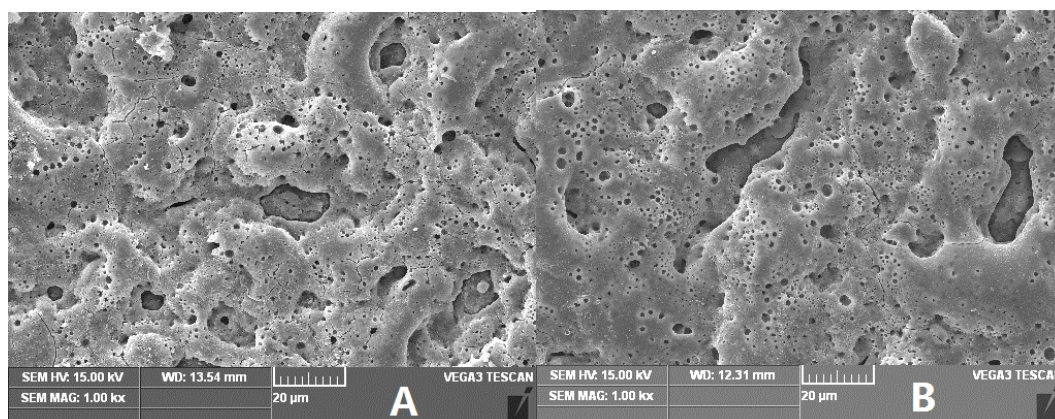
Fig. 5 shows the SEM images of AZ31B alloy surface after anodized in the electrolyte containing various concentrations of  $\text{NH}_4\text{VO}_3$ . Many pores and cracks can be observed on the surface of the specimen anodized in the electrolyte without  $\text{NH}_4\text{VO}_3$ . It suggests the density of film consisted of  $\text{MgO}$  and the  $\text{SiO}_3^{2-}$ ,  $\text{C}_6\text{H}_5\text{O}_7^{3-}$  are greater than the magnesium alloy, which is the source of the

crack appearing. However, by the addition of  $\text{NH}_4\text{VO}_3$ , the amount of the pore decreases and the cracks are filled. The anodization film also becomes smoother. These structures are beneficial to enhance the anti-corrosion performance of the film. A better surface morphology of AZ31B alloy can be obtained at concentrations of 30 g/L to 40 g/L of  $\text{NH}_4\text{VO}_3$ . Then the anodization film becomes rougher and some big pores appear again at a greater concentration of  $\text{NH}_4\text{VO}_3$ .

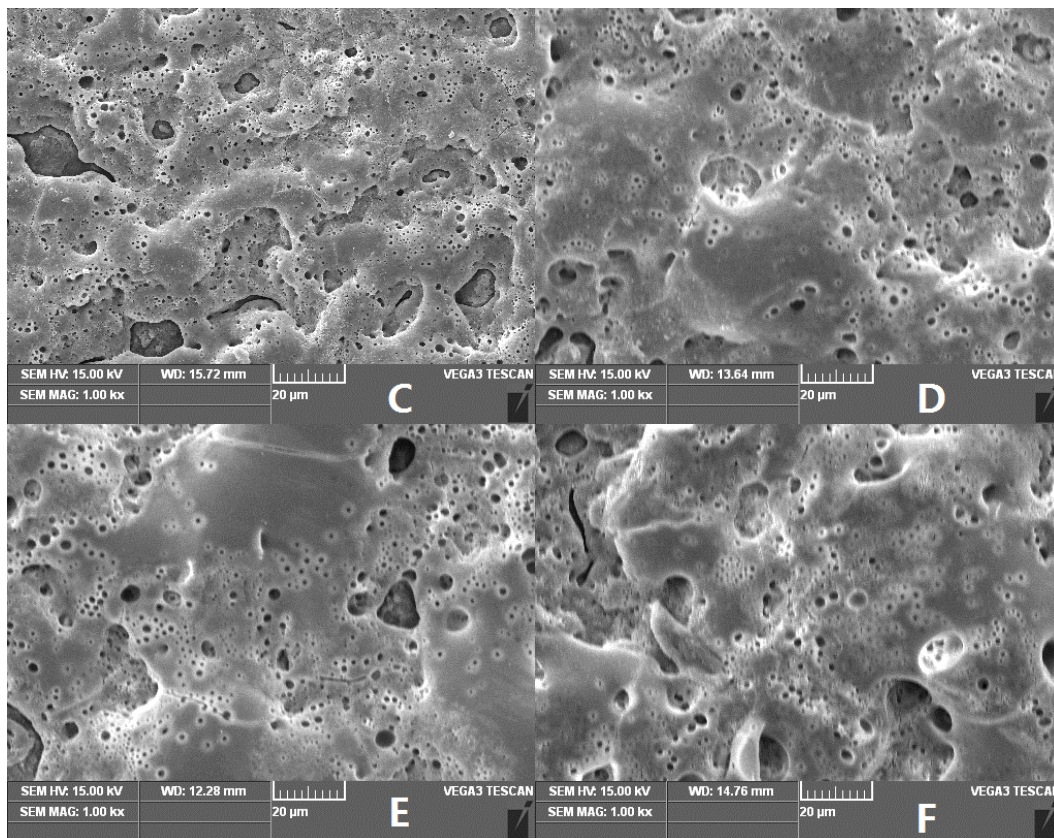
**Table 1.** Atomic percentage of different elements in the anodization film

| Concentration of $\text{NH}_4\text{VO}_3$ / g/L | V/ at % | Si/ at % | O/ at % | Mg/ at % | Na/ at % | C/ at % |
|---|---------|----------|---------|----------|----------|---------|
| 10  | 3.86    | 6.95     | 42.36   | 27.81    | 3.02     | 16      |
| 20  | 5.75    | 7.84     | 43.56   | 25.42    | 3.32     | 14.11   |
| 30  | 7.76    | 7.53     | 44.89   | 22.84    | 4.37     | 12.61   |
| 40  | 10.93   | 7.53     | 44.04   | 20.21    | 5.07     | 12.22   |
| 50  | 15.17   | 7.24     | 44.43   | 17.09    | 4.68     | 11.39   |

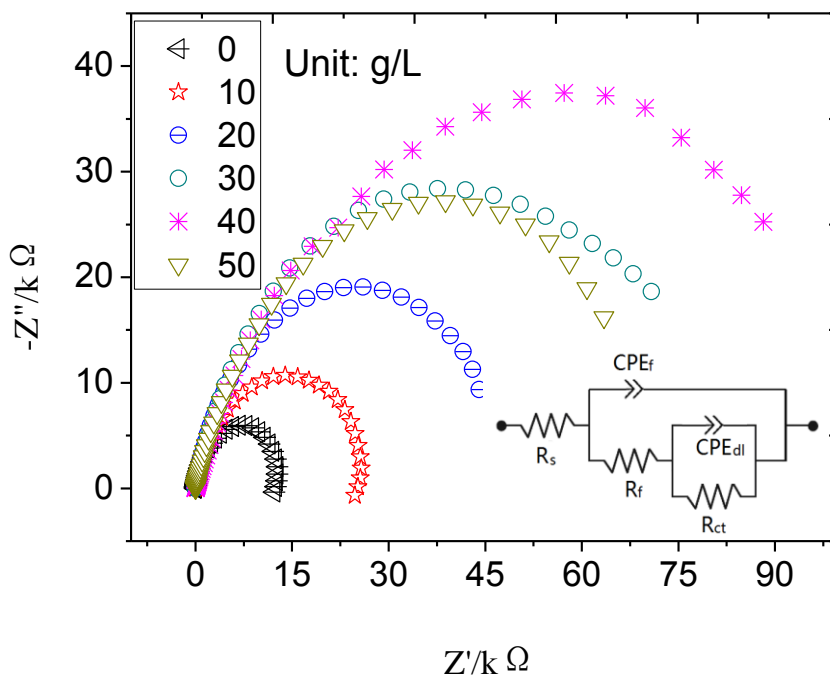
The anti-corrosion ability of the anodization film on AZ31B magnesium alloy was characterized by the EIS technique as shown in Fig. 6. The Nyquist plots of all the tests consist of one semi-circle capacitive loops. The semi-circle can be modeled by a typical equivalent circuit of porous films with five elements  $R_s$ ,  $R_f$ ,  $\text{CPE}_f$ ,  $R_{ct}$  and  $\text{CPE}_{dl}$  [3,18-21] by ZsimDemo software. Herein,  $R_s$  represents the solution resistance;  $R_f$  represents the resistance of anodization film; the  $\text{CPE}_f$  is related to the capacitance of anodization film.  $R_f$  and  $\text{CPE}_f$  reflect the properties of the anodization film. The double layer capacitance ( $\text{CPE}_{dl}$ ) models the characteristic of faradic reaction on the substrate interface; the charge transfer resistance ( $R_{ct}$ ) can be referred to the anodic dissolution of  $\text{Mg}$  into  $\text{Mg}^{2+}$ . Larger  $R_f$  indicates the anodization film is compacter, and larger  $R_{ct}$  means the anodic dissolution on the substrate becomes more difficult. Table 2 lists the fitting values of  $R_f$  and  $R_{ct}$ . It can be seen that the values of the two resistance increase by the addition of  $\text{NH}_4\text{VO}_3$  into the basic electrolyte. The values of  $R_f$  and  $R_{ct}$  are largest in the electrolyte containing 40 g/L of  $\text{NH}_4\text{VO}_3$ . Thereby, the anodization film can act as a more effective barrier and effectively protect the AZ31B magnesium alloy from corrosion.







**Figure 5.** SEM images of anodization films obtained in electrolytes containing different concentration of  $\text{NH}_4\text{VO}_3$ , (A) 0 g/L, (B) 10 g/L, (C) 20 g/L, (D) 30 g/L, (E) 40 g/L, (F) 50 g/L



**Figure 6.** Nyquist plots of the anodization films obtained in electrolytes containing different concentration of  $\text{NH}_4\text{VO}_3$  and equivalent circuit (inset)

**Table 2.** EIS fitting results of anodization films obtained in electrolytes containing different concentration of  $\text{NH}_4\text{VO}_3$ 

| Concentration of $\text{NH}_4\text{VO}_3$<br>/ (g/L) | 0     | 10    | 20     | 30     | 40     | 50     |
|--|-------|-------|--------|--------|--------|--------|
| $R_f/(\Omega \text{ cm}^2)$                          | 1873  | 4101  | 3652   | 3529   | 4355   | 4283   |
| $R_{ct}/(10^4 \Omega \text{ cm}^2)$                  | 3.701 | 7.169 | 12.497 | 19.405 | 24.043 | 17.691 |

#### 4. CONCLUSIONS

(1) AZ31B magnesium alloy was anodized in an electrolyte containing  $\text{NH}_4\text{VO}_3$ .  $\text{VO}_3^-$  ions take part in the formation of anodization film, which increases the film resistance and spark starting voltage in the process.

(2) By the addition of  $\text{NH}_4\text{VO}_3$ , the number of pores on the film reduces and the cracks can be filled. The anodization film also becomes smoother and compacter.

(3) From the result of EIS test, the anodization film resistance  $R_f$  and charge transfer resistance  $R_{ct}$  increase by anodizing the AZ31B magnesium alloy in an electrolyte containing  $\text{NH}_4\text{VO}_3$ . The best anti-corrosion of anodization film can be obtained at a concentration of 30-40 g/L of  $\text{NH}_4\text{VO}_3$ .

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