

## Properties of fluoride film and its effect on electroless nickel deposition on magnesium alloys

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**Abstract:** The physical characteristics and microstructure of the fluoride film formed during activation were investigated using SEM, XPS and SAM, and its stability in electroless nickel (EN) bath was analyzed. The effects of the fluoride film on EN deposition were studied additionally. The results show that the fluoride film on magnesium alloys is a kind of porous film composed of  $\text{MgF}_2$  with thickness of 1.6–3.2  $\mu\text{m}$ . The composition of the activation bath and pretreatment of EN processing have influence on the composition of the fluoride film. The fluoride is stable and dissolves little in EN bath; as a result, the fluoride film can protect magnesium substrate from the corrosion of EN bath. The composition of fluoride determines the initial deposition of EN and part of the fluoride film finally exists as inclusion in EN coating.

**Key words:** magnesium alloys; electroless nickel plating; fluoride film

### 1 Introduction

Magnesium and its alloys, with one quarter of the density of steel and only two thirds that of aluminium and specific strength far exceeding either of these two, fulfill the role admirably as an ultra light alloy. Hence, these alloys have obviously become the choice for weight reduction in portable microelectronics, telecommunications, aerospace and automobile applications, etc. Magnesium also has a number of other desirable features, including excellent castability, good machinability and high damping property. A serious limitation for the potential use of magnesium alloys is their susceptibility to corrosion[1]. Therefore, certain surface treatments are needed to protect magnesium alloys, e.g. chromate conversion coating, anodic coating and electroless coating[2]. Compared with the first two treatments, electroless nickel plating (EN) not only offers high corrosion and wear resistance, but also achieves good uniformity with complex objects. It is irreplaceable

when thermal or electrical conductivity and solderability of the surface are needed.

There are two promising methods for EN deposition on magnesium alloys: zinc immersion and direct EN procedures. Compared with the former, direct EN procedure has the advantages of simplicity and suitability for high aluminum content alloys[2–5]. American society for testing and materials (ASTM) has provided a standard for the two procedures. HF acid is commonly used in the activating treatment in EN procedure, and a thin layer of protective fluoride film forms on the magnesium base metal to reduce the oxidation of magnesium and the corrosion of EN plating bath to magnesium. It is obvious that fluoride is not catalytic to the EN bath, nor can it react with nickel ions in the EN bath to form an immersion deposit[6]. However, the microstructure and chemical state of the fluoride film has a great impact on the EN process[7–10]. It's necessary to conduct in-depth study on the characteristics and microstructure of the fluoride film. However, there is so far little report on such subject. DING[11] investigated

the composition and structure of fluoride film formed in different concentrations of HF and found that dense and thin film is obtained when the concentration of HF is high, while osteoporosis and thick fluoride film are obtained when the concentration of HF is low. Ding also proposed the fluoride film formed by  $\text{MgF}_2$  and  $\text{Mg}(\text{OH})_2$  that was composed of hydroxyl  $\text{MgF}_2 \cdot \text{Mg}(\text{OH})_{2-x}\text{F}_x$ . However, no more evidence supports the assumption except XPS. The thickness of the fluoride film has not been measured yet. To further understand the properties of the fluoride film and its influence on the process of EN plating, the thickness of the fluoride film was measured by dissolution method. The chemical state and microstructure of the fluoride film were studied by means of scanning electron microscope (SEM), X-ray photoelectron spectrometer (XPS) and scanning Auger microscope (SAM). The stability of the fluoride film in EN bath was analyzed through theoretical calculation.

## 2 Experimental

AZ91 alloy castings were used as the substrates, the nominal composition of which was Mg-9Al-1Zn. The reason to choose this alloy is that it is the most widely used cast magnesium alloy with high mechanical strength and good castability. Fig.1 shows its original metallograph. Analysis from EDAX and phase diagram shows that the alloyed elements Al and Zn segregate at grain boundaries and an intermetallic compound  $\text{Mg}_{17}\text{Al}_{12}$  ( $\beta$  phase) forms. All samples were pre-treated in alkaline cleaning solution. The alkaline cleaning formulation was 60 g/L NaOH and 10 g/L  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ .

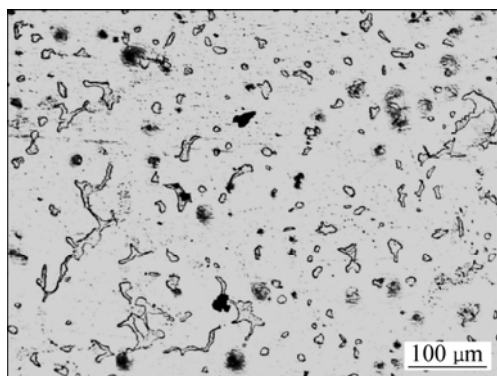


Fig.1 Metallograph of original AZ91 alloy casting

The fluoride film was generated in hydrofluoric acid solution. In order to analyze the influence of the factor on the fluoride film, the characteristics of the fluoride film obtained from different activation solutions were compared.

The thickness of the fluoride film was estimated by dissolution method. The magnesium alloy samples with

dimensions of  $d$  30 mm×3 mm were just activated, and the concentration of hydrofluoric acid was 15%. The samples lost fluorine in dilute nitric acid. The total amount of fluorine dissolved was determined by model Dionex 500 ion chromatography. The thickness of fluoride film could be calculated based on the density of fluoride and the total amount of fluoride over the surface.

The surface composition and the chemical states of elements were analyzed by XPS with  $\text{Mg K}_{\alpha}$  radiation. The samples were cleaned by ion sputtering for 2 min prior to analysis. The cross section morphology was observed by SEM and the composition of cross section surface was analyzed by X-ray energy dispersion analysis (EDS). The morphology and the composition of the fluoride film were observed and analyzed by SAM.

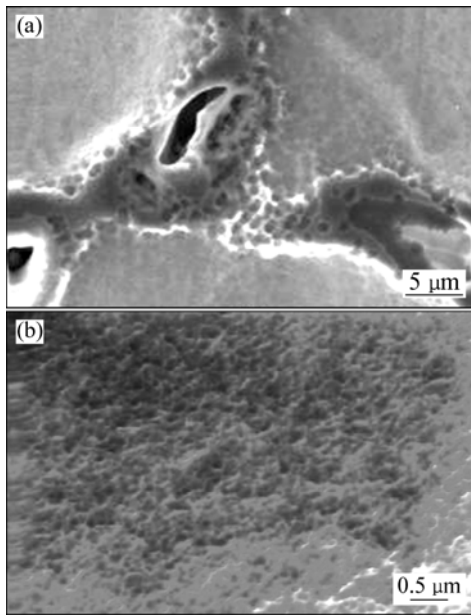
The variation of open circuit potential in different activation solutions of magnesium alloy was measured at room temperature by a ZF-3 potentiostat to reveal the electrochemical properties of the fluoride film. A three-electrode cell arrangement was used for the electrochemical measurements, where the sample acted as the working electrode, the saturated calomel electrode (SCE) was the reference electrode and a platinum sheet formed the counter electrode. The working electrodes were embedded in an epoxy resin to provide insulation, leaving a surface of  $1.0 \text{ cm}^2$  in contact with the electrolyte.

## 3 Results and discussion

### 3.1 Thickness and microstructure of fluoride film

Fig.2 shows the microstructures of the fluoride film after activation. It can be seen that the fluoride film is flat but not uniform. It looks like a porous film with cavities of micrometer on grain boundaries under low resolution (Fig.2(a)). However, the flat area in the fluoride film shows the similar porous characteristics with scores cavities of nanometer under high resolution (Fig.2(b)). The main reason for the formation of the porous structure of the fluoride film may be the release of hydrogen during activation. There are two phases in AZ91 alloy: the matrix phase and  $\beta$  phase, the electrochemical potentials of which are  $-1.71$  and  $-1.0 \text{ V}$ , respectively[12]. Thus, the etching of magnesium alloy may take the following course: at the partial anode (the matrix phase), magnesium is dissolved:  $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$ ; while at the partial cathode (the  $\beta$  phase),  $\text{H}^+$  ions accept the electrons and  $\text{H}_2$  gas is evolved:  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ .

The fluoride film is too thin to measure its thickness directly. In this study, the thickness of the fluoride film was measured by dissolution method. Taking a sample with area of  $0.01 \text{ m}^2$ , the density of  $\text{MgF}_2$  is  $3.148 \text{ g/cm}^3$  and the span of the porosity is 0–50%, it could be



**Fig.2** SEM images of magnesium alloy after activation

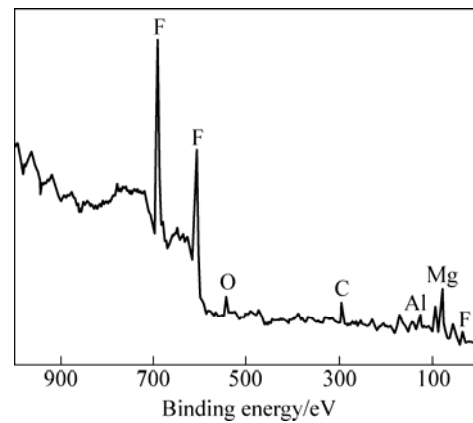
figured out that the thickness of  $\text{MgF}_2$  on the surface of activated magnesium is approximately 1.6–3.2  $\mu\text{m}$ .

### 3.2 Chemical composition of fluoride film

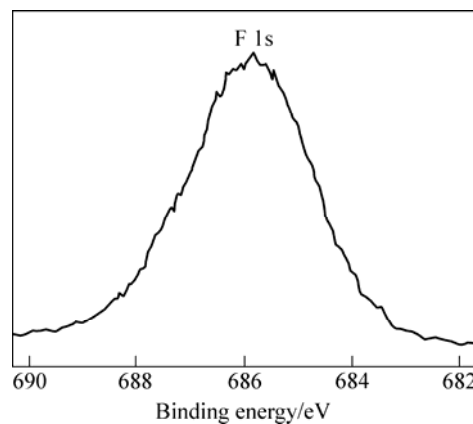
XPS was used to study the surface composition and chemical states of the elements of fluoride film. Fig.3 shows the XPS spectrum of the fluoride film on magnesium alloy after activation. It can be seen that F was the main element on the surface, as well as micro constituent O and Al. Fig.4 shows the high-resolution spectrum of F 1s which is found at 685.5 eV corresponding to  $\text{MgF}_2$ . This indicates that  $\text{MgF}_2$  is the main component of the fluoride film[13–14]. Fig.5 shows the high-resolution spectrum of Al 2p. Al 2p peak corresponding to  $\text{AlF}_3$  is found at 76.2 eV, indicating that aluminum involves the formation of fluoride film.

Table 1 shows the composition of the fluoride film calculated from the XPS spectra according to the atomic sensitivity factor(s) method after several different pretreatments.

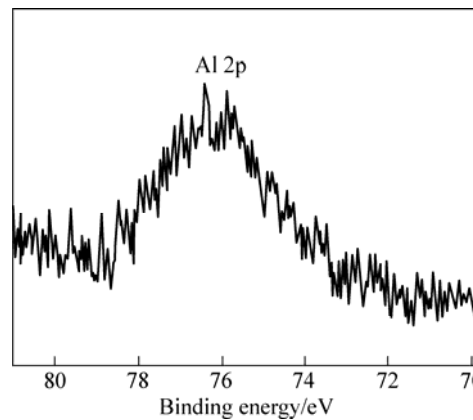
It is evident from Table 1 that F is the main element of the surface after activation. From F 1s high-resolution



**Fig.3** XPS spectrum of fluoride film



**Fig.4** High resolution spectrum of F 1s



**Fig.5** High resolution spectrum of Al 2p after activation

**Table 1** Surface composition of fluoride film after activation in different solutions

| Number | Activation solution       | Pre-treatment                                                    | Composition of fluoride film(molar fraction, %) |    |    |    |    |    |    |      |
|--------|---------------------------|------------------------------------------------------------------|-------------------------------------------------|----|----|----|----|----|----|------|
|        |                           |                                                                  | O                                               | F  | Mg | Al | Cr | Si | Na | C    |
| 1      | HF(15%)                   | $\text{CrO}_3$ 120 g/L,<br>$\text{HNO}_3$ 110 ml/L etching 1 min | 16                                              | 27 | 15 | 5  | —  | 2  | —  | Bal. |
| 2      | HF(15%)                   | $\text{CrO}_3$ 200 g/L,<br>KF 1 g/L etching 10 min               | 14                                              | 41 | 14 | 8  | —  | 1  | —  | Bal. |
| 3      | HF 4%                     | —                                                                | 10                                              | 48 | 15 | 9  | —  | —  | —  | Bal. |
| 4      | HF 4%+ $\text{NaNO}_3$ 2% | —                                                                | 24                                              | 30 | 15 | 8  | —  | —  | 1  | Bal. |

spectrum, it is determined that F exists in the form of  $\text{MgF}_2$ , with 1 s peak at 685.8 eV. It is the formation of insoluble  $\text{MgF}_2$  film that prevents the substrate from further dissolution.

O element is also present on the surface, which indicates that the fluoride film formed is not complete or dense. The surface of the magnesium sample is made rough during pretreatment; a complete coverage of fluoride film is hard to form on a rough surface when being activated.  $\text{H}_2$  is evolved during activation, which would make the fluoride film porous. On the sites where the fluoride film is not complete or dense, oxide ( $\text{MgO}/\text{Mg}(\text{OH})_2$ ) can be formed after samples are taken out of the activation solution, since magnesium has a very high chemical activity and the formation of magnesium oxide on the surface is rapid.

Additionally, the different activation solutions and pretreatment affect the composition of fluoride film, particularly on the F/O ratio. Na could even be detected in the fluoride film after activation in the solution with low concentration of  $\text{NaNO}_3$ .

Fig.6 shows the chemical composition of the fluoride film at different places (line 1 and 2), which indicates the presence of F, Mg and O. The results from SAM are similar to those from XPS. Line 3 in Fig.6 is the composition of the fluoride film after ion sputtering. It can be seen that the fluoride film is composed of Mg and F at the bottom of the film. This indicates that the oxide ( $\text{MgO}/\text{Mg}(\text{OH})_2$ ) which may be formed after the sample is taken out of the activation solution forms on the surface of the film.

The fluoride film is too thin to analyze the phase structure by XRD. The phase structure and the phase composition of the fluoride film can not be obtained through XPS only. DING's proposal on the phase structure of the fluoride film could not be demonstrated. On the other hand, the results from SAM and XPS indicate that the fluoride film is mainly composed of  $\text{MgF}_2$ , the oxide ( $\text{MgO}/\text{Mg}(\text{OH})_2$ ) on the surface of the film may be formed after the sample is taken out of the

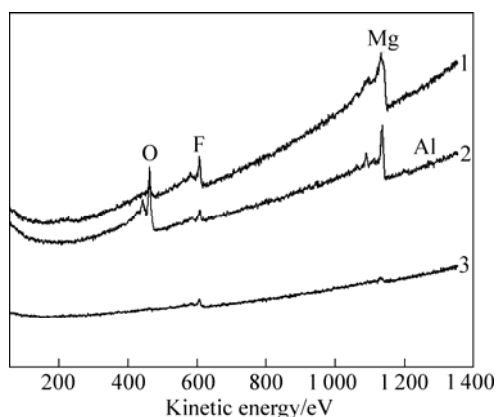


Fig.6 SAM spectrum of fluoride film

activation solution.

### 3.3 Potential of fluoride film

The fluoride film will be generated rapidly on the surface of magnesium alloy in activation bath, which results in the change of open circuit potential. This means that the open circuit potential could reflect the generation of the fluoride film and reveal the electrochemical properties of the fluoride film. Fig.7 shows the variation of open circuit potential of magnesium alloy in different activation solutions. It is seen that the potential increases gradually at the initial stage and then reaches a stable value, which indicates the generation of fluoride film and its stabilization. When there is a certain amount of  $\text{NO}_3^-$  in the activation bath, the potential increases at first and then decreases gradually after it reaches the maximum. The final stable potential has little change compared with the original open circuit potential. The increase of the potential in the first stage indicates the generation of fluoride film. However, the existing  $\text{NO}_3^-$  results in the destruction of the fluoride film and destroys the protection of fluoride film on magnesium substrate. So, the potential decreases subsequently.

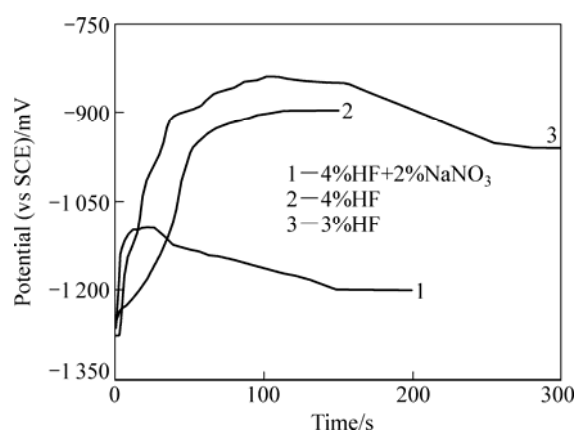


Fig.7 Open circuit potential of magnesium alloy in different baths

### 3.4 Stability of fluoride film

The stability of the fluoride film is referring to the stability of the fluoride film in the EN bath. There are three important reactions during the dissolution of magnesium fluoride in the plating bath when considering the composition in plating bath:

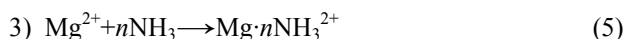


where  $k_s$  is the solubility product of  $\text{MgF}_2$ ;  $[\text{Mg}^{2+}]$  and  $[\text{F}^-]$  refer to the balance concentrations of  $\text{Mg}^{2+}$  and  $\text{F}^-$ , respectively.



$$[\text{MgF}^+]/([\text{Mg}^{2+}][\text{F}^-])=k_1 \quad (4)$$

where  $k_1$  is the stability constant of  $\text{MgF}^+$ .



$$[\text{Mg}\cdot n\text{NH}_3^{2+}]/([\text{Mg}^{2+}][\text{NH}_3]^n)=k_2 \quad (6)$$

where  $k_2$  is the stability constant of  $\text{Mg}\cdot n\text{NH}_3$ . Only the condition of  $n=1$  was taken into account in calculations, since the stability constant is too small if  $n\geq 2$ .

$[\text{NH}_3]$  is calculated by the dissociation constant of  $\text{NH}_4^+$ .



$$[\text{NH}_3][\text{H}^+]/[\text{NH}_4^+]=k_3 \quad (8)$$

The pH value of the EN bath is 6.5, the initial concentration of  $[\text{NH}_4^+]$  is 0.37 and  $k_3=10^{-9.24}$ , then calculated  $[\text{NH}_3]=0.0018[\text{NH}_4^+]$ .

In addition,  $\text{Mg}^{2+}$  in the plating bath also has a complex reaction with citric acid, but its complexation reacting ability is much less than that of nickel with citric acid. As a result, citric acid mainly reacts with  $\text{Ni}^{2+}$  in the plating bath, and the reaction of citric acid with  $\text{Mg}^{2+}$  is neglected. Taking  $k_3=10^{-8.18}$ ,  $k_1=10^{1.31}$  and  $k_2=10^{0.23}$ [15–17], the total solubility of  $\text{MgF}_2$  in the plating bath can be calculated as

$$\begin{aligned} s &= [\text{Mg}^{2+}] + [\text{MgF}^+] + [\text{Mg}\cdot\text{NH}_3^{2+}] \\ &= [\text{Mg}^{2+}] + k_1[\text{Mg}^{2+}][\text{F}^-] + k_2[\text{Mg}^{2+}][\text{NH}_3] \\ &= k_s \cdot (1 + k_1[\text{F}^-] + k_2[\text{NH}_3]) / [\text{F}^-] \\ &= 1.5 \times 10^{-5} \text{ g/L} \end{aligned}$$

Taking the plating area of the EN bath as  $0.01 \text{ m}^2$  and the density of  $\text{MgF}_2$  as  $3.148 \text{ g/cm}^3$ , it could figure out that the dissolution of  $\text{MgF}_2$  in EN bath is approximately  $0.47 \text{ nm}$ , while the thickness of  $\text{MgF}_2$  on the surface of the activated magnesium is  $1.6\text{--}3.2 \text{ }\mu\text{m}$ . This approves that the dissolution of fluoride in EN plating bath is negligible.

In addition,  $\text{MgO}$  will be dissolved first to make the concentration of  $\text{Mg}^{2+}$  reach its dissolution balance in the plating bath, so that little  $\text{MgF}_2$  will be dissolved.

It can be seen from the Pourbaix diagram of magnesium that magnesium oxide is not thermodynamically stable in aqueous solutions. If the solution has a pH value higher than 10, magnesium oxide is converted into magnesium hydroxide. If the pH value of the solution is lower, such as in the case of the EN solution, it will dissolve to form magnesium ion. However, the magnesium ions form fluoride film since there is a certain amount of HF in the EN plating bath.

XPS was used to analyze the surface composition and chemical state of the elements after the samples were plated for 5 min. The results show that the surface of the magnesium alloy still consists of magnesium fluoride

and magnesium oxide. The peak value of F 1s corresponds well to that of  $\text{MgF}_2$ , indicating that F is presented mainly in the form of  $\text{MgF}_2$ . This also proves that magnesium fluoride is stable in the EN plating bath.

### 3.5 Influence of fluoride film on EN initial deposition

Because of the dissolution of magnesium oxide, magnesium substrate is exposed to the EN bath, thus the replacement reaction between magnesium and nickel is possible. Nickel nucleates can be formed and the substrate is then catalytically active. The initial deposition may take the following courses:

1) The magnesium oxide is dissolved and the magnesium substrate is exposed;

2) At the partial anode (the matrix phase), magnesium is dissolved:



While at the partial cathode ( $\beta$  phase), nickel is deposited:



3) The chemical deposition then occurs on the nickel nuclei.

From the analysis above, it can be deduced that the initial deposition of EN on magnesium is faster when the O content of the surface is higher and the F/O ratio is lower, since more nickel nucleates can be formed from the dissolution of the oxide, which is confirmed by the experimental results[8].

### 3.6 Influence of fluoride film on EN bonding

After peeling off the plating from the substrate mechanically, the compositions of both sides of the fracture surface were analyzed by means of SAM. Fig.8 shows the composition analysis of fracture morphology on the base metal side. It can be seen that the surface layer of the fracture mainly consists of Mg, F, O, Ni and Na. The results from both point and surface analysis are identical. Only a few areas are composed of pure nickel, and no area is found that only pure magnesium exists without F and Ni. This indicates that fluoride exists in the plating and some bath composition is also trapped in the plating. The fact that nickel is detected but base metal elements are undetectable indicates that nickel layers would break while base metal wouldn't during peeling.

A flat and level area was chosen to carry out the ion sputtering, and then the composition was analyzed. The composition after ion sputtering is similar to that of the surface. This shows that the mixed layer of the fluoride film, nickel and plating bath composition has a certain thickness. With the increase of sputtering time, base metals are exposed and the peak of the characteristic element Al of the base metal appears.

The magnesium fluoride does not involve into a

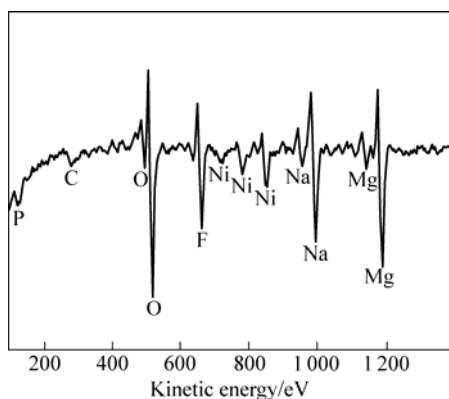


Fig.8 SAM pattern of fracture surface of nickel coating

redox reaction nor have any chemical linkage with the nickel since its property is inert. Therefore, the fluoride does not disappear but is trapped in the coating during plating. Meanwhile, there is also the bath composition included in the coating, so a certain thickness of the mixed layer is formed. As a result, the fluoride mixed layer becomes the weakest part in the coating and reduces the bonding strength. The coating breaks at this place when peeling. Therefore, the layer in the plating is mainly composed of the fluoride, and the bath composition and nickel can be seen from the composition analysis of the plating fracture.

The presence of a mixed layer of the fluoride and nickel could also be demonstrated by composition analysis of the cross section of the plating. Fig.9 shows

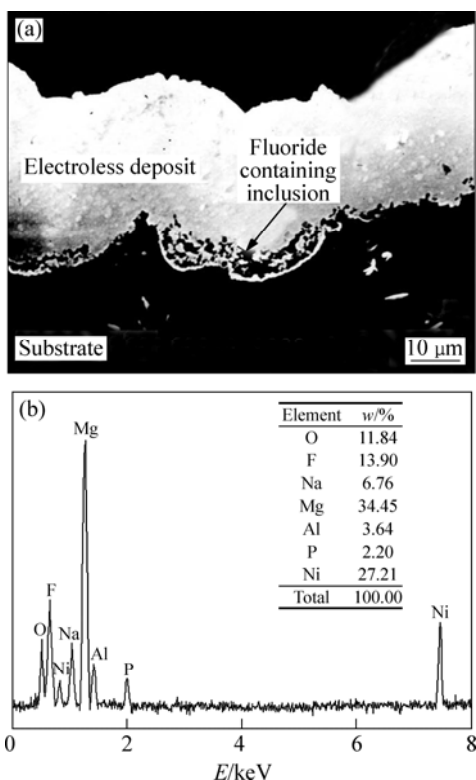


Fig.9 SEM morphology (a) and EDX spectrum (b) of cross section of nickel coating

the cross section morphology of the plating. It can be seen that some substances look like inclusions in the plating layer near the base. Energy dispersion analysis of X-ray (EDAX) indicates that there is a considerable amount of fluorine, oxygen and sodium in this place, which fully proves the existence of a mixed layer here.

## 4 Conclusions

1) The fluoride film on the magnesium alloys formed during activation is a kind of porous film with the thickness of about 1.6–3.2  $\mu\text{m}$  and is mainly composed of  $\text{MgF}_2$ . The composition of the activation bath and pretreatment of EN processing have an influence on the composition of the fluoride film.

2) The fluoride is stable and dissolves little in EN bath, which results in the protection of magnesium alloys base. However, the fluoride would be trapped in the plating layer.

3) The composition of fluoride determines the initial deposition rate of EN and part of the fluoride film finally exists as inclusion in EN coating.

## References

- [1] SHI Chang-xu, KE Jun, CAHN R W. A series of materials science and technology [M]. Beijing: Science Press, 1999, 18: 105–106. (in Chinese)
- [2] AVEDESIAN M, BAKER H. ASM specialty handbook: Magnesium and magnesium alloys [M]. Ohio, USA: ASM International, 1999: 139.
- [3] ASTM B480–88. Standard guide for preparation of magnesium and magnesium alloys for electroplating [S].
- [4] DELONG H K. Plating on magnesium [J]. Metal Finishing Guideline, 1978, 76(1): 175–183.
- [5] MAHALLAWY N E L, BAKKAR A, SHOEIB M, PALKOWSKI H, NEUBERT V. Electroless Ni-P coating of different magnesium alloys [J]. Surface and Coatings Technology, 2008, 202(21): 5151–5157.
- [6] GUO Dong, FAN Zhan-guo, YANG Zhong-dong, ZHAO Lin, GAO Peng. Effects and characteristics of  $\text{MgF}_2$  during electroless nickel plating of magnesium alloys [J]. The Chinese Journal of Nonferrous Metals, 2007, 17(5): 789–794. (in Chinese)
- [7] RAJAN AMBAT, ZHOU W. Electroless nickel-plating on AZ91D magnesium alloy: Effect of substrate microstructure and plating parameters [J]. Surface and Coatings Technology, 2004, 179(2/3): 124–134.
- [8] XIANG Yang-hui, HU Wen-bin, SHEN Bin, ZHAO Chang-zheng, DING Wen-jiang. Initial deposition mechanism of electroless nickel plating on magnesium alloys [J]. Journal of Shanghai Jiao Tong University, 2000, 34(12): 1638–1644. (in Chinese)
- [9] LIU Xin-kuan, XIANG Yang-hui, HU Wen-bin, DING Wen-jiang. Bonding mechanism of electroless nickel coating with magnesium alloys [J]. Journal of Chinese Society for Corrosion and Protection, 2002, 22(4): 233–236. (in Chinese)
- [10] LIU X, XIANG Y, HU W, DING W. Effect of fluoride film on bonding of electroless nickel coating with magnesium alloys [J]. Transactions of the Institute of Metal Finishing, 2005, 83(6): 1–4.

- 286–290.
- [11] DING Pei-pei. The electroless nickel plating of magnesium alloys and its mechanism [D]. Hangzhou: Zhejiang University, Department of Materials Science & Engineering, 2008: 77–94.
- [12] LUNDER O, LEIN J E, AUNE T Kr, NISANCIOGLU K. Role of Mg<sub>17</sub>Al<sub>12</sub> phase in the corrosion of Mg alloy AZ91[J]. Corrosion, 1989, 45(9): 741–748.
- [13] WANG Jian-qi, WU Wen-hui, FENG Da-ming. Introduction of electro spectrum (XPS/XAES/UPS) [M]. Beijing: Defense Industry Press, 1992: 520–536. (in Chinese)
- [14] WAGNER C D. Handbook of X-ray photoelectron spectroscopy [M]. Minnesota: Perkin-Elmer, 1979: 44–45.
- [15] SMITH R M, MARTELL A E. Critical stability constants [M]. New York: Plenum, 1976: 252–254.
- [16] MARTELL A E, SMITH R M. Critical stability constants [M]. New York: Plenum, 1982: 178–179.
- [17] HU Wen-bin, XIANG Yang-hui, LIU Xin-kuan, LIU Lei, DING Wen-jiang. A study on surface state during the pretreatment of electroless nickel plating on magnesium alloys [J]. Journal of Chinese Society for Corrosion and Protection, 2001, 21(6): 340–344. (in Chinese)

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