Electrodeposition of a protective copper/nickel deposit on the magnesium alloy (AZ31)

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Abstract

An environmental-friendly Cu electrodeposition process was proposed for the Magnesium alloy (AZ 31). Experimental results show that a good bonding between Cu deposit and Mg alloy surface can be achieved with a pretreatment of galvanostatic etching and then copper electrodeposition in the alkaline copper-sulfate plating bath. Microstructures between Cu deposit and Mg alloy substrate were examined with scanning electron and energy-filtering transmission electron microscopes (SEM and EF-TEM). The Cu-deposited Mg alloy can be further electroplated in acidic Cu and Ni plating baths to acquire a protective Cu/Ni deposit.

Keywords: A. Magnesium; B. Galvanostatic etching; B. EF-TEM; B. SEM

1. Introduction

Mg alloys have been attracted much more attention in recent years owing to their properties of high strength to weight ratio, high thermal conductivity, good electromagnetic shielding and easy recycling. These properties make them valuable in many applications including components used in automobile, computer, aerospace, mobile phone, and handheld tools, etc. However, Mg alloys show poor corrosion and wear resistance that limits its widespread usage [1]. Several surface coating treatments have been proposed to meet the requirement of corrosion protection for Mg alloys, such as metal coating [2], conversion coatings [3], anodizing [4], hydride coatings [5], organic coatings [6] and vapor-phase processes [7]. Compared with these surface coating treatments, the electroplating is a relatively economical and convenient method for operation. Therefore, it is worth to develop a suitable protective coating method for magnesium alloys.

Because Mg alloys are very active in nature, it is very difficult to obtain a protective deposit through an electroplating method in an aqueous plating bath. An oxide or hydroxide layer could be developed immediately when Mg alloys are immersed in water or even in air [8]. Because of their low electrical conductivity and bonding ability, this oxide layer could impede further electroplating on its surface. Thus, several pretreatments on the surface of the Mg alloy have being proposed for electroplating. Many reports have shown that activation of Mg alloy can be accomplished by first mechanical polishing, then dipping in alkaline solution, and finally pickling in the acid bath containing chromic acid or hydrofluoric acid [9–12]. Gray et al. [13] have demonstrated that a non-uniform deposit could be obtained on Mg alloy owing to different discharging capacities between intermetallic compound, Mg17Al12, and eutectic a presented in the electroplating surface. Nevertheless, a uniform copper deposit can be achieved with electroplating in a highly toxic Cu-cyanide bath, which is inappropriate for operation and environment.
In this study, an environment-friendly electroplating method is proposed for the protective coating on Mg alloy (AZ 31). To obtain a protective layer, four sequential processes are recommended; namely, galvanostatic etching, copper electroplating in the alkaline Cu plating bath, Cu electroplating in the acidic Cu bath, and Ni electroplating in the Watt’s bath. The corrosion behavior of the deposited specimens was evaluated by means of an anodic polarization test in 3.5 wt.% NaCl solution at 27 °C.

2. Experimental procedure

As-rolled magnesium alloy, AZ 31, in bar type with a 12 mm diameter was used in this study. Main compositions of the alloy were composed of 3.1 wt.% Al, 0.63 wt.% Zn, 0.13 wt.% Mn, 0.001 wt.% Fe and Mg balance. Electroplating was conducted in a typical electrochemical three-electrode cell. The AZ 31 specimen was used as the working electrode and shaped into the rotating cylinder electrode (RCE) with a diameter of 12 mm and a length of 5 mm. Plantized Ti-mesh and Ag/AgCl in saturated KCl solution were used as the counter and the reference electrodes, respectively. To obtain a Cu deposit on AZ 31 surface, the AZ 31 RCE specimen was electroplated in the alkaline Cu-sulfate bath with a constant plating charge of 24 C/cm² for 500 s. Before electroplating, two different pretreatments, a mechanical grinding and a galvanostatic etching, were used to obtain a copper deposit from the alkaline Cu-sulfate bath. With the mechanical grinding, the RCE surface was dry-ground with 600-grit emery paper, ultrasonically cleaned in de-ionized water, and then prepared for electroplating. Galvanostatic etching was conducted in the same bath as that used for Cu electroplating cell by applying a constant anodic current density of 25 mA/cm². Before electroplating, two different pretreatments, a mechanical grinding and a galvanostatic etching, were used to obtain a copper deposit from the alkaline Cu-sulfate bath. With the mechanical grinding, the RCE surface was dry-ground with 600-grit emery paper, ultrasonically cleaned in de-ionized water, and then prepared for electroplating. Galvanostatic etching was conducted in the same bath as that used for Cu electroplating cell by applying a constant anodic current density of 25 mA/cm² for 500 s.

To evaluate the bonding strength between the Cu deposit and AZ 31 substrate, the ASTM D3359-02 Standard Test Method for Measuring Adhesion by Tape Test was performed with a Cu deposited specimen. The test was accomplished by scratching five 1 mm wide parallel lines in both longitude and latitude directions on the Cu deposited specimen with a diamond knife. The scratched specimen was then adhered tightly with the 3 M type (3 M Core Series 4-1000) for ca. 60 s, and then the type was peeled rapidly in a direction parallel to the deposit surface. The bonding strength can be evaluated with appearance of the deposited specimen after peeling. A bad bonding strength can be found when the deposit is broken and peeled from the substrate; whereas, a good bonding strength can be found when merely scratched marks are revealed on the deposited specimen.

The corrosion behavior of the deposited RCE specimen was evaluated by means of the anodic polarization test in 3.5 wt.% NaCl solution at 27 °C. The same electrochemical three-electrode cell as that used in the electroplating cell was conducted. The deposited RCE specimen was used as a working electrode. The anodic polarization behavior of the deposited specimen was evaluated by potentiodynamic scanning with a scan rate of 5 mV/s from -0.25 V (vs. open circuit potential) to noble potential direction until breakdown of the deposit was detected.

Morphologies of the deposits were examined with a scanning electron microscope (SEM, ZEISS DSM 982 Gemini) equipped with an energy-dispersive X-ray spectrometer (EDS) allowing for chemical composition analysis. The microstructures and chemical composition of the deposited RCE was analyzed by energy-filtering TEM (EFTEM) using a FEI Tecnai F20 electron microscope. To avoid the oxidation of Mg alloy specimen during preparation, SEM and TEM specimens were prepared by focused-ion beam machining (FIB, FEI STRATA FIB 205). In FIB preparation, a beam of Ga⁺ ions was used for milling. To produce the TEM samples in this investigation the so-called ‘lifout’ technique was used [14]. The technology has recently been used to produce TEM samples of biomaterials such as bone and teeth [15]. The thickness of TEM samples for investigation was about 150 nm.

3. Results and discussion

3.1. Pretreatments with galvanostatic etching and mechanical grinding

To evaluate the pretreatment effect on the Cu electrodeposition, a Cu electroplating with a constant plating charge of 24 C/cm² on the AZ 31 specimen was conducted direct after galvanostatic etching in the alkaline Cu plating bath and mechanical grinding. Fig. 1 (a) and (b) show the surface morphologies of copper deposits on the AZ 31 surfaces pretreated with mechanical grinding and galvanostatic etching, respectively. With mechanical grinding, a non-uniform Cu deposit was observed [see Fig. 1(a)]. The results of EDS analysis at the concave position of the Cu deposited AZ 31 specimen show that only the intensity of element Mg was detected; whereas, at the convex position only the copper element was measured. It means that coverage of the Cu deposit on the AZ 31 surface is incomplete. Thus, further Cu or Ni electroplating on this Cu-deposited specimen in acid bath is not feasible owing to high chemical reaction of the exposed Mg substrate. This can be visually seen by immersing the Cu-deposited AZ 31 specimen in the acidic Cu-sulfate bath, in which several bubbles escaped from the AZ 31 surface leading to an etched rough surface. As shown in Fig. 1(b), a uniform copper deposit on the AZ 31 surface can be achieved with the pretreatment of galvanostatic etching. Moreover, the result of EDS analysis on the Cu-deposited specimen shows that only the intensity of the Cu element was measured. It indicates that complete coverage of the Cu deposit on the AZ 31 surface was achieved. Immersing the Cu-deposited specimen in the acidic Cu-sulfate bath, no chemical reaction was observed by naked eyes. It implies that the Cu-deposited specimen is suitable for further Cu and Ni electrodeposition in acidic baths to increase its corrosion resistance.
Many researchers [9–13] have pointed out that uniform coverage of the metal deposit is especially difficult to achieve on the magnesium alloys. Because intermetallic species such as Mg$_x$Al$_y$ are formed at the grain boundaries, resulting in a non-uniform surface potential across the substrate, and therefore further complicating the plating process. Gray [13] proposed that to obtain an equal potential surface a pretreatment is needed which requires many precisely controlled steps and consumes much time. In this study, we propose a simple method to obtain a uniform Cu deposit on the AZ 31 specimen with a pretreatment of galvanostatic etching and then Cu electrodeposition in an environment-friendly alkaline Cu-sulfate plating bath.

Fig. 1. The surface morphologies and EDS analyses of the AZ 31 specimens pretreated with (a) mechanical grinding and, (b) galvanostatic etching.

Fig. 2(a) and (b) shows the cross-sectional SEM micrographs of the Cu-deposited specimens with pretreatments of the mechanical grinding and the galvanostatic etching, respectively. As expected, some pores at the Cu/Mg interface were found when the AZ 31 specimen was pretreated with mechanical grinding (see Fig. 2(a)). It implies that the bonding between the Cu deposit and the AZ 31 surface is not well-built. On the other hand, a dense and pore-free Cu/Mg interface was obtained with a pretreatment of galvanostatic etching, as shown in Fig. 2(b). That is, the bonding strength between the Cu deposit and AZ 31 substrate could be improved.

Cross-sectional EFTEM micrographs of the Cu-deposited specimens with pretreatments of mechanical grinding

Fig. 2. The cross-sectional SEM micrographs of Cu-deposited AZ 31 specimens pretreated with (a) mechanical grinding and (b) galvanostatic etching.
and galvanostatic etching are shown in Fig. 3(a) and (b), in which three main elements of Cu, O and Mg are presented in red, blue and green, respectively. It can be clearly seen that an oxygen-rich layer with a width of ca. 80 nm was detected along the Cu/Mg interface when the AZ 31 specimen was pretreated with mechanical grinding and then Cu electrodeposition in the alkaline Cu-sulfate bath. It suggests that an oxide or a hydroxide layer exists on the surface of Mg alloy. Compared with the results of SEM observation, it can be concluded that pores at the interface between the Cu deposit and the AZ 31 substrate surface were markedly affected from the surface oxide or hydroxide. As shown in Fig. 3(b), the oxygen-rich layer was not found along the Cu/Mg interface anymore when the AZ 31 specimen was pretreated with galvanostatic etching. It has been accepted that the oxide or hydroxide layer on Mg alloy surface is not suitable for further metallic electroplating owing to its high electrical resistance [13,16,17]. Therefore, with the pretreatment of galvanostatic etching, a dense and uniform Cu deposit on the AZ 31 surface can be achieved when it was electroplated in the alkaline Cu-sulfate bath.

As mentioned above, with the pretreatment of galvanostatic etching, the oxide-rich layer formed on the AZ 31 specimen was removed. Moreover, the bonding strength between the Cu deposit and the AZ 31 surface was significantly improved. This can be realized from the results of the ASTM D3359-02 standard test. Merely scratched marks were observed on the Cu deposited specimen with the pretreatment of galvanostatic etching (see Fig. 4(a)). On the other hand, a broken and peeled Cu deposit was seen adjacent to the scratched marks in some places on the Cu-deposited specimen pretreated with mechanical grinding (see Fig. 4(b)). It means that the bonding strength between the Cu deposit and the AZ 31 surface is obviously improved with the pretreatment of galvanostatic etching. The results of bonding strength in relation with pretreatments of mechanical grinding and galvanostatic etching are fully in agreement with the observation results with the cross-sectional SEM and EFTEM micrographs shown in Figs. 2 and 3.

3.2. Protective Cu/Ni electroplating in acidic plating baths

To prepare a protective coating on the surface of an AZ 31 RCE specimen, four sequential processes were conducted. The first step is a galvanostatic etching in the alkaline Cu-sulfate plating bath. As mentioned above, the aim of this process is to remove the oxide or hydroxide developed on the RCE surface. The second process is a Cu electroplating (Cu1 plating) in the alkaline Cu-sulfate solution. The purpose of this process is to obtain a uniform, dense and pore-free copper deposit on the AZ 31 RCE surface. The Cu1 deposit inhibits a chemical reaction with the AZ

![Fig. 3. The cross-sectional EFTEM micrographs of Cu-deposited AZ 31 specimens pretreated with (a) mechanical grinding and (b) galvanostatic etching. Three main elements, Cu, O and Mg, are presented in red, blue and green, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 4. The optical micrographs showing (a) good and (b) bad bonding strength of Cu-deposited AZ 31 specimens pretreated with galvanostatic etching and mechanical grinding, respectively.](image)
31 substrate during the copper electroplating in the acidic Cu-sulfate plating bath, in which a copper electroplating (Cu2 plating) was performed and designated as the third process. This process aims to further increase the Cu deposit effectively on the AZ 31 specimen and to improve bonding property between Cu and Ni deposits. The Ni electrodeposition in the Watt’s Ni bath is the last process. To improve the corrosion resistance of the AZ 31 specimen, the Ni deposition with a thickness of ca. 15 μm was performed on the AZ 31 specimen [18].

Fig. 5 presents the cross-sectional optical micrograph of the RCE with protective coatings. According to the processes mentioned above, there are three deposits, Cu1, Cu2 and Ni, on the AZ 31 surface and their corresponding thickness values are 3, 6, and 15 μm, respectively. As shown in Fig. 5, each deposit can be clearly differentiated and uniformly distributed on the AZ 31 surface.

To evaluate the corrosion resistance of the non-deposited and the deposited AZ 31 specimens, their anodic polarization curves were tested in the 3.5 wt.% NaCl solution at 27 °C. The anodic polarization curves of the non-deposited and the deposited AZ 31 specimens are presented in Fig. 6. The corrosion resistance of a specimen can be evaluated from its anodic polarization curve with its corrosion potential and corrosion current density. The higher corrosion potential and the lower corrosion current density of the specimen show the higher corrosion resistance. As shown in Fig. 6, the lowest corrosion potential of -1.5 V and the highest corrosion current density of $2 \times 10^{-3}$ A cm$^{-2}$ was found with the non-deposited AZ 31 specimen. That is, the AZ 31 specimen has the lowest corrosion resistance. The corrosion potential increases and corrosion current density decreases with increasing the electrodeposition processes mentioned above. It means that the corrosion resistance of AZ 31 alloy had been improved by electroplating. Interestingly, different corrosion resistances were seen between Cu1 and Cu2 deposited AZ 31 specimens. The corrosion potential of the Cu1-deposited specimen is lower than that of the AZ 31 specimen electroplated with Cu2 deposit. On the other hand, the corrosion current density of the Cu1-deposited specimen can be improved further by a Cu2 electrodeposition on its surface. This is properly attributed to a relatively thin Cu deposit on the AZ 31 surface. The highest corrosion potential of $-0.25$ V and the lowest corrosion current density of $2 \times 10^{-5}$ A cm$^{-2}$ were obtained for the AZ 31 specimen after Ni electrodeposition. Besides, an obvious passive potential region from $-0.25$ V to 0.61 V was found when the AZ 31 specimen after Cu1, Cu2 and Ni electrodeposition processes. Similar results of the Ni-deposited AZ 31 specimens were reported by several researchers [18,19], by whom Ni electrodeposition was also used as the final electroplating process to increase the corrosion resistance of Mg alloy.

4. Conclusions

In this work, a simple and environment-friendly method was proposed to obtain a Cu-deposited Mg alloy (AZ 31). The method comprises of galvanostatic etching and then Cu electrodeposition in the alkaline Cu-sulfate plating bath. The full coverage Cu deposit on Mg alloy surface can be used as the substrate for further Cu and Ni electrodeposition in the acidic plating baths to achieve a protective coating for Mg alloy.

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References