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A zinc transition layer in electroless nickel plating

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Abstract

A new process, which is characterized with zinc transition layer obtained by combining immersing zinc in an improved zinc bath containing $FeCl_3$ and electroplating zinc, is used to plate Magnesium alloy AZ91D. Corrosion testing and SEM images indicate that the immersion zinc layers obtained in zinc immersion baths with $FeCl_3$ are more compact. Peel testing shows that there is good adhesion to the subsequent electrodepositing layer. The electroplating zinc can further promote the coverage of zinc transition layer on the magnesium alloy substrate before electroless nickel plating and reduce the galvanic corrosion effect between Mg alloy and Ni–P alloy. The good zinc deposit can be obtained by electroplating zinc in pH 9~10 zinc pyrophosphate bath at 40 °C under the current density of 2~3 A/dm^2. The developed new process of electroless nickel plating greatly improves the adhesion and coverage of Ni–P coating. The zinc transition layer obtained by the developed process can supersede copper transition layer obtained by cyanide plating process in electroless nickel plating on magnesium alloy.

Keywords: Magnesium alloy AZ91D; Zinc immersion; Zinc electroplating; Electroless nickel plating

1. Introduction

Magnesium has established itself as the panacea of the metal die-casting during the last decade. Its abundant supply – it comprises 2% of the earth's crust – ensure price stability, and its inherent features make it ideal for precision engineering in the fields of advancing technology. Lightweight, thermal conductivity, high dimensional stability, good electromagnetic, good machinability and easily recycled make magnesium and magnesium alloys valuable in a number of applications including automobile and computer parts, aerospace components, mobile phones, sporting gods, handheld tools and household equipment [1–4].

Nevertheless, a number of undesirable properties of magnesium including poor corrosion and wear resistance, poor creep resistance and high chemical reactivity that have hindered its widespread use in many applications. Several different methods have been developed for plating on magnesium alloys. Some of these using poisonous cyanide which is harmful to environment; others are inadequate because of limited adhesion and corrosion resistance.

Because the electrode potential of magnesium is much more negative than that of nickel, poor adhesion of Ni–P coating without zinc transition layer on magnesium alloys will be produced by direct electroless nickel plating on the substrate of magnesium alloys. Magnesium, as an anode, would be usually thought to be corrode in a form of galvanic corrosion cell when the positive metal coatings such as copper, nickel etc. are deposited on magnesium alloy surface, especially in salt or marine environments, unless the depositing coatings are very compact or pore-free. Copper is deposited in an alkaline–cyanide-type copper bath after immersing zinc at first, but the cyanide copper plating process is harmful to the environment. Only zinc immersion film is too thin, but compact zinc film can be produced by Electroplating zinc and the thickness can be controlled by adjusting the depositing time. It is quite encouraging to note that, when zinc alloy electroplating [5] or zinc electroplating is applied as the initial film to separate the more noble metals deposits from the magnesium surface instead

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of cyanide copper layer, a much-improved result is obtained in regarding to the protective value of the subsequent plated coating [6,7]. The presence of the zinc electro-layer with high coverage does much to reduce the galvanic cell effect normally encountered once corrosion begins in porous areas of the deposit. So if a compact layer of zinc has been deposited, the nickel and many other more positive metals can be applied to obtain high quality plating coating.

In this article, a new process, which applied zinc transition to supersede copper transition layer plated with cyanide bath, is discussed in electroless nickel plating.

2. Experimental

The research works were performed on the specimens of magnesium alloy AZ91D, the chemical composition are: Al 8.5–9.5%, Zn 0.45–0.9%, Mn 0.17–0.4%, Si <0.05%, Cu <0.025%, Fe <0.004%, Ni <0.001%, others <0.01%, balance Mg. The AZ91D specimens were cut into pieces of 20×30×4 mm.

The process flows of electroless nickel plating, including ultrasonic cleaning→acid pickling→activation→immersing zinc→cathodic depositing zinc→electroless nickel plating, are listed in Table 1 [8–11].

Pure Ni–P alloy usually resists corrosion of 5% NaCl solution. But if there is porous Ni–P plating on magnesium alloy surface, strong galvanic corrosion on the porous surface will take place because there is a big standard potential difference between Mg (−2.47 V) and Ni (−0.25 V). Ni–P alloy as cathode of corrosion cell is protected, but the uncovered Mg alloy substrate as anode is fiercely dissolved. The corrosion weight lost testing cannot be used to evaluate corrosion resistance of the Ni–P coating because the corrosion occurs on the uncovered magnesium alloy substrate, not on Ni–P plating. Therefore, the coverage of the Ni–P plating was evaluated by observing the corrosion spots through immersion in 5% NaCl solution for 15 or 30 h.

Table 1
The process flow of electroless nickel plating

1. Ultrasonic cleaning
Acetone degrease
2. Acid pickling
$C_2H_2O_4$ 10 g/L, Wetting agent, Room temp. 1 min
3. Activation
$K_4P_2O_7$ 65 g/L, Na_2CO_3 15 g/L, KF 7 g/L, 75 °C, 2 min
4. Immersion zinc
Immersion in $K_4P_2O_7$ zinc bath, $ZnSO_4{\cdot}7H_2O$ 50 g/L, $K_4P_2O_7{\cdot}10H_2O$ 150 g/L, LiF 3 g/L, Na_2CO_3 5 g/L, pH 10.2~10.4, 65 °C, 3 min
5. Electroplating zinc
① Zinc pyrophosphate bath, Zn salt 21 g/L, $K_4P_2O_7{\cdot}10H_2O$ 260 g/L, $C_6H_{17}O_7N_3$ 25 g/L, Thiourea 1~2 g/L, lustre-coating agent 0.02~0.05 g/L
② Zincate bath, ZnO 10 g/L, NaOH 100 g/L, proper additives, proper lustre-coating agent
6. Electroless nickel plating
$NiSO_4{\cdot}6H_2O$ 20 g/L, HF (40%) 12 mL/L, $H_3C_6H_5O_7{\cdot}2H_2O$ 5 g/L, NH_4HF_2 10 g/L, $NH_3{\cdot}H_2O$ (25%) 30 mL/L, $NaH_2PO_2{\cdot}H_2O$ 20 g/L, Thiourea 1 mg/L, pH 4.0, Temperature: 95 °C, Time: 60 min
7. Passivation treatment
CrO_3 2.5 g/L, $K_2Cr_2O_7$ 120 g/L, Temperature: 90~100 °C, Time: 10 min

Rinse each step.

Table 2
The adhesion and corrosion spots of Ni–P coatings obtained by various zinc immersion processes and then electroless nickel plating

Test	Zinc immersion operation	Electroless plating	Adhesion	Corrosion spots of Ni–P for 15 h in NaCl (cm^{-2})
1	No zinc immersion	Operation based on the flow of Table 1	x	2.04
2	Immersing zinc in $K_4P_2O_7$ zinc bath (10 min)		O	0.33
3	Immersing zinc in $K_4P_2O_7$ zinc bath (20 min)		Δ	0.51
4	Double immersion in $K_4P_2O_7$ zinc bath (10+10 min)		O	0.14
5	Immersing zinc in $K_4P_2O_7$ zinc bath+$FeCl_3$ (10 min)		O	0.00

Note: "x" stands for very poor adhesion and plating continuously sloughed-off. "Δ" indicates sometimes small plating swell occurs but no peeling off. "O" represents good quality plating without swell and peel off.

Evaluation of adhesion was conducted with reference to the following criteria at timings of direct after the plating and directly after 150 °C×one hour, wherein a state of swell occurrence on a plating surface or a state of peeling-off occurrence was observed on respective samples. The plating adhesion is classified into three grades. "x" stands for very poor adhesion and plating continuously sloughed-off. "Δ" indicates sometimes small plating swell occurs but no peeling off. "O" represents good quality plating without swell and peel off.

A common three-electrode cell was used to perform polarization curves in 5% NaCl solutions at room temperature. A platinum electrode and SCE are used as counter and reference electrode, respectively. Microstructure of the layers was charactered with SEM.

3. Results and discussion

3.1. Zinc transition

3.1.1. Improvement of zinc immersion process

The standard zinc immersion baths are based on aqueous solution of pyrophosphate, in which there are some zinc salts, and a fluoride salt as well as a small mount of carbonate in order to adjust the alkalinity [12]. It is known that loose zinc layer with less adhesion will be only obtained owing to magnesium alloy corrosion.

A successful application about zinc alloys immersion film on aluminum alloys has been reported in the literature [13]. This method is also applied in the pretreatment of electroless plating on Mg alloys. After electroless nickel plating was conducted based on the process of Table 1, omitting Step 5, the results of adhesion and corrosion testing of Ni–P coatings are shown in Table 2.