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Effects of ultrasonic dispersion on structure of electrodeposited Ni coating on AZ91D magnesium alloy

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Abstract: To obtain the refined electrodeposited nickel layer on AZ91D magnesium alloy, ultrasonic technology was applied in the processes of pre-treatment and electrodeposition. The phases of pre-treatment layer and the nickel coating were analyzed by X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS), and the microstructure was observed by scanning electron microscopy (SEM). Then, the effects of ultrasonic dispersion on the microstructure of pre-treatment layer and the grain refinement of electrodeposited nickel layer were discussed. The results showed that the pre-treatment electrodeposited Cu-Sn layer with compact microstructure could be synthesized in alkaline copper-tin liquid with ultrasonic agitation, as a result, smooth and refined nickel coating formed on AZ91D magnesium alloy. On the other hand, preferred orientation in the coating decreased because of the refined grains.

Key words: AZ91D magnesium alloy; Cu-Sn layer; Ni coating; electrodeposition; ultrasonic dispersion

1 Introduction

Magnesium alloys have many advantages, such as low density, high specific strength, good castability, machinability, shock resistance, heat conductivity, electrical conductivity, non-toxicity and recoverability[1]. However, the application of magnesium alloys is restricted by their poor corrosion resistance[2−3]. Surface treatment is one of common and effective ways to improve the performance of magnesium alloys which mainly includes chemical conversion treatment, anodic oxidation, micro-arc oxidation, ion implantation, laser surface alloying, chemical plating and electrodepositing, etc[4−12]. One simple and effective way is to plate metal or alloy onto the magnesium alloy through electro-chemical methods, which is known as electrodepositing or electroless plating. Many works in plating nickel on magnesium alloys were done in previous studies[13−16], and a better performed layer through electroless plating is obtained through electrodepositing nickel, but in a difficult process and at a high cost. Technology of galvanizing cyanide copper as the substrate and then electrodepositing was used to plate layers with a better binding strength and a good corrosion resistance, but the application of toxic cyanide caused serious pollution. In the present work, alkaline copper-tin alloy electrolyte was applied to replace cyanide electrolyte to pre-plate substrate on magnesium alloy, then nickel was plated on magnesium alloy using Watt bath under ultrasonic. The effect of ultrasonic on the structure of electrodeposited coating was analyzed.

2 Experimental

2.1 Sample

AZ91D magnesium alloy specimens with dimensions of 20 mm×10 mm×2 mm were used as substrate in the experiment.

2.2 Plating processes of magnesium alloy

Surface pre-treatments and plating processes of magnesium alloy were as follows: pre-grinding, washing, pickling activation, plating copper-tin alloy and plating nickel. The formulation of electrolyte and process conditions are listed in Table 1.

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Table 1 Composition of electrodeposited solution and process conditions of surface treatments

Stage	Process operation	Treatments and solution
1	Caustic washing	NaOH 60 g/ L , (60 ±5) ˚C, 8−10 min
2	Activation	HF (40%) 350 mL/L , 20 ˚C, 8−10 min
3	Galvanizing	$ZnSO_4$ 30 g/L, $Na_4P_2O_7$ 120 g/L, Na_2CO_3 5 g/L, NaF5g/L, (80±2) ˚C, 6−10 min, with ultrasonic
4	Plating copper-tin alloy	$C_6H_8O_7·H_2O$ 140 g/L, $CuCO_3·Cu(OH)_2$ 18 g/L, H_3PO_4 8 ml/L, $Na_2SnO_3·3H_2O$ 22 g/L, KOH 135 g/L, pH 10−11, J_K 1−1.5×10^{-4} A/dm^2, (25±5) ˚C, with ultrasonic
5	Plating nickel	$NiSO_4·6H_2O$ 270 g/L, $NiCl_2·6H_2O$ 40 g/L, $C_{12}H_{25}NaO_4S$ 2 mg/L, H_3BO_3 40 g/L, Additives: 0.01 g/L, pH 3.5, J_K 1−3×10^{-4} A/dm^2, (50±2) ˚C, with ultrasonic

2.3 Coating examination

Phase identification of the deposits was performed by X-ray diffraction (XRD, D/max 2500PC) and XPS VG ESCALAB MKⅡ. Surface morphology of the deposits was observed by a scanning electron microscope (SEM, JSM-5600).

3 Results and discussion

3.1 Effect of ultrasonic on structure of galvanizing layer

After caustic washing and hydrofluoric acid treatment, the sample was galvanized for 5 min before XPS analysis. The XPS pattern shows that the main element of the surface is Zn. The 2p peaks of Zn locate at 1 020.85 and 1 043.66 eV, respectively, corresponding to simple substance Zn, which proves that Zn exists in the form of simple substance, as shown in Fig.1.

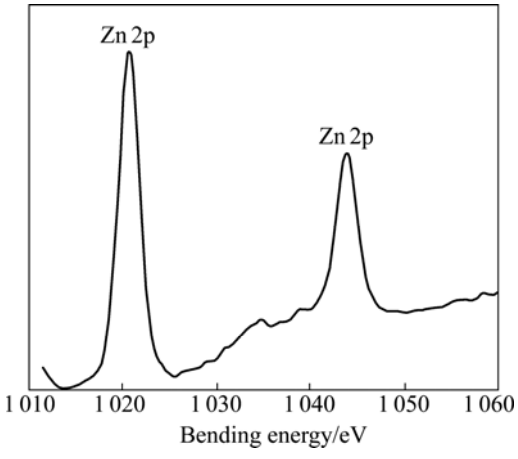

Fig.1 High-resolution XPS spectra of Zn 2p

The deposition of Zn on the AZ91D alloy included: 1) The replacement reaction of magnesium with zinc occurred to form a layer for the substrate is not covered by MgF_2, or coverage layer is less compact. 2) Zn firstly reacted with pyrophosphate, then deposited on magnesium alloy with electrochemical manner. The reactions are

$$Mg^{2+}+2OH^- \longrightarrow Mg(OH)_2 \quad (1)$$

$$Mg+Zn^{2+} \longrightarrow Mg^{2+}+Zn \quad (2)$$

$$Zn^{2+}+2P_2O_7^{4-} \longrightarrow [Zn(P_2O_7^{4-})_2]^{6-} \quad (3)$$

$$[Zn(P_2O_7^{4-})_2]^{6-}+2e \longrightarrow Zn+2P_2O_7^{4-} \quad (4)$$

XRD pattern of the sample galvanized for 20 min is shown in Fig.2. It can be seen that the coating is mainly composed of Mg and Zn. The Zn layer is too thin to be penetrated into the substrate. The main reasons are based on reactions (1) and (2). Once a complete galvanizing layer is formed, dissolution rate of magnesium alloy declines sharply in accordance with the speed of the replacement reaction. The zinc layer is not a catalytic surface, so there is no continuous formation condition like electroless plating, as a results, reactions (3) and (4) are terminated. Though the thickness and density of zinc layer are very low, it is chosen as the bottom layer for pre-plating Cu-Sn alloy.

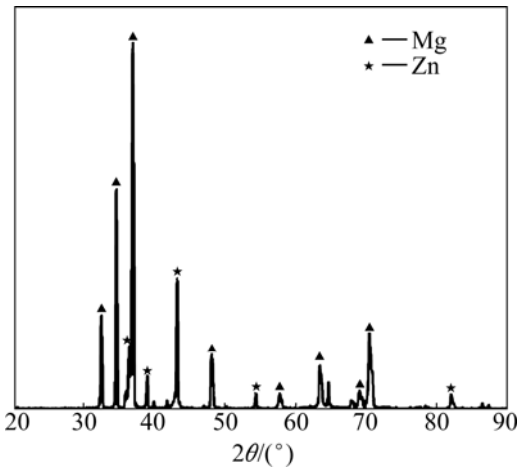

Fig.2 XRD pattern of sample galvanized for 20 min

The surface morphology of galvanizing sample is shown in Fig.3. It can be seen from Fig.3(a) that there are many holes, and the galvanizing layer which is composed of coarse particles is non-uniform and non-compact. In Fig.3(b), the surface of deposition is uniform

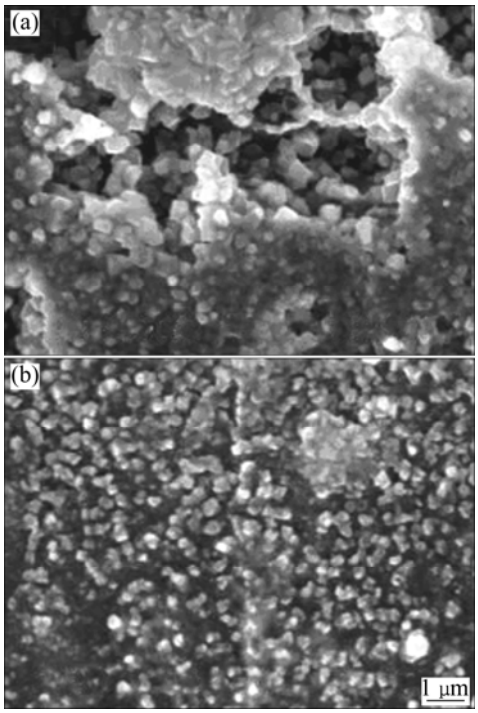

Fig.3 SEM images of surface morphology of galvanizing layer: (a) Without ultrasonic; (b) With ultrasonic

and dense by ultrasonic galvanizing. The quality of subsequent deposition of Cu-Sn alloy is improved by the uniform and dense galvanizing layer.

3.2 Effect of ultrasonic on structure of electroplated Cu-Sn alloy coating

Cu-Sn alloy coating acts as the transitional bottom layer which has a strong effect on the quality of the deposited nickel layer on the magnesium alloy. One of the methods of pre-plating copper or copper alloy is the regular cyanide electroplating. Two complexing agents, sodium cyanide and sodium hydroxide, are used to mix with univalent copper ions and quadrivalent tin ions for tin and copper, respectively. Because of the non-interfering character between the two agents, the plating solution is stable. Co-deposition of Cu-Sn alloy is obtained by adjusting the complexing agent; both the capacity of deep plating and uniform plating are appreciable. However, the toxicity of cyanide brings great harm to human beings and environments, which should be avoided as much as possible. In this experiment, if an acidic solution is chosen, although the substrate of magnesium alloy can be galvanized, the substrate will be corroded easily because of the quite thin and non-dense zinc layer. Based on these considerations, alkaline solution is introduced, and ultrasonic is used to enhance the capacity of equal plating electrolyte and refine microstructure, which also contributes to the bonding of coating on the substrate.

XRD patterns of Cu-Sn coatings with and without ultrasonic agitation in alkalic solution are shown in Fig.4. The coating formed with ultrasonic agitation was composed of a single phase of $Cu_{13.7}Sn$, while the coating without ultrasonic agitation is composed of $Cu_{13.7}Sn$ and Zn.

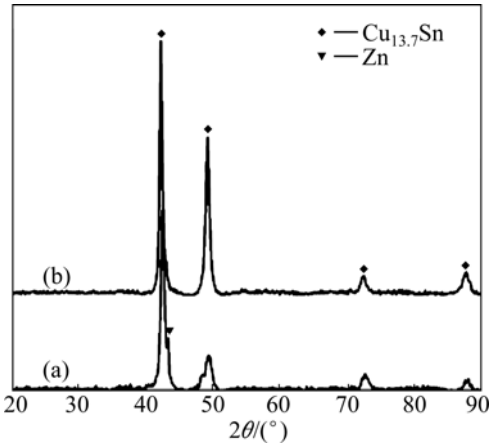

Fig.4 XRD patterns of plating Cu-Sn alloy layers: (a) With ultrasonic; (b) Without ultrasonic

The surface morphology of Cu-Sn coating is shown in Fig.5. It can be seen that the coating without ultrasonic agitation is not dense and has obvious holes, and its grains gather together. By comparison, the coating with ultrasonic agitation is uniform and compact. The main reason is that under the effect of ultrasonic cavitations, ultrasonic oscillation box emits signals with high-frequency, high-pressure and strong vibration; the signal is converted to mechanical vibration by the transducer

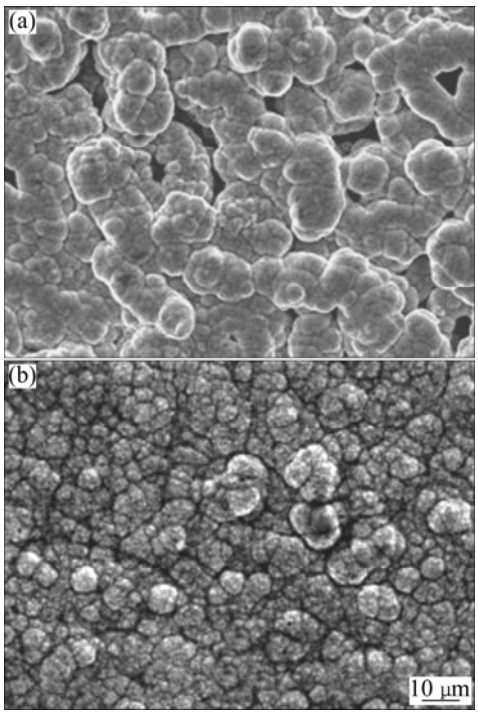

Fig.5 SEM images of electroplating copper-tin alloy: (a) Without ultrasonic; (b) With ultrasonic

then sent into the bath. This signal spreads in a mode of continuous, radial and straight line. Tens of thousand of small negative-pressure bubbles are produced when the ultrasonic beams spread in the medium, and these bubbles produce series of intensive explosions under a certain pressure near the surface of cathode, which impacts on the cathode surface constantly to enhance the surface activity of cathode substrate and increases the rate of nucleation. As a result, the uniform and dense surface coating is formed. At the same time, equal plating ability of the electrolyte is improved.

3.3 Effect of ultrasonic on structure of electro-deposited Ni coating on magnesium alloy

Fig.6 shows the XRD patterns of electrodepositing nickel layer after pre-plated Cu-Sn alloy with or without ultrasonic agitation. From the result, it can be seen that the diffraction intensity of plating nickel layer obtained under different deposition conditions are different. The crystal surface are corresponded to three diffraction peaks of nickel (111), (200) and (220). The intensity of these diffraction peaks turned weak gradually. However, as shown in Fig.6, among the diffraction peaks of nickel layer obtained from two different conditions, (200) crystal plane without ultrasonic is the most intense, followed by (111) crystal plane without ultrasonic. With the effect of ultrasonic, the diffraction intensity of nickel layer (111) crystal plane is the most intense, followed by (200) crystal plane, which is the same as nickel diffraction peaks. This indicates that general electrodepositing nickel coatings result in a preferred orientation in (200) crystal plane. In the process of electrodeposition, nickel atoms are easily taken by crystals perpendicular to the surface of cathode, which makes this direction a faster growth surface and causes a preferred orientation of nickel deposition layer. However, effects of ultrasonic stirring destroy the original growth mode of the deposited layer, which makes the nickel atoms oritate randomly in crystallization process in front of the deposition interface, and eventually it decreases the preferred orientation of depositing layer.

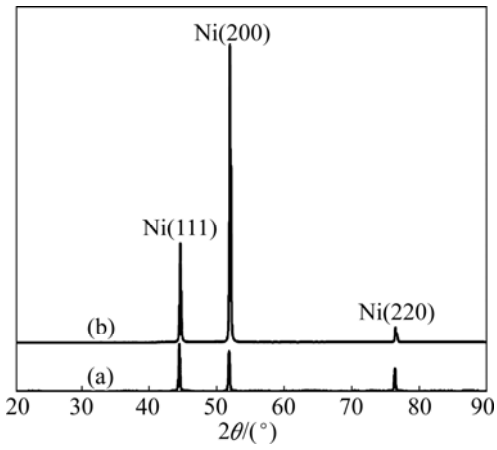

Fig.6 XRD patterns of plating nickel: (a) With ultrasonic; (b) Without ultrasonic

Fig.7 shows the SEM images of electrodeposited nickel. From Fig7(a), it can be seen that the grains of the coating are thick, and most of them are pyramid. Fig.7(b) shows that the grains of coating are cellular and their size are uniform, which indicates that nickel grains are refined by ultrasonic. The reason is that cavitation bubbles generated by ultrasonic cavitations exploded, creating a strong shock pressure. The ultrasonic energy activates the surface of electrode, and destroys the normal growth of grains, which makes the grains form new smaller nucleus and nuclear proliferation create, thus the rate of nucleation is increased. When the rate of nucleation exceeds the rate of growth, the grains will be refined. “Interferences” of ultrasonic cavitations in the process of grain growth make the growth direction change from the preferred orientation to the random orientation, and nickel grains also change from large pyramid shape to cellule shape.

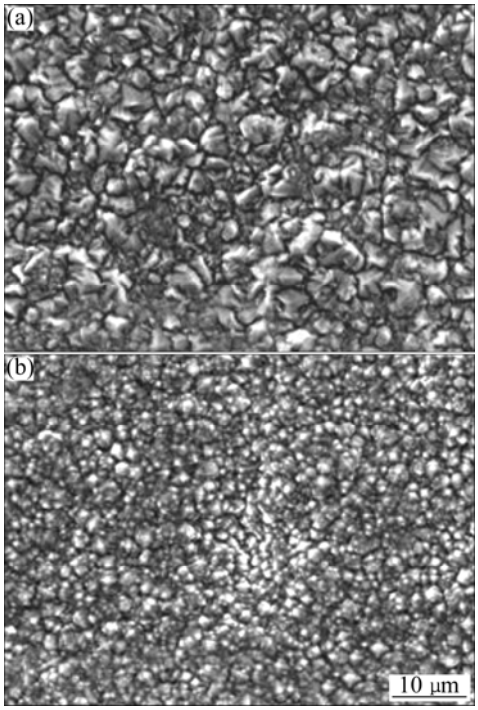

Fig.7 SEM images of electrodepositing nickel layer: (a) Without ultrasonic; (b) with ultrasonic

At the same time, ultrasonic vibration and cavitations phenomenon are thought to have extremely strong mixing effects, which makes adsorptive hydrogen on the substrate (cathode) surface generated from plating magnesium alloy dissolve fast, diffuse rapidly and not stay on the substrate surface. As a result, the porosities and internal stress of the coating decrease, and the bonding force of the coating on the substrate is improved.

4 Conclusions

1) On the surface of magnesium alloy, nickel coating was fabricated by pre-plating Cu-Sn alloy as the bottom layer. During the process of plating Cu-Sn alloy with ultrasonic agitation, cyanide plating bath was replaced by alkaline. Therefore, uniform and compact coating of Cu-Sn alloy was fabricated.

2) Tests and observation results show that ultrasonic vibration and cavitations could refine the grains in the crystallization process of each layer, improve the uniformity of the coating surface, reduce the preferred orientation of nickel coating and change the grains from pyramid shape to exiguous cellular shape.

References

[1] SHI Chang-xu, LI Heng-de, WANG Dian-zuo, LI Yi-yi, ZUO Tie-yong. Propose of acceleration development of China magnesium industry [J]. Materials Review, 2001, 15(4): 5−6. (in Chinese)

[2] GU Chang-dong, LIAN Jian-she, HE Jin-guo, JIANG Zhong-hao, JIANG Qing. High corrosion-resistance nanocrystalline Ni coating on AZ91D magnesium alloy [J]. Surface and Coatings Technology, 2006, 200(18/19): 5413−5418.

[3] FROES F H, WARD-CLOSE C M. Processing of light metals for enhanced performance [J]. Materials Processing Technology, 1995, 48(1): 667−673.

[4] GRAY J E, LUAN B. Protective coatings on magnesium and alloys —A critical review [J]. Journal of Alloys and Compounds, 2002, 336(1/2): 88−113.

[5] JIANG Y F, LIU L F, ZHAI C Q, ZHU Y P, DING W J. Corrosion behavior of pulse-plated Zn-Ni alloy coatings on AZ91 magnesium alloy in alkaline solutions [J]. Thin Solid Films, 2005, 484: 232−237.

[6] SONG Guang-ling, ATRENS A. Understanding magnesium corrosion ― A framework for improved alloy performance [J]. Advanced Engineering Materials, 2003, 5: 837−857.

[7] HAWKE D, ALBRIGHT D L. A phosphate-permanganate conversion coating for magnesium [J]. Metal Finishing, 1995, 93(10): 34−38.

[8] DMITRI G, YOSHIO B, MASANORI M, KEITA F, TANG C C. Boron nitride nanotubes as nanocrucibles for morphology and phase transformations in encapsulated nanowires of the Mg-O system [J]. Acta Materialia, 2004, 52(11): 3295−3303.

[9] SACHIKO O. Oxide films formed on magnesium and magnesium alloys by anodizing and chemical conversion coating [J]. Corrosion Reviews, 1998, 16(1/2): 175−190.

[10] SUBRAMANIAN R, SIRCAR S, MAZUMDER J. Laser adding of zirconium on magnesium for improved corrosion properties [J]. Journal of Materials Science, 1991, 26: 951−956.

[11] SHARMA A K, SURESH M R, BHOJRAJ H, NARAYANAMURTHY H, SAHU R P. Electroless nickel plating on magnesium alloy [J]. Metal Finishing, 1998, 96(3): 10−17.

[12] HIROYUKI U, MATSUFUMI T, TETSUJI I. Corrosion resistance of the casting AZ91D magnesium alloys with paint finishing [J]. Journal of Japan Institute of Light Metals, 1998, 48(5): 248−255.

[13] CHEN Jue-ling, YU Gang, HU Bo-nian, LIU Zheng, YE Li-yuan, WANG Zhen-feng. A zinc transition layer in electroless nickel plating [J]. Surface and Coatings Technology, 2006, 201(3/4): 686−690.

[14] GEORGE R, VENKATACHALAM S, NINAN K N. Electrochemical impedance measurements on Ni-P coated magnesium alloy, chromated magnesium alloy, and anodized aluminium alloys in aqueous salt solutions [J]. British Corrosion Journal, 2002, 37(1): 37−42.

[15] LI Jian-zhong, SHAO Zhong-cai, ZHANG Xin, TIAN Yan-wen. The electroless nickel-plating on magnesium alloy using $NiSO_4·6H_2O$ as the main salt [J]. Surface and Coatings Technology, 2006, 200(9): 3010−3015.

[16] GU Chang-dong, LIAN Jian-she, LI Guang-yu, NIU Li-yuan, JIANG Zhong-hao. Electroless Ni-P plating on AZ91D magnesium alloy from a sulfate solution [J]. Journal of Alloys and Compounds, 2005, 391(1/2): 104−109.

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