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Analysis on the Effects of Mechanical Attrition on the Mechanical Properties of Electroless Alloy Surface Coating

Liying Huang*[a], Kuaishe Wang[a], Pengfei Jia[b], Wen Wang[a]

[a]School of Metallurgy Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China
[b]Xingtai Polytechnic College, Xingtai 054035, China
huangliying00002@163.com

In this paper, we design a method that uses mechanical attrition to apply the electroless plating on the alloy surface, and compare the effect of electroless plating with that of traditional electroless plating. Based on the comparison results, we study the effects of mechanical attrition on the properties of electroless alloy plating during the electroless Ni-P plating. The results show that the mechanical attrition changes the growth pattern of Ni and P atoms in the traditional electroless plating. The resulting impact causes more energy to be transferred to the surface of the coating and brings plastic changes to the surface. The increase of the ion transport rate in the solution helps improve the uniformity of the coating. After mechanical attrition, the coating shows a very smooth and flat surface, indicating that this method effectively increases the coating density and at the same time saves a lot of coating resources. Mechanical attrition reduces the amorphism of the electroless coating so that the coating achieves the amorphous conversion from high to low energy. It can also make the zinc alloy coating harder and more resistant to corrosion. The surface of the magnesium alloy shows “cauliflower-like” structure. The “cauliflower” structure on the traditional electroless coating is not uniform, while the surface structure after the mechanical attrition is relatively smooth and flat, with tighter particle binding and no obvious pores. Amorphous Ni-P coating has an unstable mechanical shape in high temperature. Using the traditional chemical plating to coat the magnesium and zinc alloy can easily cause the coating to peel off or fail, while in the mechanical attrition method, the glass balls continuously impact the coating, increasing the atomic energy in the coating and inhibiting the galvanic corrosion between the coating and the magnesium alloy.

1. Introduction

The mechanical attrition treatment technology for alloy surface is a new type of electroless plating method developed from the traditional plastic deformation treatment technology. Electroless plating of alloy surface using mechanical attrition have such advantages like small grain size, few pores, good bond between the coating and the alloy surface, high toughness and universality. As a result, in recent years, the mechanical attrition technology has been widely used in electroplating and electroless plating (Cai et al., 2015; Liu et al., 2015; Balusamy et al., 2013; Kumar et al., 2012; Balusamy et al., 2012).

Regarding the mechanism of electroless plating with mechanical attrition, many scholars have been conducted researches (Arifvianto et al., 2012; Li et al., 2012). Most of the researches focus on changing the mechanical barrier layer, in-situ mechanical treatment of coatings, crystallization of amorphous coatings and effects of thermal treatment on the properties of coatings (Chen et al., 2013; Guo et al., 2014; Sun, 2013). At present, crystallization of Ni-P coatings has been gradually applied in the industry.

Electroless plating of zinc alloy and magnesium alloy surfaces is currently a common application of electroless plating. The research on zinc alloy plating mainly focuses on thermal treatment and gas shield (Ping et al., 2009; Inoue, 2015); and the research on magnesium alloy surface plating mainly focuses on surface modification, anodic oxidation and application of organic coatings (Gray and Luan, 2002; Ambat and Zhou, 2004; Song et al., 2006).

In this paper, we design a method that uses mechanical attrition to apply the electroless plating on the alloy surface, and compare the effect of electroless plating with that of traditional electroless plating. Based on the

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comparison results, we study the effects of mechanical attrition on the properties of electroless alloy plating during the electroless Ni-P plating.

2. Testing materials and methods

2.1 Mechanical-attrition-based electroless plating

Figure 1 shows the device that uses mechanical attrition to apply electroless coating on the surface of the sample. It consists of a temperature meter, a beaker, an open cup, a stirring paddle and glass balls. During the test, add a certain number of glass balls into the Ni-P electroless plating bath, and use the stirring paddle to make the glass balls move in the bath, and at the same time, conduct mechanical attrition and electroless nickel plating on the sample. The sample surface plating process includes sample grinding, cleaning (using ultrasound, caustic wash and acid pickling process to remove impurities on the sample surface), activation, pre-plating, electroless plating (acid plating + mechanical attrition) and drying. The basic liquid for electroless plating consists of nickel sulfate, sodium hypophosphite, accelerator, buffer and potassium iodate, with a pH of 4.5-5.0. The electroless plating duration is 2-3h.

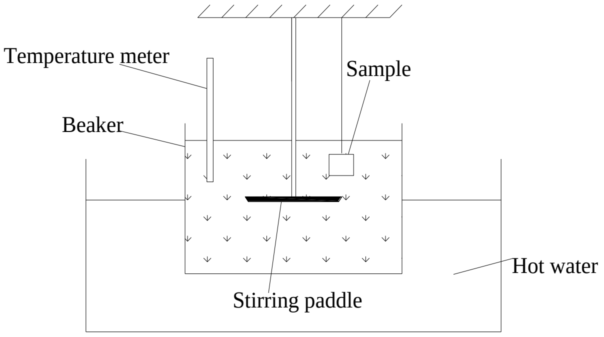


Figure 1: Schematic diagram of electroless plating with mechanical attrition test treatment

2.2 Testing method

We use the scanning electron microscope and atomic force microscope to observe the coating surfaces in the traditional and mechanical-attrition-based electroless plating, and test the Ni-P content in the coating. We use the diffractometer to analyze the coating phase structure and use the Vickers microhardness tester to measure the fiber hardness. The working electrode and auxiliary electrode are sample and platinum sheet, respectively. The reference electrode is calomel electrode, the corrosion medium is NaCl, and the scanning speed is set to 0.015V/s.

3. Test results and analysis

3.1 Analysis on the effects of mechanical attrition on the properties of electroless zinc alloy plating

The reaction rates of coatings in the mechanical-attrition-based and traditional electroless plating methods at different temperatures are shown in Table 1. From the table, we can see that in the mechanical-attrition-based method, the coating thickness can be effectively reduced. When the temperature is higher than 75°C, the mechanical-attrition-based method is more cost-saving.

Table 1: The reaction rate of electroless nickel plating at different temperatures

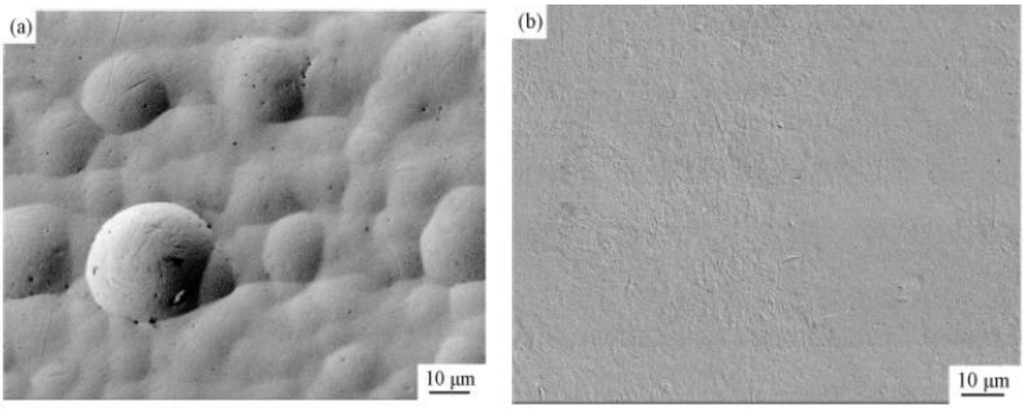
	Temperature/°C	65	75	85	90	95
Reaction rate (μm/h)	MAE-plate coating	2.9	6.3	10.86	11.57	12.02
	CE-plate coating	2.8	6.6	11.37	12.89	14.37

The relationship between the chemical reaction rate and the activation energy E_m is as follows:

$$\lg v = C - E_m / (2.3RT) \tag{1}$$

C is a constant; T is the temperature at which the electroless plating is applied; R=8.3J/(mol•k). Through calculation of the activation energy in the two electroless plating methods according to Formula 1, we find that mechanical attrition can effectively reduce the activation energy of the reaction. This is due to the fact that the glass balls in the electroless plating bath can enhance the energy of the active center, and that the impact of the glass balls on the sample increases the energy of the reaction.

The microscanning results of the traditional and mechanical-attrition-based electroless plating methods are shown in Figure 2. From the figure, it can be seen that, in the traditional method, there are a large number of cell structures in the surface of the Ni-P coating, and there are many pores on the surface; in the mechanical-attrition-based method, the coating has a very smooth and flat surface. By comparison of the two figures, it can be found that the electroless coating under the mechanical-attrition-based method is smoother. This method not only effectively increases the coating density, but also saves a lot of plating resources.



(a) Traditional electroless plating (b) Mechanical grinding

Figure 2: SEM micrographs showing morphology of Ni-P between traditional and mechanical grinding electroless plating

The electroless plating process is a process where there are deposited particles formed on the active surface and continuously increase, and the Ni and P atoms grow in a spherical shape during the deposition process. Mechanical attrition changes the growth pattern of Ni and P atoms in the traditional electroless plating. The resulting impact causes more energy to be transferred to the surface of the coating and brings plastic changes to the surface. The increase of the ion transport rate in the solution helps improve the uniformity of the coating.

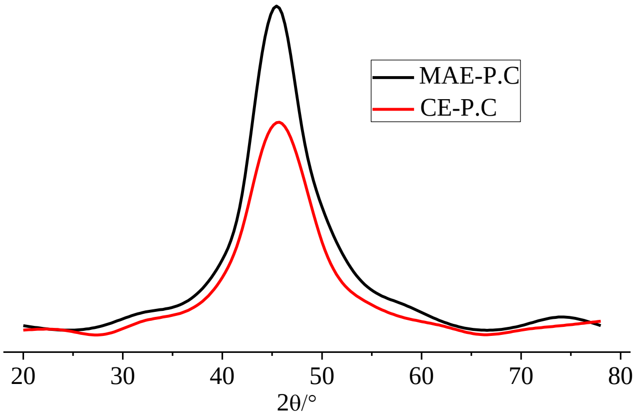


Figure 3: XRD patterns of Ni-P coatings on zinc alloy by MAE and CE plated coating

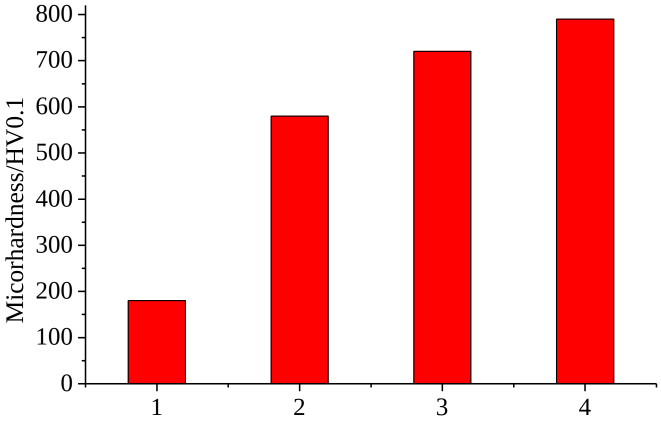
Figure 3 shows the X-ray diffraction patterns of the traditional and mechanical-attribution-based electroless plating. It can be seen from the figure that when 2θ=42-47°, the diffraction peak appears in the nickel diffraction direction and the coating shows a typical amorphous structure. The peak in the traditional electroless plating tends to be sharp, while in the mechanical-attrition-based method, this characteristic is even more obvious, indicating that mechanical attrition reduces the amorphism of the electroless coating so that the coating achieves the amorphous conversion from high to low energy.

The EDS results of the two methods are shown in Table 2. The P content in the coating in the mechanical-attribution-based method is about 1.01% less than that in the traditional method, while the Ni content is increased to 92.52%. The decrease in the P content makes the amorphous structure in the coating convert to crystalline structure.

Table 2: EDS analysis of Ni-P coatings (%)

Element	P	Ni
MAE-plate coating	7.48	92.52
CE-plate coating	8.49	91.51

The microhardness in the traditional and mechanical-attribution-based method is shown in Figure 4. When there is any coating, the mechanical-attrition-based electroless coating is harder than the traditional electroless plating, which is 745HV0.1, and in the traditional electroless plating, the hardness can reach 776 HV0.1 only after being thermally treated at 250°C, indicating that the mechanical attrition can greatly improve the hardness of electroless coatings. The is because the continuous impact of glass balls in the mechanical attrition results in plastic deformation, and eventually forms a uniform stress layer after a long time of attrition. At the same time, the deposition of single atoms leads to the continuous growth of the coating and makes the coating transform to the crystalline state.



1-Substrate; 2-CE; 3-MAE; 4-CE(250°C)

Figure 4: Microhardness of the substrate and coatings

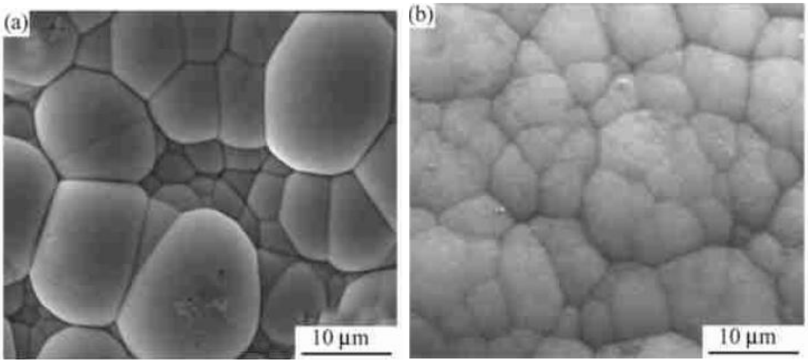
3.2 Analysis on the effects of mechanical attrition on the properties of electroless magnesium alloy coating

Based on the previous sections, we further analyze the effects of mechanical attrition on the properties of electroless magnesium alloy coating.

Figure 5 shows the scanning electron microscope results of the traditional electroless plating and the mechanical-attrition-based electroless plating. From the figure, it can be seen that the surface of the magnesium alloy coating shows a “cauliflower-like” structure. The “cauliflower” structure on the traditional electroless coating is not uniform, while the surface structure after the mechanical attrition is relatively smooth and flat, with tighter particle binding and no obvious pores. The thickness of the electroless coating through mechanical attrition is about 5μm less than that of the traditional coating, with lower roughness.

Figure 6 shows the micro-hardness test on the Ni-P coating. In the figure, Trad-1 represents the Ni-P coating in the traditional electroless plating method while Trad-2 stands for the traditional Ni-P electroless plating plus heat treatment at 400°C; MG-1 represents the mechanical-attrition-based electroless Ni-P plating; and MG-2 represents the mechanical-attrition-based electroless Ni-P plating plus heat treatment at 400°C. It can be seen from the figure that the hardness of the coating after the heat treatment at 400°C is improved to some extent compared with that at room temperature. The hardness of the traditional electroless coating after the heat treatment at 400°C is increased by 153HV0.1 on average; and that in the mechanical-attrition-based electroless plating after the 400°C heat treatment is increased by 290HV0.1 on average. Meanwhile, both after the heat treatment at 400°C, the hardness of the mechanical-attrition-based electroless plating is about

304HV0.1 greater than that of the traditional one. The results also show that when the content of sodium hypophosphite in the solution increases, the hardness of the coating also increases.



(a) Traditional electroless plating (b) Mechanical grinding

Figure 5: Coating surface on magnesium alloy between traditional and mechanical grinding electroless plating

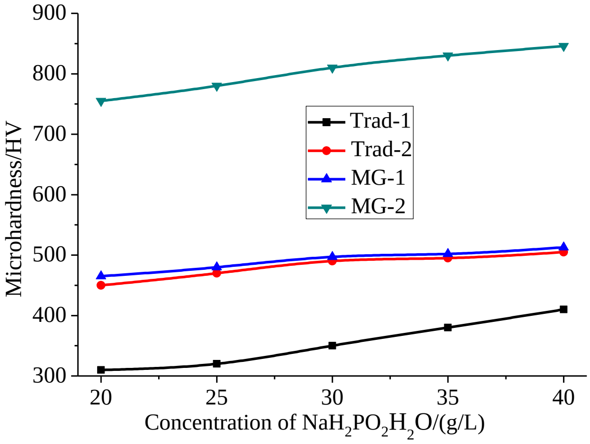


Figure 6: Micro-hardness test results of Ni-P coatings with different $NaH_2PO_2.H_2O$ contents

Amorphous Ni-P coating has an unstable mechanical shape in high temperature. Using the traditional chemical plating to coat the magnesium and zinc alloy can easily cause the coating to peel off or fail, while in the mechanical attrition method, the glass balls continuously impact the coating, increasing the atomic energy in the coating and making the coating transform from being amorphous to being crystalline. The mechanical-attrition-based electroless plating not only increases the chemical properties and abrasive resistance of the coating, but also inhibits the galvanic corrosion between the coating and the magnesium and zinc alloy.

4. Conclusions

In this paper, we design a method that uses mechanical attrition to apply the electroless plating on the alloy surface, and compare the effect of electroless plating with that of traditional electroless plating. Based on the comparison results, we study the effects of mechanical attrition on the properties of electroless alloy plating during the electroless Ni-P plating. And the conclusions are as follows:

(1) Mechanical attrition changes the growth pattern of Ni and P atoms in the traditional electroless plating. The resulting impact causes more energy to be transferred to the surface of the coating and brings plastic changes to the surface. The increase of the ion transport rate in the solution helps improve the uniformity of the coating. After mechanical attrition, the coating shows a very smooth and flat surface, indicating that this method effectively increases the coating density and at the same time saves a lot of coating resources.

(2) Mechanical attrition reduces the amorphism of the electroless coating so that the coating achieves the amorphous conversion from high to low energy. It can also make the zinc alloy coating harder and more resistant to corrosion.

(3) The surface of the magnesium alloy shows “cauliflower-like” structure. The “cauliflower” structure on the traditional electroless coating is not uniform, while the surface structure after the mechanical attrition is relatively smooth and flat, with tighter particle binding and no obvious pores. Amorphous Ni-P coating has an unstable mechanical shape in high temperature. Using the traditional chemical plating to coat the magnesium and zinc alloy can easily cause the coating to peel off or fail, while in the mechanical attrition method, the glass balls continuously impact the coating, increasing the atomic energy in the coating and inhibiting the galvanic corrosion between the coating and the magnesium alloy.

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