Vol. 7 № 3 **Trans. Nonferrous Met. Soc. China** Sep. 1997

ELECTRODEPOSITION OF AMORPHOUS Ni-P ALLOY COATINGS①

Fang Zhaoheng
Institute of Chemical Metallurgy, Chinese Academy of Sciences, Beijing 100080

ABSTRACT A process to produce amorphous Ni-P alloy coatings from nickel sulfate and hypophosphite bath by electrodeposition was investigated. The influence of the concentration of phosphorous and pH in the bath, the plating temperature and the organic additives ware determined. The X-ray energy dispersive spectroscopy (EDAX) was used to evaluate the composition of the alloy coatings. The alloy coatings containing over 10% ~ 12% P(mole percent) were distinguished to be amorphous by X-ray diffraction, they were found to have better corrosion resistance than the conventional Ni-Cr stainless steel in 5% HCl, H_2SO_4, NaCl and NaOH solutions. The effective mechanism of organic surfactants was studied by voltammetry on a copper rotating disk electrode.

Key words electrodeposition amorphous alloy coating nickel phosphorus

1 INTRODUCTION

Amorphous materials have a short-range order only over a few atomic distances and lack a long range atomic order characteristic. They therefore possess uniqueness to their structure and isotropy to their properties, and have not disadvantages characterizing crystalline materials, such as crystal boundary, lattice defect, segregation, crystal anisotropy and so on.

Amorphous metals or alloys are usually produced by rapid solidification of liquid components. In the area of surface processing thin layers of amorphous alloys can be formed by electrodeposition, this technology shows a simple way to be easy to control the layer composition and structure, to plate coatings on the surface of various parts with various shapes or large size, made by metals, alloys, or plastics and other non-metal materials. It has advantages to be suitable for formation of coatings with non-equilibrium phases and for scale-up production in industrial lines.

Since nickel is sensitive to be oxidized in the atmosphere and tend to build up a passivated film on the surface, its coatings have superior resistance to the corrosion from moist atmosphere containing alkaline or acid components. However, these coatings are micro-porous, need multi-plating to build enough thickness to act as defense film. An effective way to improve the property of corrosion resistance is the technique of alloying. Ni-P alloy coating is the most wide-used way[1]. Ni-P alloys are easy to be became amorphous. This paper describes the process to produce amorphous coatings by electrodeposition, and the effects of various factors in the process, the conversion role between crystalline and amorphous of the alloy, as well as the corrosion behaviors of amorphous coatings.

2 PRINCIPLES AND EXPERIMENTAL

Alloy coatings are formed from an electrolyte by simultaneous reduction and codeposition of component metal ions. P in the coatings is resulted from reduction reactions of hypophosphite or/and phosphorus, as

$$H_2PO_3^- + 4H^+ + 3e^- \rightarrow P + 3H_2O \qquad (1)$$

$$E_0/V = -0.419(r), -0.467(w)$$

$$H_2PO_2^- + 2H^+ + e^- \rightarrow P + 2H_2O \qquad (2)$$

$$E_0/V = -0.248(r), -0.391(w)$$

---

① Received Aug. 20, 1996; accepted Dec. 10, 1996

It may have a step reaction during the reduction process of the phosphorus, i. e.

$$H_2PO_3^- + 2H^+ + 2e^- \rightarrow H_2PO_2^- + H_2O \quad (3)$$

As a component of the alloy, nickel ions are simultaneously reduced from bath, for example,

$$Ni^{2+} + 2e^- \rightarrow Ni \qquad E_0/V = 0.250 \quad (4)$$

In alloy plating, the conditions for simultaneous codischarge and codeposition of metal ions depend on the cathodic behavior and concentration of individual cations, pH and additives in the bath. These conditions have not been prescribed by the theory on alloy plating so far and would be determined by tests.

The by-reactions on the cathode are reduction of hydrate protons, as

$$2H^+ + 2e^- \rightarrow H_2 \quad (5)$$

$$H^+ + e^- \rightarrow H_{ads} \quad (6)$$

These reactions result in decreasing the current efficiency, in increasing structure defects as gas holes or pin-pricks in coatings, and therefore in weakening the corrosion resistance and deteriorating the surface appearance. It also results in increasing the internal stress in coatings.

Electrodeposition was performed under constant current conditions. The Ni and Pt plate was used as anode electrode, and Cu plate as cathode. The Cu plates were emerged in a dilute HNO_3 solution for 10 min., and then washed subsequently with de-ionized water and acetone prior to plating. Elemental composition of coatings was determined by X-ray energy dispersive spectroscopy analysis (EDAX), and the structure by X-ray diffraction (XRD).

3 RESULTS

3.1 Effect of bath composition

A basic bath, which consists of 240 g/L $NiSO_4 \cdot 6H_2O$, 50 g/L $NiCl_2 \cdot 6H_2O$, 30 g/L H_3PO_3 and 50 g/L H_3PO_4, was used in the study. The pH was adjusted with phosphate acid and sodium alkaline solution, and was maintained at 2.5 ±0.1. The phosphorus content in coatings, as determined by EDAX, was found to be increased with enhancing concentration of hypophosphorus in the bath, as shown in Fig. 1. The coatings, in which over 10% ~ 12% P (mole percent) was contained, were distinguished as amorphous structure by XRD, as shown in Fig. 2.

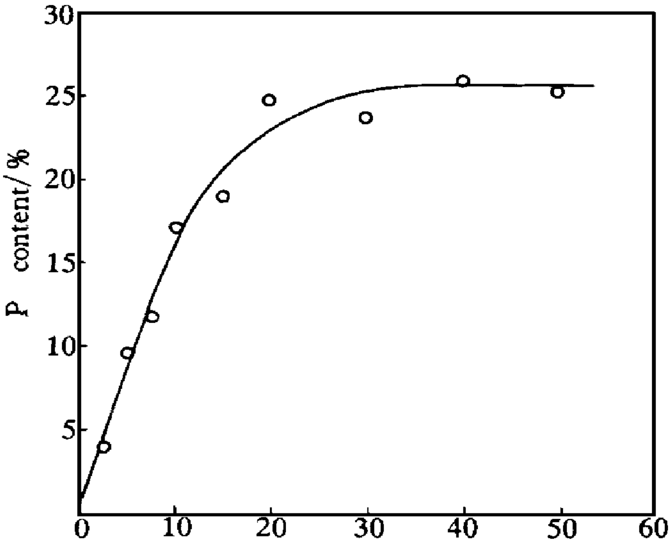

Fig. 1 The correlation between P contents in coatings and the concentration of hypophosphorus in the bath

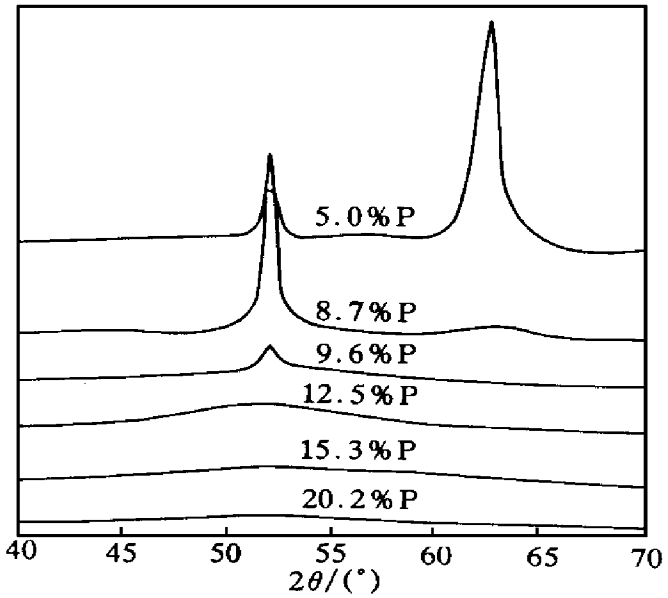

Fig. 2 The diffraction patterns of coatings containing various P

3.2 Effect of additives

It is known, the surfactants and other organic additives have strong influence on the grain size and the appearance of coatings[2-4]. In this study several additives were tested, among them the dodecyl sulfate and saccharine were found to be more effective.

It was observed that the appearance of coatings was much more improved when electrodeposition performed in a bath containing a few content of dodecyl sulfate. As a surfactant, dodecyl sulfate is adsorbed on the surface of the cathode and plays a role as wetting agent to reduce boundary tension between the cathode surface and the electrolyte. The hydrogen bubbles, evolved on the cathode surface during deposition, would be therefore released more easily from it, as a result, the structure defects in coatings would be minimized.

The test results show that the phosphorus content in coatings would decrease with enhancing concentration of saccharine in the bath, as seen from Fig. 3. A trace of sulfur may contained in the coatings because saccharine includes a $-SO_3$ group. This therefore affects the chemical and physical properties of coatings. However, the sulfur content in the coatings is too low to be determined by EDAX in the study.

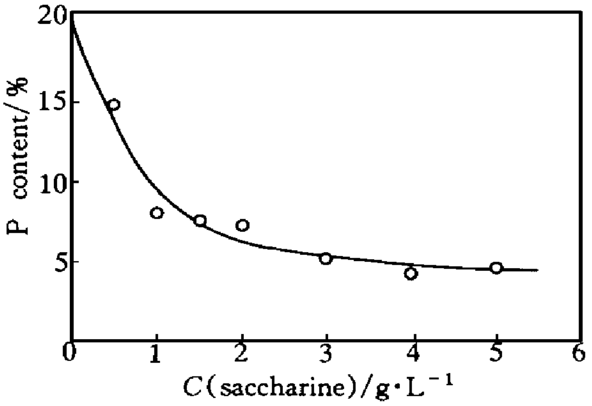

Fig. 3 Correlation of P content in coatings with the concentration of saccharine in bath

Saccharine is used as brightening agent in the bath. It increases the polarization of the cathode and plays a role in refining grain of the deposit[4]. Test results show that the critical P content which determines the conversion from crystal to amorphous structure in coatings is reduced when a certain quantity of saccharine is added to the bath. As observed from XRD, the coatings containing over 8% P would become amorphous structure when 1.5 g/L saccharine is contained in the bath.

3.3 Effect of plating temperature

The test results indicate that phosphorus content in coatings increases a little with increasing plating temperature. In the conditions under study the chemical composition of coatings would not change in the temperature range from 35 ℃ to 55 ℃.

3.4 Current efficiency

Based on the reactions (1) to (3) above, the current efficiency is calculated from the increased weight of the cathode and the electricity measured with a coulometer during plating. These tests were carried out at 1 A current for 25 min. The results show that the current efficiency was reduced with increasing phosphorus content in coatings.

The current density might be another active factor affecting the current efficiency. As increasing the current density, the efficiency was decreased.

3.5 Cathodic polarizing behavior in plating

The cathodic polarization in plating was investigated by voltammetry in a cell, in which a copper rotating electrode was used as the working electrode, a Pt plate as the auxiliary, and a calomel electrode as the reference. As observed with SEM, the appearance and composition of the coatings were affected by the rotating rate. It was indicated that the composition of coatings would not change when the rotating rate higher than 800 r/min was used. The voltammetry curves are shown in Fig. 4.

As shown in Fig. 4, the curve from addition of saccharine would shift to the negative direction. It suggests that saccharine inhibits discharge of hydrate protons on the cathode and therefore makes effect on improving the physical properties of coatings. In the case under the study, the current efficiency is less than 40%, and the discharge of protons is a dominant reaction in plating.

3.6 Corrosion rate of coatings

Based on ASTM31-72 criteria, the corrosion behaviors of amorphous Ni-P coatings in different solutions were determined with a classical method of weight losses in the solution, and the test results are listed in Table 1.

Table 1 Corrosion rate of amorphous Ni-P coatings in various solutions

Solution	Test time/d	Corrosion rate/mm•a^{-1}
5% HCl	30	0.073
5% H_2SO_4	30	0.009
5% NaOH	30	0.001
5% HNO_3	10	2.12
5% NaCl	30	0.002

It was indicated that the corrosion resistance of the amorphous coatings was more superior than that of the conventional Ni-Cr stainless steel in the non-oxidizing solutions, such as dilute HCl, H_2SO_4, NaOH and NaCl solutions. It is known, the corrosion rate of the stainless steel in those solutions is higher than 1.5 mm/a.

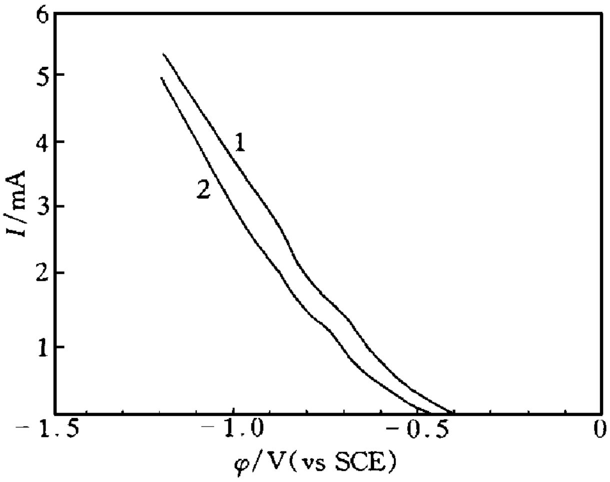

Fig. 4 Cathodic polarizing curves
1 —without organic additives;
2 —with 2 g/L saccharine added

4 DISCUSSION

The test results show that the chemical composition of Ni-P alloy coatings mainly depends on the concentration of Ni and hypophosphorus in the bath, the current density and the organic additives.

By determining the composition and diffraction patterns, amorphous structure of coatings can be observed, as P content in coatings is above a certain quantity; but it is no possibility to form amorphous structure when coatings contain a P content lower than a critical value which is 10% ~ 12% P in the bath without any additive.

This phenomenon suggests that P plays a role in refining deposit grains. In the codeposition process a nickel ion receives two electrons at an active center on the cathode surface and becomes nickel atom, the nickel atom then moves onto a point of the crystal lattice by atomic surface diffusion. Reduction and codeposition of phosphorus might inhibit surface diffusion of nickel atoms and growth of crystal nuclei. In the result, the rate of nucleus growth goes slower when P is more deposited. With increasing of P content in alloy, the rate of nucleus formation is much higher than the rate of nucleus growth, and finally no nucleus is in growthing when a critical P content is achieved in deposits. In this point, an amorphous structure that has a short-range order only over a few atomic distances and lacks a long range atomic order characteristic is formed. For the same reason, some type of additives, e. g. saccharine, plays the role of refinement of grains and then makes the critical value of amorphous formation decreased.

REFERENCES

1 Wang Yihe *et al*. Amorphous Alloys, (in Chinese), Beijing: Publishing House of Metallurgy Industry, 1989.

2 Oniciu L *et al*. J Applied Electrochem, 1991, 21: 565.

3 Krauss C J. J Metals, 1976, 28: 4.

4 Franklin T C *et al*. J Electrochem Soc, 1988, 135 (7): 1638.

(Edited by Wu jiaquan)