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Deposition and Characterization of Electroless Nickel-Phosphorus-Boron Coatings From Acidic Bath

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Electroless plating is a chemical redox process, which depends upon the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent and the subsequent deposition of the metal without the use of electrical energy. During the past five decades electroless plating has gained popularity due to its ability to produce coatings with high performances. Although there exists variety of electroless plating process such as electroless nickel, copper, silver, platinum, palladium, gold, etc., electroless nickel has proved its supremacy for producing coatings with excellent corrosion and wear resistance^[1~2].

Electroless nickel are mostly classified as nickel-phosphorus, nickel-boron, and pure nickel based on the respective reducing agents used in the bath, i. e. hypophosphite, borohydride or dialkyl amino borane, or hydrazine. These processes have often involved solutions containing a single reducing agent. Recently a combination of two or more reducing agents in the electroless bath has been attempted to develop nickel-phosphorus-boron coatings^[3~5]. These studies, however, have been conducted in alkaline bath, which is more sensitive to decomposition and does not function below 80 °C. Therefore, a more stable electroless nickel plating bath needs to be used to improve alloy properties. In this paper, a stable acidic bath for Ni-P-B alloys with both sodium hypophosphite and sodium borohydride as reducing agents has been developed and the deposits with various boron content have been obtained. The effects of codeposition of boron on the structure and properties of the deposits have also been investigated.

1 Experimental

The solutions used for the Ni-P-B deposition were composed of 30g/L NiSO₄·6H₂O, 20 g/L NaH₂PO₂·H₂O, 0.2~1.0 g/L NaBH₄, 20 mL/L HCOOH, 10 g/L CH₃COONa·3H₂O and 10 mL/L additive EN07. The pH value of the solution was adjusted with NH₃·H₂O and was controlled in the range of 5.5~6.0. Both sodium hypophosphite and sodium borohydride were used

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as the reducing agents. The quantity of borohydride alone was varied to produce deposits with various boron content. The electroless Ni-P coating, for comparison, were deposited from the bath composed of 30 g/L $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 20 g/L $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, 16 g/L $\text{CH}_3\text{CH}(\text{OH})\text{-COOH}$, 8 g/L $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, pH 4.8 ~ 5.0. All solutions were prepared using reagent grade chemicals and distilled water. The deposition was carried out on low carbon steel or stainless steel substrates for 90 minutes at 88 °C with stirring.

The chemical composition of the deposits was determined by inductively coupled plasma (ICP) emission spectrometry and atomic absorption spectrometry. Heat treatment was carried out in a nitrogen atmosphere with a 10 °C/min heating rate for 1 h at temperatures of 200 °C, 300 °C, 400 °C and 500 °C respectively. Hardness test was carried out using a Vickers diamond microhardness meter under a load of 25 grams. X-ray diffraction data were collected using D/max-RC X-ray diffractometer with Cu K α radiation. For transmission electron microscopic (TEM) studies, the separated deposits from stainless steel substrates were cut to 3mm diameter discs, both sides of which were thinned by mechanic polishing and further thinned to a suitable thickness by jet polishing. The atomic force microscopic (AFM) tests were carried out using Model NANOSCOPE IIIa made by Digital Instrument.

Potentiodynamic polarization studies for various deposits were made in 3.5 wt % NaCl and 40 wt % NaOH solutions at ambient temperature using CHI-660 potentiostat. The specimens were masked with lacquer so that only 1 cm² area was exposed to the electrolyte. In 3.5 wt % NaCl solution, a saturated calomel electrode (SCE) was used as reference electrode whereas a Hg/HgO electrode was used in 40wt. % NaOH solution. The counter electrode was a coil of platinum 2 × 4 cm. The corrosion potentials (E_{corr}) and corrosion currents (i_{corr}) were measured from polarization curves using the Tafel extrapolation method.

2 Results and Discussion

Numerous preliminary experiments for choosing a suitable complexing agent have been carried out for a stable acidic electroless Ni-P-B process. The results show the bath stability, deposition rate, and properties of the deposits are greatly influenced by the type of the complexing agent and its quantity. We have also achieved an effective additive EN07 to further improve the bath stability. The NaBH_4 concentration in the bath has a great effect upon the chemical composition of the deposits. Fig. 1 shows an increase of NaBH_4 concentration in the bath results in great increase in boron

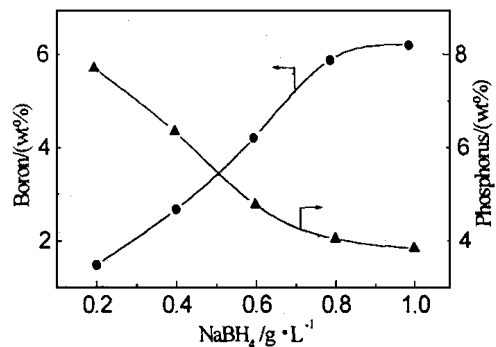


Fig. 1 Dependence of boron and phosphorus content of Ni-P-B deposits on NaBH_4 concentration in the bath

content of Ni-P-B deposits and a subsequent decrease in phosphorus content. The NaH_2PO_2 concentration in the bath, however, has an opposite effect on the chemical composition of the deposits. The results also show that the NaBH_4 concentration has little effect on the deposition rate, but the tendency for bath decomposition increases with increasing the NaBH_4 concentration. All the electroless Ni-P-B deposits obtained are uniform. They are semibright in appearance and are highly adherent when tested by the bend test and the thermal shock method. Table I shows the chemical composition of Ni-P-B deposits obtained by varying the NaBH_4 concentration in the bath.

Tab. 1 Chemical composition of Ni-P-B and Ni-P deposits

Specimen	$\text{NaBH}_4/\text{g L}^{-1}$	Chemical composition		
		Ni	P	B
a	0	91.80	8.20	—
b	0.2	90.96	7.78	1.26
c	0.4	89.80	6.83	3.37
d	0.8	90.07	4.04	5.89

The atomic force microscopy provides a powerful means of characterizing the microstructure and growth process of the films deposited by both chemical and electrochemical methods^[6~7]. Fig. 2 shows the AFM images of electroless Ni-P and Ni-P-B coatings with various boron content. When the deposit contains only nickel and phosphorus, the surface morphology of deposit is more uniform and smooth than that of the deposits in which boron is incorporated (Fig. 2a). When the boron content is low, as shown in Fig. 2b, the deposit is composed of phosphorus-boron islands with fine nickel nodules in random internal orientation. When the boron content increases, both phosphorus-boron islands and nickel nodules become larger and the deposits show a coarse grain size and less uniform crystal structure (Fig. 2c). This may be due to a distortion in the lattice of the deposited nickel because of codeposition of boron.

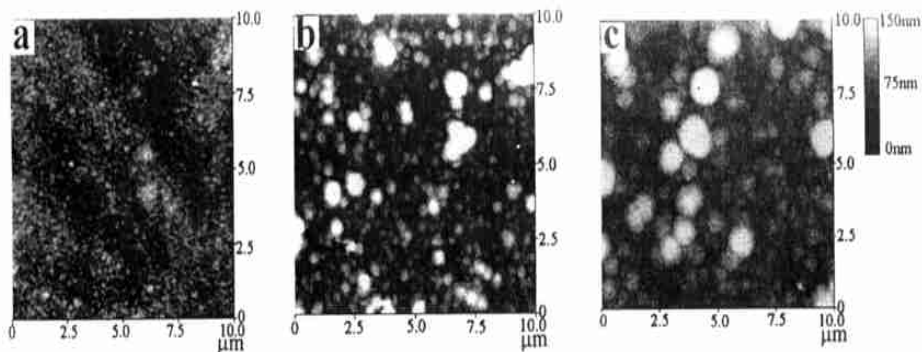


Fig. 2 AFM images of electroless Ni-P and Ni-P-B deposits with various boron content.

(a) Ni-8.20P (b) Ni-7.78P-1.26B (c) Ni-6.83P-3.37B

The hardness of the as-deposited Ni-P-B coatings with various boron content is shown in Fig. 3. The results show that the Ni-P-B coatings have higher hardness compared with Ni-P deposit, and the hardness increases with the boron content increasing. The increase in hardness of Ni-P-B coatings, as compared with Ni-P coatings, is probably attributed to the incorporation of boron in the Ni-P matrix^[8]. Boron is expected to occupy the interstitial voids of the nickel, causing a distortion in the lattice of the deposited nickel, thereby impeding the dislocation movement in the deposit, which is shown in terms of increased hardness and better wear resistance. On the other hand, earlier reports^[2] show the electroless Ni-P deposits with lower phosphorus possess higher hardness. So a great decrease of phosphorus in the deposits, which is caused by the incorporation of boron, may be another factor of causing higher hardness.

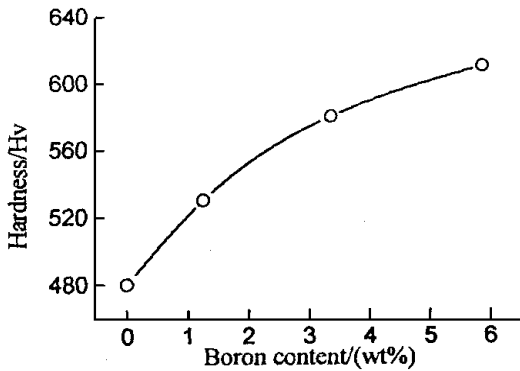


Fig. 3 Hardness of electroless Ni-P-B deposits as a function of boron content

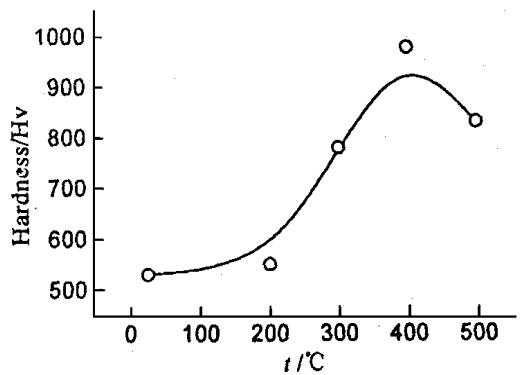


Fig. 4 Effect of heat treatment on hardness of the electroless Ni-7.78P-1.26B deposit

Fig. 4 shows variation of hardness of the Ni-7.78P-1.26B deposit with heat treatment temperature. There is not much change in the hardness at temperatures below 200. With further increase in temperature the hardness increases rapidly as its structure begins to change. Rapid increase in hardness is noticed up to a temperature of 400. Over this temperature the hardness decreases. It is evident that the hardness follows typical precipitation hardening behavior with the peak hardness temperature corresponding well with the completion of the precipitation reaction. After the peak hardness reaches, further annealing results in decrease of hardness, a result of general growth and conglomeration of the precipitates associated with the softening of the matrix. Previous studies on Ni-P-B de-

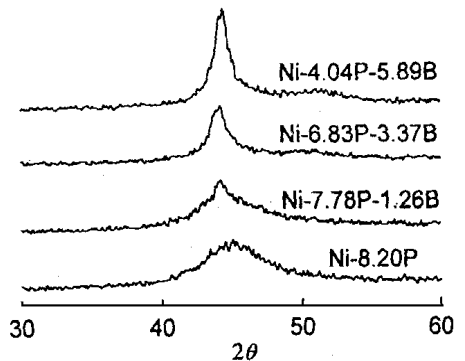


Fig. 5 X-ray diffraction patterns of Ni-P and Ni-P-B deposits with various boron content

posits, showed the hardened phase of Ni_3P and Ni_3B precipitated along with crystalline nickel when heat treated^[3], which supports the observation in this work. The variation of hardness of Ni-P and other Ni-P-B deposits obtained with heat treatment temperature also follows above tendency.

Fig. 5 shows the X-ray diffraction patterns(XRD) of the as-plated coatings with boron contents. The X-ray diffraction pattern of Ni-8.20P deposit has only a single broad peak around a 2θ value of 45° . The peak broadening can be attributed to the amorphous nature of the deposit. This is in good agreement with the literature where the deposits with more than 7 wt % phosphorus are shown amorphous in the as-plated form^[9]. When boron is incorporated into the deposits, relatively sharp XRD patterns of the deposits are observed, indicating the presence of microcrystalline and amorphous mixture. Moreover, the increase in boron content in the deposits results in a much sharper pattern. The formation of microcrystalline phase in Ni-P-B deposits may be due to the great decrease in phosphorus in the deposits caused by codeposition of boron.

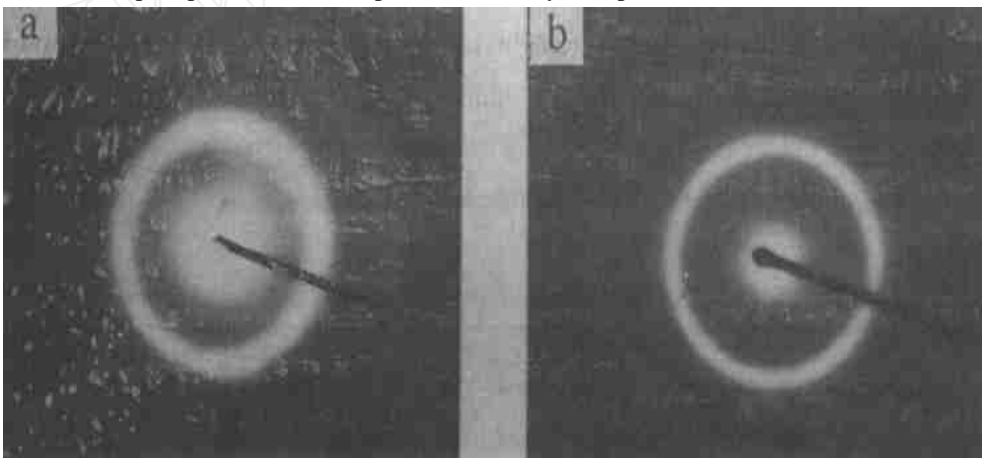


Fig. 6 Selected area diffraction patterns of Ni-P and Ni-P-B deposit

(a) Ni-8.20P (b) Ni-7.78P-1.26B

The TEM micrographs of as-plated Ni-P-B deposits with various boron content show that the deposit with higher boron content presents larger grain size. This result is consistent with AFM observation. The diffraction pattern from Ni-P deposit exhibits a diffuse ring pattern (Fig. 6a), which is typical of an amorphous structure and supports the from X-ray diffraction measurements. However, the diffraction patterns from all Ni-P-B deposits show a diffuse inner ring and a relatively sharp outer ring (Fig. 6b), and the outer ring becomes much sharper with increasing boron content. The presence of such sharp ring in the diffraction patterns indicates that the Ni-P-B deposits are not fully amorphous phases. This result is also in good agreement with the X-ray diffraction measurement.

The corrosion resistance of Ni-P and Ni-P-B coatings in 3.5 wt % NaCl solution and 40 wt % NaOH solution was investigated by electrochemical methods. The results in Table II show that there is a great improvement in corrosion resistance of Ni-P-B coatings compared with Ni-P deposit. With the boron content in the deposits increasing from 1.26 to 5.89 wt %, the corrosion current density decreases and the corrosion potential shifts toward positive in both test solution. This result seems to be inconsistent with the XRD and TEM results given in this paper, which show the deposit with higher boron content exhibits more microcrystalline structure and usually reveals less corrosion resistance^[10]. Mital and Shrivastava^[8] investigated the corrosion resistance behavior of Ni-P-B coatings by salt spray test. They found the deposits with a certain quantity of boron yielded superior corrosion resistance; however, with an increase of B/P ratio, more corrosion spots were seen in the tested samples. This observation is somewhat different from our results.

The role of phosphorus in the anodic inhibition of an amorphous Ni-P alloy in acidic and alkaline electrolytes have been investigated by many authors^[11~14]. A commonly accepted mechanism is that phosphorus can accelerate the early stage of dissolution during passivation and thereby cause enrichment of the formation of element phosphorus in the resultant passive film. However, there are little reports about the role of boron in the improvement of corrosion resistance of such amorphous alloys as Ni-B and Fe-B. Therefore, it is necessary to deeply study the effects of boron on properties of Ni-P alloys, the further investigations are in progress.

Tab. 2 Corrosion parameters from potentiodynamic polarization data

Specimen *	3.5 wt % NaCl solution		40 wt % NaOH solution	
	$E_{\text{corr}}/\text{mV (vs. SCE)}$	$i_{\text{corr}}/\mu\text{A cm}^{-2}$	$E_{\text{corr}}/\text{mV (vs. Hg/HgO)}$	$i_{\text{corr}}/\mu\text{A cm}^{-2}$
a	- 425	12.7	- 228	2.9
b	- 369	3.6	- 161	1.8
c	- 278	1.7	- 128	1.1
d	- 248	0.5	- 117	0.2

* The specimen in this table is consistent with that in Table 1

3 Conclusions

Electroless Ni-P-B coatings with various boron content have been deposited from a stable acidic bath which contains both sodium hypophosphite and sodium borohydride. The introduction of NaBH₄ into the bath has led to a marked decrease of phosphorus content in the deposits. Compared with Ni-P deposit, the Ni-P-B deposits have shown a coarse grain size and less uniform crystal structure, which is characterized by AFM observation. Both X-ray diffraction and selected

XRD diffraction reveal that the as-deposited Ni-P-B coatings are a mixture of microcrystalline and amorphous phase in nature. The hardness of the Ni-P-B deposits increases with increasing the boron content in the deposits, and follows typical precipitation hardening behavior when heat treated. Potentiodynamic polarization studies in both 3.5 wt % NaCl solution and 40 wt % NaOH solution show that the co-deposition of boron can significantly improve corrosion resistance of the electroless Ni-P deposit, which increases with increasing the boron content in the deposit.

Key words: Electroless plating, Ni-P alloy, Ni-P-B alloy, Sodium borohydride, Sodium hypophosphite, Electrochemical corrosion

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酸性溶液化学镀 Ni-P-B 合金及结构性能表征

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摘要: 联用次亚磷酸钠和硼氢化钠两种还原剂, 从酸性镀液中沉积出不同硼含量的 Ni-P-B 镀层, 并用原子力显微镜、X-射线衍射、透射电镜、动电位扫描等实验技术对其镀态结构及性能进行了表征。实验表明, 镀液中硼氢化钠含量对沉积速度影响不大, 但能显著影响镀层的化学组成。硼的共沉积使镍晶格点阵产生扭变, 导致镀层晶粒增大, 表面粗糙, 颗粒分布不均匀, 并使镀层由非晶态向微晶结构转变, 且微晶成分随镀层中硼含量的增加而增多。Ni-P-B 镀层的硬度随镀层中硼含量的增加而增大, 热处理能显著提高镀层的硬度, 且服从沉淀硬化机理。在 3.5 wt % NaCl 和 40 wt % NaOH 两种介质中, Ni-P-B 合金的耐腐蚀能力优于 Ni-P 合金。镀层中硼含量越高, 其耐腐蚀能力越强。

关键词: 化学镀, Ni-P 合金, Ni-P-B 合金, 硼氢化钠, 次亚磷酸钠, 电化学腐蚀

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