# Structure of Electroless Nickel Deposits From Baths Containing Sodium Hypophosphite And Potassium Borohydride

By A. Talaat El-Mallah, M. Hassib Abbas, M. Farid Shafei, M. El-Sayed Aboul-Hassan and I. Nagi

The results of scanning electron microscopy and thermal analysis of deposits obtained in electroless baths containing sodium hypophosphite and/or potassium borohydride indicated that Ni-P, Ni-B and Ni-P-B deposits were amorphous. Heat treatment at 290-300° *C* induced little crystallinity in Ni-P deposits but precipitated Ni<sub>3</sub>B in Ni-B and Ni-P-B deposits. Heating to 430° C caused the formation of NiP<sub>2</sub> in Ni-B and Ni-P-B alloys.

ince the discovery of electroless (autocatalytic) nickel plating by Brenner and Riddell' in 1944, its use has continued to grow because of its useful combination of properties and characteristics. Strong reducing agents used for electroless nickel plating include hypophosphite ions, borohydride ions, boranes and hydrazine. Ni-P alloy is produced in baths prepared with hypophosphite ions. Ni-B alloys are obtained in solutions containing borohydride ions or boranes, whereas relatively pure nickel is deposited in baths that use hydrazine. Most studies have involved solutions containing a single reducing agent whereas baths using more than one reductant have been somewhat neglected. Little information is available on Ni-P-B alloy deposition in baths containing both hypophosphite and borohydride ions, for example.

Amino boranes are sometimes added to borohydride baths<sup>2</sup>to enable operation in neutral and, acid solutions, whereas solutions prepared with borohydride ions alone are highly alkaline.

#### **Experimental Procedure**

In our studies of nickel deposition in baths prepared with hypophosphite and/or borohydride ions, rolled, low-carbon steel samples were catholically degreased in an alkaline solution, rinsed and treated for 1 min in 20 percent hydrochloric acid at room temperature. Thereafter, the specimens were rinsed thoroughly in distilled water, plated in an electroless bath, quickly rinsed first in tap water and then in distilled water, dried and stored in a desiccator if not immediately examined by scanning electron microscopy (SEM) or X-ray diffractometry.

An X-ray diffractometer was used for identifying the phases present in deposits before and after heat treatment. Co K $\alpha$  radiation filtered with Fe was adopted at 40 kV with a 25-mA current. Scanning speed was 2 degrees/min.

Cross sections of deposits were metallographically polished and examined by SEM in the unetched condition. Differential thermal analysis (DTA) and thermogravimetry (TG) data were derived by using 530 mg of powdered sample heated at 10° C/min to 950° C with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as a reference material.



Fig. 1—X-ray diffraction patterns of unheated Ni-P (top) and Ni-P deposit heat treated one hour at 300° C (bottom).



Fig. 2—X-ray diffraction patterns of unheated Ni-B (top) and Ni-B deposit heat treated one hour at 300° C (bottom).

An aluminum foil strip was used as a carrier material for the determination of chemical and thermal analyses of the unheated Ni-P-B alloy deposits listed in Table 1. These deposits were produced by using the procedure detailed in the Appendix.<sup>3</sup>The nickel and phosphorus contents of the deposits were determined gravimetrically. Boron was calculated by weight difference.

The solutions for depositing Ni-P alloys contained 0.6 M formic acid. Baths for plating Ni-B or Ni-P-B contained 0.6 M ethylene diamine. Table 2 gives the concentrations of the reducing agents in all of the 0.1 M nickel chloride solutions prepared for SEM and X-ray diffraction studies. Good deposits were obtained when the ratio of the solution volume to specimen surface area was 25 cm<sup>3</sup>/cm<sup>2</sup>. No agitation was used.

## **Results and Discussion**

Figures 1 and 2 show the X-ray diffraction patterns of unheated Ni-P and Ni-B deposits, respectively. Two diffused lines corresponding to (111) and (200) Ni are evident in Fig. 1 but only one diffused line corresponding to (111) Ni exists in Fig. 2. Materials with X-ray diffraction curves showing nothing more than one or two broad maxima can be characterized as amorphous although they may have a microcrystalline structure. The X-ray diffraction curves for unheated Ni-P-B deposits in Figs. 3 and 4 (top) indicate an amorphous condition. These results are con-

		Table 1		
			warmen and a second sec	and statement of the second
	Compo	sition of Ni-I	P-B Denosi	1e
	Compo		and the second second second	er egste ogs round
6 . J. 25.		and a state of the second second		
	All the second second		Blatal In	Dependent**
1 m 1	NaH.D	0.* KHR.*	werai II	Debosit
요즘 같이 많다.	INGI 12F		이 아이는 아이는 아이는 아이는 아이는 아이는 아이는 아이는 아이는 아이	
Samn	ole conc	M conc I		R
Amula				Persected in the second
	a set in the set of the	State State State State		
	61	0.015	950	169 031
		0.010	JOHN MARK 18	
8	0.2	0.015	91.75	3.04 2.21
en en fi	영양은 집에 그 바퀴	. 2011년 - 1921년 1911년 1911년 1911년 - 1911년 19	per su di	Philosophic and the second
1	a se an is national and a second		A State of the second second	
*Conr	entration in ele	ctroless solution		

\*\*Weight percent

 Table 2

 Electroless Nickel Baths Used for Preparing

 Deposits for X-Ray and SEM Examinations\*

		KHR.	Plating time	e, min
Sample	conc., M	conc., M	for X-ray f	or SEM
1. Ni-P	0.1		90	90
2. INI-P 3. NI-B	U.1	0.015	90 45	90 120
4. NI-B 5. NI-P-B	0.1	0.015 0.015	45 45	120 120
6. NI-P-B 7. NI-P-B	0.1 0.1	0.015 0.015	45 45	120 120
8. Ni-P-B 9. Ni-P-B	0.2 0.2	0.015 0.015	50 50	90 90
10. Ni-P-B 11. Ni-P-B	0.2 0.2	0.015 0.020	50 60**	90

\*NiCl<sub>2</sub> concentration was 0.1 M. Solution temperature was 80° C. The pH of the Ni-P bath, which contained 0.6 M formic acid, was 5.0 and the pH of the Ni-B and Ni-P-B baths, which contained 0.6 M ethylene diamine and 1 M NaOH, was 12.33 to 12.39. Samples 2, 4, 6 and 9 were heat treated for an hour at 300° C. Samples 7 and 10 were heated for an hour at 500° C.

\*\*Prepared for thermal analysis









Fig. 4—X-ray diffraction panels of unheated Ni-P-B sample 8 (top), Ni-P-B sample 9 heated one hour at 300°C (center) and Ni-P-B sample 10 heated one hour at 500°C (bottom).



Fig. 5—Thermal behavior of electroless nickel sample 11 containing 85.74 percent Ni, 0.2 percent P and 14.06 percent boron.

sistent with those obtained by Mital and Shrivastav for deposits produced with hypophosphite ions and dimethylamine borane as reducing agents.<sup>4</sup>

Little crystallinity was induced in a Ni-P deposit heat treated at 300° C for an hour (Fig. 1, bottom). However, this heat treatment for a Ni-B alloy deposit resulted in strong evidence of crystallinity in the X-ray diffraction curve for this deposit (Fig. 2, bottom). Lines that corresponded to Ni<sub>3</sub>B were readily identified. Matsuoka and Hayashi<sup>5</sup> detected Ni<sub>3</sub>B after a 400° C heat treatment and Gawrilov<sup>6</sup> also reported the appearance of Ni<sub>3</sub>B after heating to about 300° c.

X-ray diffraction curves for our Ni-P-B deposits heat treated at 300° C showed the formation of Ni<sub>3</sub>B (Figs. 3 and 4, center). After similar deposits were heat treated for an hour at 500° C, X-ray patterns indicated the formation of both Ni<sub>3</sub>B and NiP<sub>2</sub>(Figs. 3 and 4, bottom). Although the appearance of the peak at about 61° could be attributed to (200) Ni, the absence of this peak for the Ni-B deposit in Fig. 2 supports the conclusion that (130) NiP<sub>2</sub> was formed during the 500° C heat treatment of the Ni-P-B deposits.

Figure 5 shows TG and DTA data for a Ni-P-B deposit (Sample 11) that contained 0.2 percent phosphorus and 14.06 percent boron. The increase in weight shown by the TG curve after heating to 950° C was equal to 120 g/530 g of sample. This change is indicative of an oxidation process. The characteristic thermal behavior is illustrated by the DTA curve showing endothermic behavior at 120,500 and 820° C and five exothermic peaks at 290,430,580 and 890° C. The exothermic peak observed at 290° C strengthens the conclusion from the X-ray diffraction data that Ni<sub>3</sub>B was formed during heat treatment at 300° C. The exothermic peak at 430° C supports the finding that NiP<sub>2</sub> was precipitated during the 500° C heat treatment.

The SEM examinations of deposit cross sections showed that the type of reducing agent and its concentration affected the structure of the alloy deposits. The photomicrograph of the unheated Ni-P sample in Fig. 6 is indicative of a fine dispersion of thin layers of precipitated phosphorus in nickel, whereas the structure of the sample heated at 300° C appears to be a dispersion of nickel in a matrix of nickel phosphide. Recrystallization began to cause a nodular effect.

Figure 7 reveals a dispersion of short, thin, horizontal layers of boron in a matrix of nickel in the unheated Ni-B



Fig. 6—SEM photographs of cross sections of Ni-P deposits (a) unheated and (b) heated one hour at 300° C.



Fig. 7-SEM Photographs of cross sections of Ni-B deposits: (a) unheated and (b) heated one hour at 300° C.

sample No. 3 and the formation of Ni<sub>s</sub>B in sample No. 4, heated to 300° C. The SEM photograph at a magnification of 1000 shows a distinct diffusion layer between the steel substrate and the electroless nickel deposit.

The microstructure of unheated Ni-P-B sample No. 5 that contained 4.69 percent boron and 0.31 percent phosphorus is shown in Fig. 8. Particles of boron and phosphorus can be seen in the nickel matrix. The SEM photograph of sample No. 6 heated at 300° C resembles the appearance of the heat-treated Ni-B sample No. 4 in Fig. 7. Fig. 8c shows a similar Ni-P-B deposit after a 500° C heat treatment. Although the layer structure has disappeared, it appears that a dispersion of Ni<sub>3</sub>B and NiP<sub>2</sub> particles remains.

Figure 9 shows the microstructure of unheated Ni-P-B sample No. 8. The structure shows arrays of discontinuous parallel striations characteristic of variations in the P and B

contents of the deposit. The similar sample 9 heated to 300° C had a similar, but more pronounced laminar structure, whereas heat treatment at 500° C (Fig. 8c) resulted in a dispersion of nickel in a matrix of Ni<sub>3</sub>B and NiP<sub>2</sub>.

#### Conclusions

Based on this study, it can be concluded that heat treating electroless Ni-P alloy at 300° C introduces little crystallinity, whereas strong crystallinity was observed for electroless Ni-B alloy deposited in an alkaline chloride solution with potassium borohydride as the reducing agent. Unheated Ni-P-B also is amorphous according to X-ray diffraction data. However, the exothermic effect revealed at 290° C by differential thermal analysis is attributed to the formation of Ni<sub>3</sub>B. The exothermic peak detected at 430° C revealed the precipitation of NiP<sub>2</sub>.



Fig. 8—SEM photographs of cross sections of Ni-P-B deposits (a) unheated sample 5, (b) sample 6 heated one hour at 300° C and (c) sample 7 heated one hour at 500° C.



Fig. 9—SEM photographs of cross sections of Ni-P-B deposits: (a) unheated sample 8, (b) sample 9 heated one hour at 300°C and (c) sample 10 heated one hour at 500°C.

# Appendix

Aluminum specimens were prepared for chemical and thermal analysis<sup>3</sup> as follows:

- 1. Degrease with acetone.
- 2. Chemical polishing of test specimen.
- 3. Rinse and soak in mild alkaline degreaser (at 40° C for 2 min).
- 4. Rinse and immerse in 50% (V/V) HNO<sub>3</sub> (15 sec.
- 5. Rinse and immerse in zincating solution at room temperature for one minute.
- 6. Rinse and immerse in 0.5% (V/V) H<sub>2</sub>SO<sub>4</sub> (15sec).
- 7. Rinse.
- 8. Repeat steps 5-7 until the zinc coating completely covers the basis metal.
- 9. Immerse immediately in electrless nickel plating solution.
- 10. Rinse and strip the nickel deposit (unadhered-about 7 min).
- 11. Immerse the deposit in an Al-etching solution (2 min).
- 12. Rinse the deposit in cold, then hot water.
- 13. Immerse the deposit in alcohol and dry in an oven at 70°c.

SEM examinations of cross sections of Ni-P-B deposits showed the formation of thin layers of Ni<sub>3</sub>B and NiP<sub>2</sub> after heat treatment for an hour at 300° C. After heating to 500° C, dispersions of Ni in a matrix of Ni<sub>3</sub>B and NiP<sub>2</sub> were detected.

## References

- 1. A. Brenner and G. Riddell, *J. Res. Nat. Bur. Stds.*, 37,31 (1946).
- 2. M. Pushpavanam and B.A. Shenoi, *Finishing Industries*, 1, 48 (June, 1946).
- 3. G.O. Mallory, Plating, 58,319, (1971).
- 4. C.K. Mital and P.B. Shrivastav, *Metal Finishing*, 84, 67 (Oct., 1986).
- 5. M. Matsuoka and T. Hayashi, *Plating& Surf. Fin.,* 73,66 (July, 1981).
- G.G. Gawrilov, *Chemical (Electroless) Nickel Plating,* H.E. Warne & Co., Ltd., St. Austell, Cornwall, England, 1979.





Shafei





Nagi

Aboul-Haasan

# About the Authors

Dr. Ahmed Talaat El-Mallah is research professor and head of the electrochemical research group in the Pilot Plant Laboratory component of the Egyptian National Research Center. He received his PhD in metallurgical engineering from Cairo University in 1976. His interests are electroplating, electroless deposition, phosphating and corrosion protection. He is a member of AESF.

Dr. Mohamed Hassib Abbas is associate professor in the electrochemical research group, Pilot Plant Laboratory component of the Egyptian National Research Center.

Dr. Maha Farid Shafei is associate professor at the Pilot Plant Laboratory component of the Egyptian National Research Center.

Dr. Mahmoud El-Sayed Aboul-Hassan is professor of chemical engineering, Cairo University, Giza, Egypt.

Ismail Nagi is a chemical engineer in the chemical engineering department of Cairo University, Giza, Egypt.