# Study of Electroless Ni-P-Nanometer Diamond Composite Coatings

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Composite coating of Ni-P-Nanometer diamond was prepared by electroless plating. The effects of agitation mode, concentration of nanometer diamond particles and depositing speed were investigated. The results show that microhardness of the composite coating is greatly increased by the incorporation of nanometer diamond particles. The composite coating has the same amorphous structure as Ni-P matrix. Mechanism of the composite depositing process is discussed.

### Introduction

Electroless nickel is widely used because of its unique properties such as hardness, wear resistance and corrosion resistance. Composite coatings are produced by incorporating fine particulate matter within matrix in order to improve the properties. Numerous matrix/particle combinations are possible and some of them have been investigated, such as electroless nickel with SiC<sup>1-2</sup>, B<sub>4</sub>C<sup>3</sup>, Al<sub>2</sub>O<sub>3</sub>, and MoS<sub>2</sub><sup>5-6</sup>.

Nanometer diamond (ND) was synthesized by the detonation of explosives with negative oxygen balance<sup>7</sup>. The sizes of the primary diamond particles range from 3 to 10 nm and their specific surfaces are about 300-400 m<sup>2</sup>/g, but the size of the aggregates formed from the original ND particles during the synthesis process are of the order of  $\mu$ m. It was reported that the ND particle has the properties of diamond: high hardness and low sliding friction. In aggregates, it shows some lubricant properties<sup>8</sup>.

In this paper the process of electroless composite plating of Ni-P-ND has been investigated. Hardness measurement and microstructure analysis are also presented.

### Materials and Experimental Procedures

#### Nanometer Diamond

The average particle size of ND is 8.4 nm measured by small angle x-ray scattering method. After ultrasonic vibration in distilled water, the mean size of the ND aggregates is 0.47



Fig. 1—Particle size distribution of ND aggregates after ultrasonic vibration.

Table 1Bath Formulation						
	Bath A	Bath B				
$NiSO_4 \cdot 6H_2O$	25 g/L	25 g/L				
$NaH_2PO_2 \cdot H_2O$	20 g/L	20 g/L				
$CH_3COONa \cdot 3H_2O$	15 g/L	15 g/L				
$Na_{3}C_{6}H_{5}O_{7} \cdot 2H_{2}O$	10 g/L	10 g/L				
$Na_2B_4O_7 \cdot 10H_2O$	4 g/L					
Thiourea	1 mg/L	1 mg/L				
Plating Temp	89±1°C	86±1°C				
pH of Bath	4.60	4.60				

µm, as shown in Fig. 1.

### **Bath Formulation**

Two bath formulations are presented in Table 1. All chemicals used were of analytic grade.

### **Process and Measurements**

Medium carbon steel plates were used as substrate. Before electroless plating, the plates were treated by the following procedures: grinded with 900<sup>#</sup> SiC paper, degreased, washed with distilled water, chemically activated (1:1 HCl), washed again. Plating was carried out in a conical glass beaker containing 200 ml solution. The bath was heated by a thermostatically controlled water jacket as showed in Fig. 2. A special agitation mode, named "injection agitation" in this report, was adopted in which a syringe was used to stir the bath. Each bath was used only for 1.5 hr. The pH value of the bath was determined by a digital pH/ion tester at room temperature.

The coatings were treated at 400°C for 1 hr in  $N_2$  atmosphere. ND content of the composite coating was measured by Leco-334 CS analyzer. Phosphorous content and microstructure were analyzed with JSM-6400 scanning electron microscope. Hardness was measured by Foct-



Fig. 2—Schematic diagram of the apparatus for composite electroless plating.

### Table 2 Effect of agitation mode on the ND content of the composite coatings

Agitation mode	Agitation intensity	ND content of composite coating, wt %	Surface of composite coating
Injection	50 mL/min	0.23	Foggy
Mechanical	120 rpm	0.15	Semi-bright
N <sub>2</sub>	30 mL/min	0.17	Semi-bright

\* Bath A (without thiorea), 1g ND/L. Specimens were vertically placed.

7865-56 microhardness tester with a load of 100g. Five readings were taken on each coating and the values were then averaged out. X-ray analysis was performed on Rigaku 3014 x-ray diffractometer with Co K $\alpha$  radiation.

### Results & Discussion Effect of Agitation Mode on the ND Content of the Coating

Under the same plating conditions, the effect of agitation mode on the ND content of the composite coating is shown in Table 2. At the plating temperature, it is difficult for ND aggregates to deposit into Ni-P matrix because of the formation of agglomerations. Mechanical agitation results in the smallest ND content. This could be ascribed to a directional flow in the bath. Although N<sub>2</sub> agitation can avoid the directional flow, it does not decrease the extent of agglomerating of the ND aggregates. In injection agitation mode, the agglomerations of ND aggregates are constantly shattered and a turbulent flow is formed in the bath. That is why a higher ND content could be obtained with the injection agitation mode.

### Effect of the ND Concentration on the ND Content of the Coating

The release of  $H_2$  from the surface of the specimen will hinder the incorporation of ND into the matrix, therefore thiourea was added into the bath. Thiourea could be absorbed by the surface of the specimen to decrease the formation of  $H_2$  and improve the efficiency of the reducing agent. Compared with Table 2, the ND content of the coatings in Fig. 3 are largely increased at the presence of thiourea. It can be seen from Fig. 3 that ND content of the coating is relatively independent of the ND concentration in the bath. ND content varies in the range of 0.40-0.52 wt% when ND



Fig. 4—Effect of the ND concentration on the ND content. Bath B, injection agitation. Specimens were placed horizontally.



Fig. 3—Effect of the ND concentration on the ND content. Bath A, injection agitation. Specimens were placed vertically.

concentration increases from 0.5-4 g/L. A larger amount of agglomerations was observed in the bath at higher ND concentration.

### Effect of Depositing Speed

on the ND Content of the Coating

In order to increase the ND content of the composite coating, we also adopted bath B in which there was no accelerating agent  $Na_2B_4O_7 \cdot 10H_20$ . The specimen was horizontally placed in the bath and plated at 86°C. The depositing speed in bath B was 5-7 mg/cm<sup>2</sup> · hr while it was 11-13 mg/cm<sup>2</sup> · hr in bath A. It can be seen from Fig. 4 that ND content is notably increased by using bath B. The maximum ND content reaches 2.21 wt% at a ND concentration of 4 g/L.

### Structure of the Coatings

The XRD patterns of the Ni-P and Ni-P-ND coatings are shown in Fig. 5. Although the phosphorous and ND content are different, all the coatings are amorphous. The incorporation of ND does not change the amorphous structure of the matrix.

### Hardness of the Coatings

Table 3 gives the microhardness of the specimens before and after heat treatment. In as-plated state, the hardness of



Fig. 5—XRD patterns of the coatings: (a) Ni-8.0 P, Bath A; (b) Ni-7.6P-0.52ND, Bath A; (c) Ni-6.27P-2.21 ND, Bath B

Ni-P coatings is in the range of HV400-420. This value is much lower than that of composite coatings whose hardness is determined by the ND content. The hardness of the composite coatings obtained in bath B is higher than HV 600, reaching a maximum of HV755 in the upside coating of Ni-P-



Fig. 6—Microsture of the coatings: (a) Ni-8.0P, Bath A; (b) Ni-7.6P-0.52ND, Bath A; (c) Ni-6.27P-2.21ND, Bath B; (d) Ni-P-ND coating, 2g ND/L, Bath B, Plating time of 30 minutes.

2.21wt% ND. It is noticeable that for composite coatings deposited in bath B, hardness of the upside coating is higher than that of downside coating. This difference might be the result from the different ND content of the coating, which can be estimated by their surface finish. The brighter the coating, the lower the ND content. After heat treatment, hardness of the coating is mainly determined by the precipitation hardening effect of Ni<sub>3</sub>P. Because the phosphorus content of all the coatings are similar, hardness values of all the coatings are almost in the range of HV 900-1000 after heating in N<sub>2</sub> at 400°C for 1 hr.

### Microstructure of the Coatings

Microstructure views of the coatings are shown in Fig. 6. It can be seen that the surface of Ni-P coating is very smooth, but the surfaces of the composite coatings are much coarser. There are numerous nodular protrusions over the surfaces. It is noticeable that the nodular protrusions in Fig. 6 (d) are more

regular, larger in size and the surface looks glossier. This morphology might be the result of a short plating time.

## Mechanism of the Deposition of ND Aggregates

Ying Jin<sup>9</sup> reported that in an electroless nickel system with sodium citrate as complexing agent, the horizontal growth rate of the deposit is much larger than the perpendicular growth rate. In this case, the coating grows mainly by overlapping; in other words, by two-dimensional growth mode. The coating obtained in this system is smooth, compact and of low porosity, which is consistent with Fig. 6-a.

Fig. 7 schematically illustrates the mechanism concerning the deposition of ND aggregates. The deposition process can be approximately divided into three stages. At the beginning of deposition, some ND aggregates are

absorbed on the surface of the specimen and are gradually entrapped by reduced nickel ions, as shown in Fig. 7-a. With the increase of the deposition time, more and more ND aggregates are absorbed and deposited. The growth mechanism of the composite coating is also overlapping as a result of the effects of the complexing agent and the low deposition speed. This stage is schematically illustrated in Fig. 7-b, corresponding to the surface feature of Fig. 6-d. At the third stage, the surface of the composite coating becomes a little rougher because a large number of ND aggregates are entrapped. The dwelling positions for ND aggregates increase correspondingly. Much more particles deposit on the rough surface and result in numerous nodular protrusions. The surface feature at this stage is consistent with that of Fig. 6-b.

The above mechanism is also supported by the different deposition speeds of Ni-P and Ni-P-ND in the bath B. The deposition speed of composite coating is 7.0 mg/cm<sup>2</sup>

Hardness of the Coatings									
Coatings		Phosphorous content, wt%	ND content, wt%	HV100 (as-plated)	HV100 (After heat treatment)				
Roth A	Ni-P		8.0	0	410	979			
Daul A	Ni-P-0.52wt%ND		7.6	0.52	470	939			
Bath B		Ni-P	5.32	0	406	921			
	2g ND/L	Upside surface	5.16	1.89	666	912			
		Downside surface	5.03		612	892			
	$4$ g ND/L $\frac{U_{\rm F}}{Dc}$	Upside surface	6.27	2.21	755	966			
		Downside surface	5.40		604	919			
	6g ND/L Upside surface	Upside surface	5.59	1.68	642	951			
		Downside surface	5.12		606	913			

Table 3

 $\cdot$  hr when the ND concentration is 4 g/L. However, the depositionspeed of Ni-P coating is only 5.0 mg/cm<sup>2</sup>  $\cdot$  hr at the same plating condition. It is reasonable to consider the rougher surface of composite coating enlarges the area for deposition so that the deposition speed increases.

### Conclusions

- 1. Comparing with  $N_2$  and mechanical agitation modes, injection agitation could effectively increase the ND content of the composite coating. When the specimen was placed horizontally in a bath of low deposition speed, ND content in the composite coating greatly increased.
- 2. The microhardness of the composite coatings deposited in bath B is much higher than that of Ni-P matrix. Upside surface of the composite coating has a higher hardness than that of downside surface because of its higher ND content. The maximum hardness reaches HV 755 of the composite coating with 2.21wt% ND.
- 3. Incorporation of ND aggregates does not change the amorphous structure of the Ni-P matrix, but the surface is changed from bright and smooth to foggy and rough with numerous nodular protrusions covering the whole surface.

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