# Surface Nanocomposites Prepared By Electroless Plating

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**Nanometer-sized particle-reinforced nickel-phosphorus (Ni-P) matrix composites were prepared by electroless plating. By using transmission electron microscopy (TEM) and scanning probe microscopy (SPM), nanometer-sized particles were found to codeposit evenly. From the results of x-ray diffractometry (XRD) and differential scanning calorimetry (DSC), it was found that the particles caused the crystallization temperature of the nanocomposites to drop. Because of the presence of the nanoparticles, the microhardness of the coating greatly increased. With heat treatment, microhardness values as high as 1190 VHN$_{50}$ were produced.**

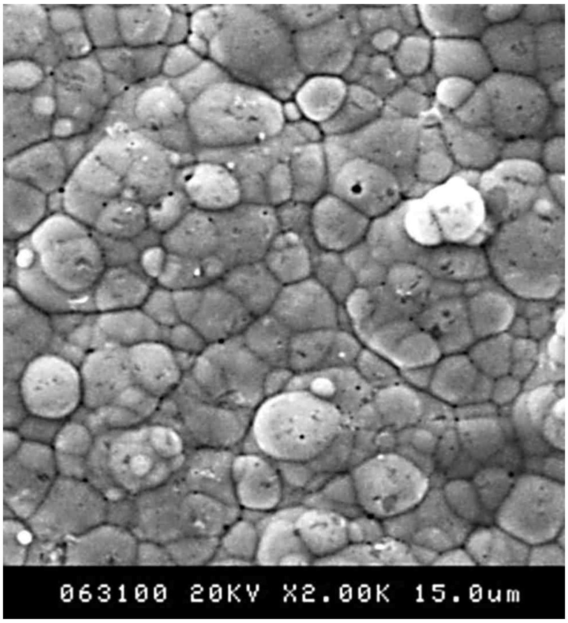

*Fig. 1—SEM morphology of as-plated Ni-P-Al$_2$O$_3$.*

## Nuts & Bolts: What This Paper Means to You

This second paper reflects the growing interest nanotechnology. Nanoparticle suspensions of alumina, silicon carbide, etc. have been added to conventional plating baths and have yielded deposits with astonishing properties. Here, the authors have looked at what can be accomplished in an electroless nickel bath, something that had not been looked at to any major extent. Once again, the results exceed what might be gotten with more traditional coatings.

Electroless nickel (EN) coatings exhibit an amorphous structure, which is thermodynamically unstable.[1] After certain heat treatments, the structure of Ni-P alloys transforms to a crystalline one. The crystallization temperature is found to be above 300°C (572°F).[2-4]

Nickel-phosphorus (Ni-P) composite coatings have been prepared by adding different particles to an electroless plating solution.[5,6] For example, wear resistant layers have been prepared with silicon carbide, diamond or alumina and self-lubricating layers have been produced with additions of PTFE or MoS$_2$.[7-11]

When compared with traditional materials, nanometer-sized particles have special properties,[12] such as large specific surface area, and they may change the crystallization behavior of the coating when added. To date, electroless composite plating with the addition of nanometer-sized particles has been given only limited study.[13,14] In this work, nanocomposites were prepared in an EN composite plating bath containing nanoparticles. Their microstructure and properties were studied by transmission electron microscopy (TEM), scanning probe microscopy (SPM), X-ray diffraction (XRD), differential scanning calorimetry (DSC) and microhardness testing.

## Experimental Procedure

A novel electroless plating bath was developed by an orthogonally designed experiment. The resulting composition is given in Table 1. The electroless composite deposits were plated on carbon steel. The substrates were degreased in a hot alkaline solution at 60°C (140°F) and lightly etched in hydrochloric acid (HCl) immediately before plating. Deposition was carried out in a 1-L plating bath, maintained at 90 ± 1°C (194 ± ~2°F) for 2 hr at a deposition rate above 10 $\mu$m/hr (0.4 mil/hr). The bath was air agitated and continuously replenished. The deposits were heat-treated at various temperatures in a baking oven.

The chemical composition of the coatings was determined by using a scanning electron microscope (SEM) with energy dispersive spectrometry (EDS) capability. The surface morphology was observed simultaneously. Transmission electron microscopy (TEM) and scanning probe microscopy (SPM) were used to observe the microstructure. The structure was studied with an x-ray diffractometer with CuK$\alpha$ radiation. The microhardness

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of the coatings was measured with a computer controlled microhardness tester.

### Table 1
### Basic Composition of the Electroless Nickel Composite Plating Bath

| | |
|---|---|
| Nickel sulfate, $NiSO_4$□$6H_2O$ | 20 g/L (2.67 oz/gal) |
| Sodium hypophosphite, $NaH_2PO_2$□$H_2O$ | 25 g/L (3.33 oz/gal) |
| Lactic acid, $CH_3CHOHCOOH$ (88%) | 33 mL/L (4.22 fl oz/gal) |
| Particulates (□-$Al_2O_3$, SiC, $SiO_2$) (Size: 50-100 nm) | 5 to 15 g/L (0.67 to 2.00 oz/gal) |
| pH | 4.3 to 4.8 |

### Table 2
### Chemical Composition of the Composite Coatings Containing Different Nanoparticles (wt%)

| Nanoparticle | SiC | | | $Al_2O_3$ | | Ni-P |
|---|---|---|---|---|---|---|
| Particle Concentration | 5 g/L | 10 g/L | 15 g/L | 5 g/L | 10 g/L | ----- |
| SiC or $Al_2O_3$ | 2.5 | 2.5 | 3.2 | 4.1 | 12.0 | 0.0 |
| P | 6.5 | 6.6 | 7.2 | 6.8 | 7.8 | 8.1 |
| Ni | 91.0 | 91.0 | 90.0 | 89.0 | 80.0 | 92.0 |

## Results & Discussion

It is inherently difficult to disperse nanoparticles in order to prepare metal matrix composites (MMC) by conventional metallurgical practice, especially at high temperatures. By contrast, nanoparticulates can be dispersed in an electroless composite plating solution by adding surfactants into the bath. With appropriate air agitation, the particles can be evenly dispersed in the bath because of their large specific surface area.

In the present study, Ni-P-$SiO_2$, Ni-P-SiC and Ni-P-$Al_2O_3$ composites were prepared by electroless deposition with different nanometer-sized particles. By doing so, this also shows that a variety of Ni-P composites can be prepared with proper pretreatment. The coatings were smooth and semi-bright. Figure 1 shows the surface morphology of the Ni-P-$Al_2O_3$ nanocomposite coating. Coating adhesion was satisfactory, as evidenced by the fact that the coatings did not exfoliate after a 180° bend test.

Figure 2 shows a TEM micrograph (bright field) and a selected area diffraction (SAD) pattern (in the corner) of the as-deposited Ni-P-$Al_2O_3$ nanocomposite coating, showing that the coating is amorphous. This shows that the nanometer-sized particles did not alter the microstructure of the basic Ni-P alloy.

The distribution of nanometer-sized particles in EN coatings (again taking Ni-P-$Al_2O_3$ as an example) was studied by TEM and SPM. The bright field TEM image and the SPM results are shown in Figs. 2 and 3, respectively. It can be seen that the particles in the coating are evenly dispersed without obvious agglomeration.

The coating composition is a critical factor in influencing the properties of the coating, especially the phosphorus content. Nanoparticles alter the composition. The chemical composition of the composites with different nanometer-sized particles is shown in Table 2. The content of particles in the coating was high, especially in the case of Ni-P-$Al_2O_3$ (12 wt%). With increasing nanoparticle concentration in the bath, the particle content in the coatings was improved.

Figure 4 shows the exothermal peak temperatures taken from the differential scanning calorimetry (DSC) curves for the EN composites at three heating rates, 20, 10 and 5 C°/min (36, 18 and 9 F°/min). From these results, the onset temperatures and the peak temperatures of the composites are found to be lower than those of the conventional EN alloys. It can be seen that the crystallization temperature of the composite is lower than that of conventional electroless Ni-P prepared under the same conditions. The nanometer-sized particles led to a decrease in the crystallization temperature.

On the other hand, the apparent activation energy of the materials can be determined by the Kissinger relation,[15] which is expressed as:

$$\ln(\beta/T^2) = -E/RT + \text{constant}$$

where β is the heating rate, T is a characteristic temperature, E is the activation energy and R is the universal gas constant. By plotting ln ($\beta/T^2$) versus 1/T one can derive the value of E from the slope of the plotted straight line. The activation energy of Ni-P-$Al_2O_3$ in the present study was found to be 226 KJ/mol, which was slightly lower than that of the conventional Ni-P alloy (228 KJ/mol).

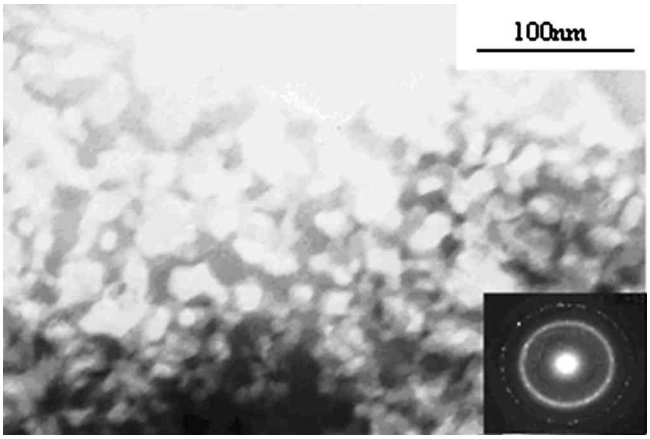

*Fig. 2—Micrograph of the bright field and diffraction pattern of Ni-P-$Al_2O_3$ composite coating (RT).*

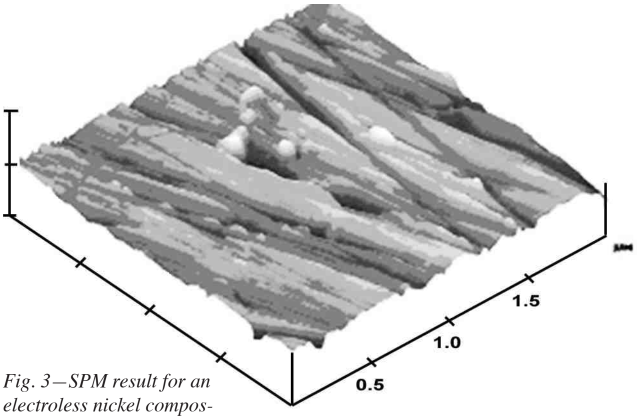

*Fig. 3—SPM result for an electroless nickel composite coating.*

Figure 5 shows the XRD patterns for the nanocomposite coatings, as-deposited and after heat-treatment. The amorphous structure of the as-plated electroless composite became crystalline after 24 hr at 230ºC (446°F). By contrast, the particle-free electroless nickel coating prepared under like conditions did not transform after heat treatment. This indicates that the particles added to the Ni-P alloy can lower the crystallization temperature.

When the coating containing nanoparticles was heat-treated at 400ºC (752°F) for 1.0 hr, the $Ni_3P$ precipitated from the Ni-P-$Al_2O_3$ composite. Figure 6 shows the TEM bright field image and

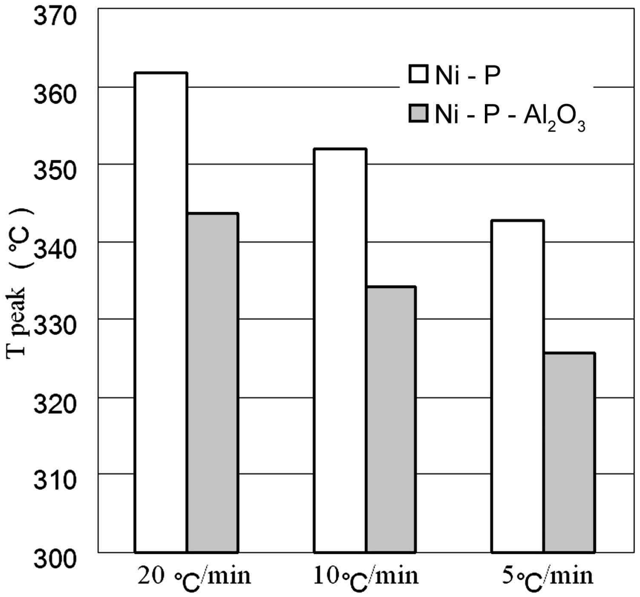

*Fig. 4—Temperatures of the exothermal peak in the DSC curves of EN composites compared with that of EN (the grey column represents Ni-P-$Al_2O_3$).*

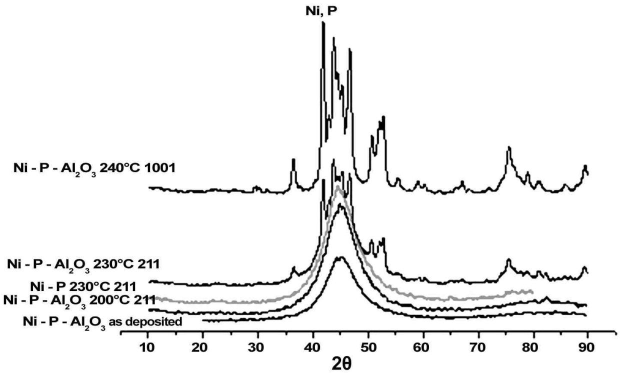

*Fig. 5—XRD spectra of electroless Ni-P-$Al_2O_3$ after various heat treatments.*

the selected area diffraction pattern of the Ni-P-$Al_2O_3$ composite, showing crystallinity after heat treatment (Compare with Fig. 2.).

Hardness is an important coating property. Microhardness values for the electroless composites are shown in Table 3. The reinforcing effect of the nanoparticles is clear. The hardness of the composites was higher than that of the conventional Ni-P alloy, increasing by 14 to 28%. The microhardness was also higher at higher coating particle contents.

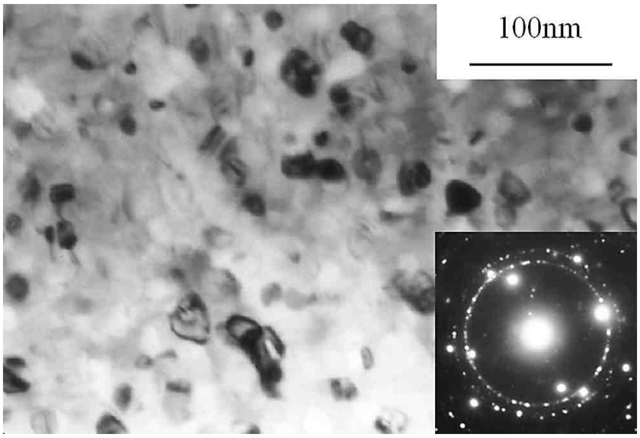

*Fig. 6—Micrograph of the bright field and diffraction pattern of Ni-P-$Al_2O_3$ composite coating after heat treatment (400°C, 1.0 hr).*

After certain heat treatments, the alloy contains crystalline nickel and nickel phosphide. Because of particle dispersion and phosphide precipitation, the hardness of the composite coating is increased. Table 4 shows the microhardness of Ni-P-$Al_2O_3$ coatings after heat treatment as well as that of the conventional particle-free EN coating for comparison. The microhardness of the Ni-P-$Al_2O_3$ coatings reached 1190 $VHN_{50}$ when the composite coating was heated for 1.0 hr at 400°C (752°F).

## Conclusions

In the present study, nanocomposite coatings were prepared by adding nanometer-sized particles into an electroless nickel bath, and certain coating properties were improved. The following conclusions could be drawn:

1. Nanometer-sized particles were dispersed by air agitation during the electroless composite plating and nanocomposite coatings were prepared. The particles content was high, up to 12 wt% in Ni-P-$Al_2O_3$ coatings.
2. The as-plated composite coatings were amorphous and their phosphorus content was 7 to 8 wt%. The nanoparticles led to a drop in the matrix crystallization temperature. After heat-treatment at 230°C (446°F) for 24 hr, $Ni_3P$ peaks appeared in the XRD spectra of the Ni-P-$Al_2O_3$ coatings. The crystallization temperature of the nanocomposites was lower than that of conventional Ni-P alloys prepared under like conditions.
3. The microhardness of the coating was improved with the codeposition of the nanoparticles. After certain heat treatments, the composites became crystalline and the microhardness of the Ni-P-$Al_2O_3$ increased, reaching 1190 $VHN_{50}$ after heat treatment at 400°C (752°F) for 1.0 hr.

Generally, electroless nickel coatings should be heat-treated at high temperature to improve their microhardness and wear properties. Thus, lowering the crystallization temperature of the coatings is important, allowing precision parts to be protected from oxidation in air as well as simplifying the overall heat treatment process.

### Table 3
### The Microhardness of As-plated Deposits Containing Different Nanoparticles

| **Nanoparticle** | **SiC** | | | **$Al_2O_3$** | | **$SiO_2$** | | **Ni-P** |
|---|---|---|---|---|---|---|---|---|
| Particle Concentration | 5 g/L | 10 g/L | 15 g/L | 5 g/L | 10 g/L | 5 g/L | 10 g/L | ----- |
| Microhardness, $VHN_{100}$ | 600 | 610 | 650 | 580 | 590 | 600 | 610 | 510 |

### Table 4
### The Microhardness of Ni-P-$Al_2O_3$ Deposits after Various Heat Treatments

| **$Al_2O_3$ Conc. (EN bath)** | **0.0** | **10.0** | **0.0** | **10.0** | **0.0** | **10.0** |
|---|---|---|---|---|---|---|
| Heat treatment | 200°C<br>24 hr | 200°C<br>24 hr | 230°C<br>24 hr | 230°C<br>24 hr | 400°C<br>1 hr | 400°C<br>1 hr |
| Microhardness, $VHN_{50}$ | 550 | 590 | 660 | 880 | 1080 | 1190 |

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