Effects of Agitation On Conventional Electroless Plating: Implications for Production of Ni-P Composite Coatings

By M. R. Kalantary, K.A. Holbrook and P.B. Wells

Studies of agitation produced by magnetic stirring, aeration and nitrogen bubbling were made on a conventional nickel-phosphorus plating bath at pH 4.5 and temperature 85 “C. Polarization curves were used to obtain the preferred stirring parameters for the production of composite coatings. The effects produced were assessed by measurement of rate of deposition, analysis for nickel and phosphorus by inductively coupled plasma spectrometry, and examination of surface topography of the coatings by scanning electron microscopy. The results are compared with those obtained for still solutions pre-saturated with air, oxygen and nitrogen. The implications for production of Ni-P-composite coatings are considered.

Electroless nickel plating has been exploited commercially for more than a decade. The main core of the published research work to date, however, concentrates on the bath chemistry, the mechanical properties of the coatings, such as wear, and the chemical composition of the coatings. In general, an electroless nickel bath contains nickel sulfate or nickel chloride, as well as one or more reducing agents, completing agents, and buffering agents, which may act as pH controllers and bath stabilizers. The bath may also contain stress reliever/brightener additives. The effects of such substances on the deposition rate and bath stability can be quite considerable. The deposited coatings normally contain nickel and some percentage of phosphorus (about 3 to 15 percent, originating from the hypophosphite ion). The alloy composition and morphology of the coated deposit have been found to depend upon the operating conditions of the plating bath, such as pH, temperature and plating time.[1] These factors were studied in order to establish the optimum operating conditions for a bath of a given composition. The effect of phosphorus content on properties of the coatings are different from those of electroplated nickel, and accounts for some of the applications of electroless nickel.[2]

In composite plating, the particles incorporated in electroplated or electroless deposits can improve the tribological properties, especially where wear is a problem. The common particles used for composite plating are silicon carbide and polytetrafluoroethene (PTFE). The use of binary or tertiary alloy coatings have also been considered by many authors because they are believed to enhance the properties for a particular specialized use.[3] Such systems have many disadvantages, however, including (a) complex bath chemistry, (b) necessary consideration of more parameters than for simpler bath systems, and (c) difficulty of bath control. These factors led to the choice of an electroless plating bath containing ions of only one metal (nickel), in which to incorporate particles of silicon carbide in this study. In general, it is important in any choice of an electroless plating system to consider both the advantages and disadvantages with regard to the coating produced and the operation of the process. These aspects are shown in Table 1.

Although the electroless nickel-phosphorus system is widely used commercially, only a few studies have seriously considered the implications of agitation on the performance of the bath. Solution stirring or agitation of the article(s) to be plated is not absolutely necessary in chemical plating, but it is generally recommended. One reason is that the higher the rates of diffusion and convection, the better both the reacting ions and SiC particles approach the coating work-piece and the reaction products removed. This is equally true for work-places having depressions or holes and for the inside coating of tubes. In electroless plating, agitation of the solution is normally achieved by aeration, stirring or continuous pumping. Agitation of the substrates, which is expensive for large or heavy work-pieces, may be achieved for mass components in baskets, or other holders.

It has been reported (Table 2) that agitation can cause changes in properties, or, in some instances, can increase the rate of deposition .[4-10] In this study, the effects of different types

Table 1
General Properties of Electroless Plating

Advantages	Disadvantages
Coating	
Uniform coating thickness	Deposition rates are slow
Good throwing power	More brittle deposit than electrodeposited metal
No leveling	Lower-melting-point deposit than electrodeposited metal
Harder coating than electroplated metal (480HV vs. 200 HV) because of the presence of other elements (e.g., phosphorus, boron)	
Deposit can be hardened by heat treatment at 400 ‘C, one hr to 1050 HV	
Unique chemical, mechanical and magnetic properties (i.e., low porosity leads to good corrosion resistance, good wear resistance, very low ductility [1-30/0 elongation])	
Process	
No electrical connection and power supplies necessary	Solutions are expensive
Deposit on nonconducting materials is possible	Higher bath temperature needed
	Shorter bath life
	Careful analytical control of the bath is required

Table 2
Types of Agitation and Electroless Bath Systems Used by Other Investigators

Authors/Reference no.	Agitation type/Solution	Remarks
Gawrilov, G. G.[4]	Ultrasound acid bath	Deposition rate increased by increase in agitation as a result of increase in the pH value of the diffusion layer. Increased porosity, bath instability can occur, depending on the bath. Large size of equipment has hindered wide application of ultrasound.
Stallman, K.[5]	Pumping Acid baths containing sodium hypophosphite (Ni-P) and Borohydride (Ni-B)	Ni-P, deposition rate decreased with increase in flow velocity. Leveling improved. Ni-B, deposition rate increased with increase in flow velocity. Tendency to form nodular deposits. General: High flow is not necessary but an intensive swirling in the region of substrate surface is decisive. Several lower-intensity stirrings produce better results than one high-intensity stirring, Filtration and a continuously pumped solution with several inlets are desirable.
Shenoi, B. and [6] Shenoi, M.; Rich, S.R.;[7] Kuzub, V.S. and Mukhlya, S. Yu[8]	Ultrasound Alkaline Ni-P	KHz-2 MHz influence on electrolytic and electroless plating. Plating rate increased 15-fold.
Ginsberg, A. and Fedotova, N[9]	Ultrasound Acid hypophosphite, Hydrazine and borohydride bath	Plating rate increased by a factor of 2-4.
Matsuoka, M. and Hayashi, T.[10]	Ultrasound Acid and alkaline hypophosphite bath with thallium nitrate as stabilizer	Quantitatively confirmed increase in deposition rate by a factor of 2.

(air, oxygen, nitrogen sparging, and magnetic stirring) and rates of agitation on the rate of deposition, morphology and composition of the deposits were examined.

Experimental Procedure

General Preparation

The substrates were prepared from cold-rolled copper sheets (99.99 percent Cu, annealed) with an exposed area of 30 cm^2, having dimensions of 15 x 100 x 0.25 mm. The pre-cleaned substrates were sensitized in a stannous chloride solution, then activated in palladium chloride solution for one min prior to plating. The substrates were washed thoroughly in distilled water before and after activation.

The electroless nickel-phosphorus bath used contained 32.1 g/L $NiSO_4 \cdot 7H_2O$, 16.6 g/L NaH_2PO_2, 28.5 mL/L lactic acid ($CH_3CHOHCOOH$), 5 mL/L propionic acid (CH_3CH_2COOH), and Pb as lead nitrate (4 ppb). The bath was operated at a pH of 4.5 and 85 °C.

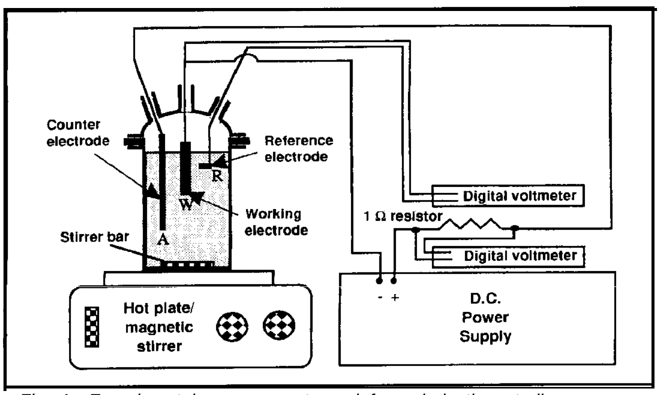

Fig. 1—Experimental arrangement used for polarization studies.

Agitation Studies

Three series of experiments were carried out as follows:

1. Using the electroless nickel-phosphorus solution described above, these types of agitation were studied:
   (a) aeration, 3.0 to 4.5 L/min;
   (b) magnetic stirring, 200 to 400 rpm
      (i) solution movement in clockwise direction
      (ii) solution movement clockwise and counter-clock wise, with change of direction every five sec

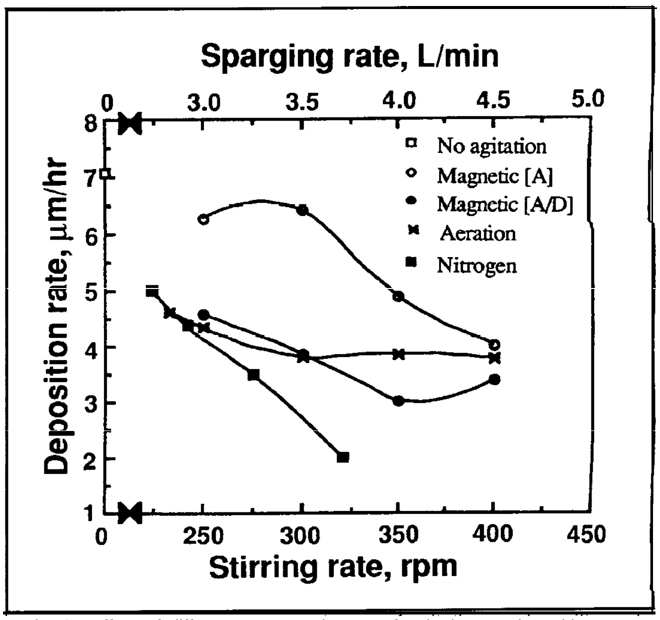

Fig. 2—Effect of different types and rates of agitation on deposition rate, using the electroless Ni-P solution operated at-pH 4.5 and 850 C

Table 3
Deposition Rate Obtained at Different Agitation Rates Using Electroless Ni-P at pH 4.5 and 80 °C

Aeration rate, L/min	Deposition rate µm/hr	Stirring rate, rpm [A]	Deposition rate, µm/hr	Stirring rate, rpm [A/D]*	Deposition rate, µm/hr	Nitrogen rate, L/min	Deposition rate, µm/hr
0	7.09						
2.8	4.62	250	6.28	250	4.58	2.69	5.01
3.0	4.33	300	6.42	300	3.86	2.9	4.37
3.5	3.79	350	4.88	350	3.0	3.31	3.49
4.0	3.86	400	4.01	400	3.38	3.85	1.99
4.5	3.75						

● Magnetic stirring clockwise [A] and counter-clockwise [D].

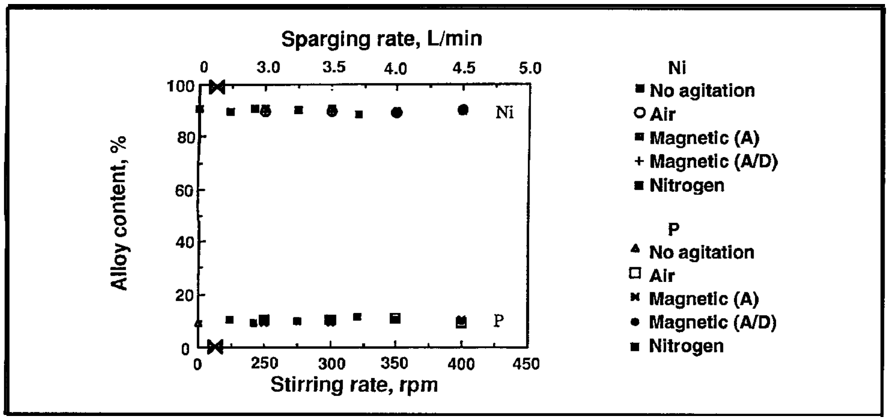

Fig. 3—Percentage of nickel and phosphorus in the deposited coatings under different agitation types and rates and their comparison to no agitation. A—magnetic stirring clockwise; D—magnetic stirring counter-clock wise.

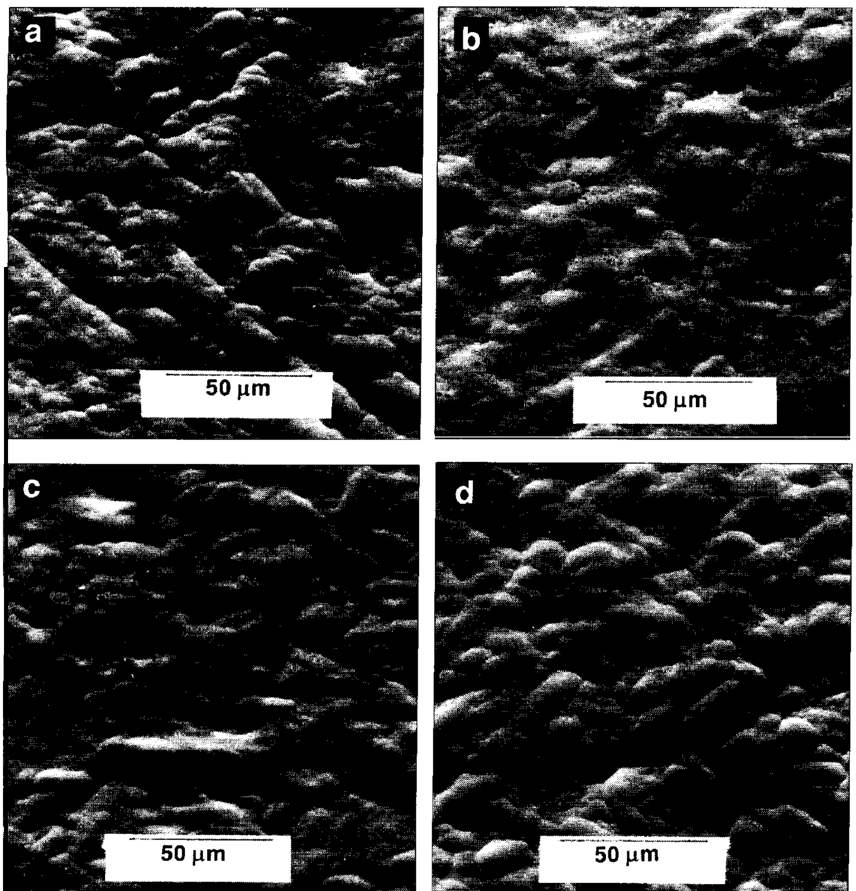

Fig. 4—Scanning electron micrographs of electroless nickel-phosphorus coatings under natural convection and different aeration rates; (a) 0 rpm, (b) 3.0 L/min, (c) 3.5 L/min, (d) 4.5 L/min, Operating conditions.. pH 4.5, 85°C; plating time, two hr.

(c) nitrogen bubbling, 2.69 to 4.4 L/min. The nitrogen bubbling was carried out using a glass frit bubbler. The effects were then examined by comparing the rate of deposition, the compositional changes (using inductively coupled plasma atomic emission spectrometry), and the morphological changes, using scanning electron microscopy (SEM), Deposition rates were measured as thickness versus time. The thickness was determined from the change in weight of the sample after plating, the known geometry (i.e., the area plated, assuming the density for nickel-phosphorus to be similar to that of nickel).

2. The effects of changing the nature of the purge gas were investigated, using air, pure oxygen and pure nitrogen. For these experiments, the rate of agitation was kept constant at 3.0 L/min. A freshly made electroless nickel-phosphorus solution was used for each type of agitation. The substrates were inserted into the plating vessel 15 min after agitation was applied. The study was carried out by:

(a) Pre-saturating the solution with the particular purge gas for 15 rein, then plating under natural convection conditions;

(b) intermittent or interrupted agitation; with the agitation switched on and off for one minute and three minutes, respectively (on-off ratio = 1 :3);

(c)continuously agitating the solution.

3. The results were compared in terms of the rates of deposition of the coating. The agitation behavior was assessed by using a polarization technique, as has commonly been used by many researchers in order to examine flow behavior.[11,12] The electrolyte used was an acid copper sulfate solution (0.3M $CuSO_4 \cdot 5H_2O$, 2.25M 99% H_2SO_4, 50 ppm Cl). The cathode and anode used were copper sheets, having an exposed area of 12 cm^2 and 36 cm^2, respectively. The polarization curves were obtained by sweeping the potential step-wise (potentiodynamically), using a mercury/mercury

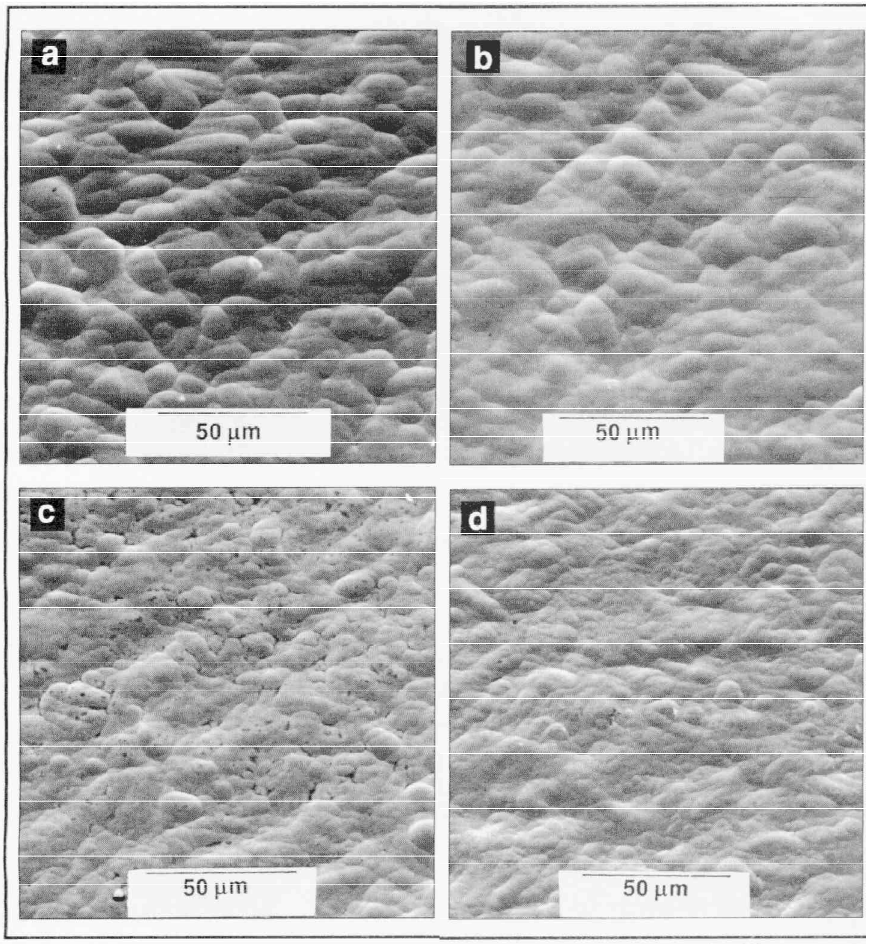

Fig. 5-Scanning electron micrographs of electroless nickel-phosphorus coatings under different magnetic stirring [clockwise] rates; (a) 250 rpm, (b) 300 rpm, (c) 350 rpm, (d) 400 rpm. Operating conditions: pH 4.5, 85 “C; plating time, two hr.

sulfate reference electrode. The electrodes were pickled for 30 sec in 50-percent nitric acid and rinsed in distilled water prior to plating. A freshly prepared copper substrate was used for different agitation conditions. The types of agitation studied were aeration and magnetic stirring. Stirring was either uni- or hi-directional. The rate of aeration ranged from 3.0 to 8.0 L/min and magnetic stirring speeds ranged from 200 to 500 rpm. The experimental arrangement used for magnetic stirring is shown in Fig. 1. Aeration was applied by admitting air through a side tube near the base of the vessel and through a sealed-in glass frit.

Electroless Composite Plating

Electroless composite plating experiments were performed, using different types of agitation. The solution used was operated as described above. The composite was silicon carbide having a mean particle size of four to seven µm, with bath loading ranging from 0-100 g/L. The substrates were pretreated according to procedures described earlier. They were then inserted in a separate electroless solution for five min as a strike, prior to composite plating and plated for two hr. The results were compared by SEM examination of the surface topography of the composite coatings obtained.

Results and Discussion

Table 3 and Fig. 2 show the effects of types and rates of agitation on the rate of deposition, using an electroless nickel-phosphorus solution operated at pH 4.5 and 85 °C. The results reveal that when the solution is not agitated, the deposition rate is high, but with increasing agitation, depending on the type of agitation, the deposition rate decreases. It was also found that after a few hours of plating, the magnetic stirrer damages the bottom of the plating vessel, a result of the rubbing action of the magnetic stirrer bar. This led to bath instability from the appearance of nickel on the bottom of the tank. From Fig. 2, it can be deduced that the deposition rate using aeration remains fairly constant upon increase of the rate of agitation, compared to the rate when using nitrogen sparging. This is an advantage over the other agitation techniques studied, especially for composite deposition where a high agitation rate is necessary to keep particulate matter in suspension, consistent with a relatively high deposition rate.

Figure 3 shows the percentages of nickel and phosphorus in the coating for different agitation types and rates. The ICP measurements were made against a solution containing a known amount of copper, because the amount of copper has an influence on the reproducibility of the ICP values. The nickel and phosphorus wavelengths used were 231.604 **nm and 253.565** nm, respectively. The **ICP measurements were made on coatings dissolved in aqua regia. The error of the results is about 10 percent, relative to a known solution containing copper, nickel and phosphorus. The re-**suits show that the composition of the coatings is fairly constant with a phosphorus content of 9.4 to 11.3 percent.

Figures 4, 5, 6 and 7 show scanning electron micrographs of the electroless nickel-phosphorus coatings for different rates of aeration, unidirectional magnetic stirring, bidirectional magnetic stirring, and nitrogen sparging, respectively. It

Table 4
Deposition Rates Obtained for Different Sparging Methods

	Pre-saturated/still, µm/hr	Interrupted agitation, µm/hr	Continuous agitation, µm/hr
Air	8.71	6.01	4.71
	8.58	7.84	5.60
Oxygen	8.40	5.27	3.14
	7.72	6.88	3.10
Nitrogen	7.11*	4.67	4.11
	9.14”	—	12.82*

“Solution decomposed during plating.

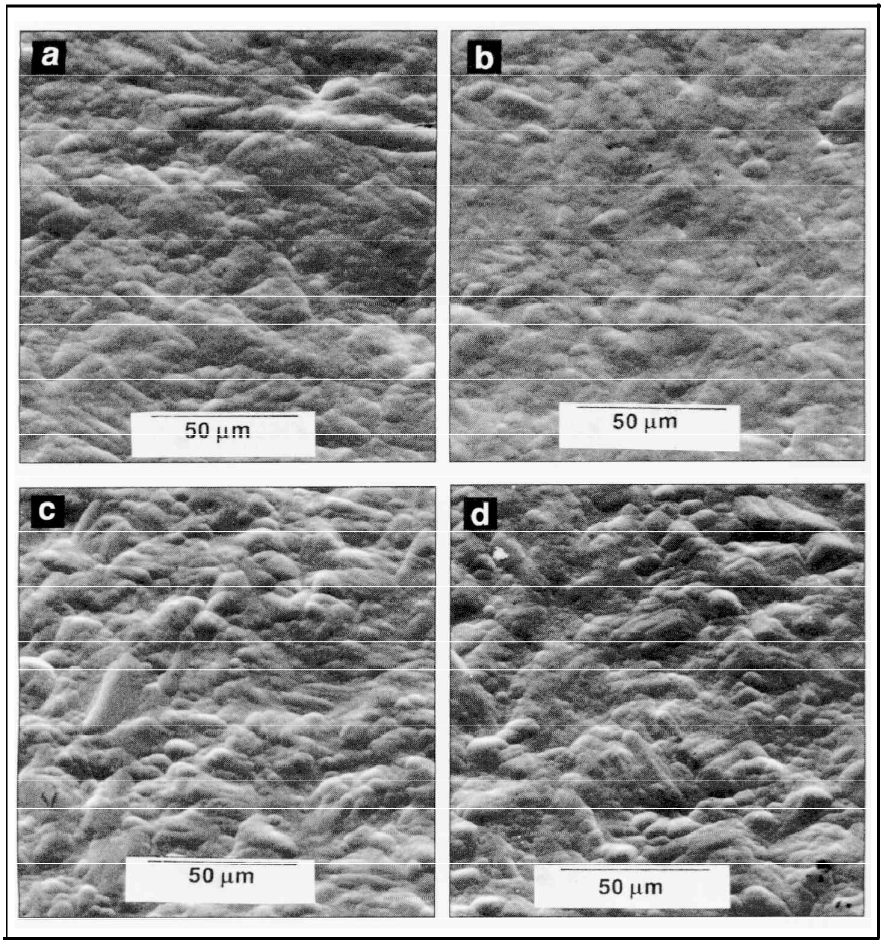

Fig. 6-Scanning electron micrographs of electroless nickel-phosphorus coatings under different magnetic stirring [clockwise/counter-clockwise (A/D)] rates; (a) 250 rpm, (b) 300 rpm (c) 350 rpm (d) 400 rpm. Operating conditions: pH 4.5, 85 °C; plating time, two hr.

can be seen that different agitation techniques and rates have some effect on surface topography, compared to the coatings obtained without agitation (Fig. 4). It can also be noted that because the coating thicknesses obtained under nitrogen were thin (Table 3) compared to other agitation methods, the surface texture has followed that of the copper substrates. If the coatings were allowed to become thicker, the surface topography would probably be similar to that obtained by the other agitation techniques. It **can** be concluded that the coating textures obtained by the different agitation techniques are broadly similar because no major structural differences have been detected.

Table 4 shows the results obtained for different methods of sparging (i.e., air, pure oxygen and pure nitrogen). It was found that the rate of deposition decreased in the order, saturated still solution > interrupted agitation > continuous agitation. The sparging rate was set at 3.0 L/min. The table also shows the reproducibility of the results obtained (± 10 percent), and the effectiveness of different types of continuous solution sparging and a comparison to saturated/still solution and interrupted agitation. The solution was saturated for 15 minutes prior to plating. The interrupted agitation was set to an on-off ratio of 1:3 min. A freshly made solution was used for each set of experiments.

The most important findings are based on the baths operated under nitrogen sparging. They show that the bath stability is affected by nitrogen. The majority of the results (Table 4) under nitrogen were obtained while the bath was decomposing, thereby increasing the apparent rate of reaction, increasing the plating rate and forming powdery deposits on the substrate surface. The rates of deposition obtained using oxygen were found to be somewhat lower than those using air sparging. No instability of the baths during the plating period was observed using either air or oxygen. The apparent beneficial effect of the presence of only 20 percent oxygen in air, compared with pure nitrogen, is surprising and, if confirmed, may be related to a specific influence on the bath chemistry. More research is needed on these aspects before firm conclusions may be drawn.

The polarization curves were obtained by sweeping the potential for different magnetic stirring, agitation and air sparging rates. From the polarization curves, a common limiting potential was established, then different limiting current density values for different agitation types and rates were obtained." Figure 8 shows the polarization curves obtained for different magnetic stirring rates, in alternate clockwise/counter-clockwise directions, **using** an acid copper sulfate solution at room temperature. Similar results were obtained for clockwise stirring and for aeration. From these curves, a common potential (known **as** limiting potential) was chosen: -0.75 V, and Figs. 9 and 10 were constructed to show the limiting current density for the various methods of agitation as functions of rate of stirring and rate of aeration, respectively. The figures may be used to describe the flow behavior as either laminar, turbulent, or as a transition region between the two. If such agitations are to be used for composite plating, the sparging or stirring rates must not be too slow, which may not disperse the particles completely, or too fast, which may not allow particles to remain on the substrates long enough to avoid reducing the amount of particles in the deposit. For these reasons, the laminar-turbulent transition region is considered to be the most effective for composite plating."

The optimum conditions for agitation, as obtained by the polarization technique, were, for magnetic stirring (either

Table 5
Deposition Rate Values Obtained at Different Air and Nitrogen Sparging Conditions
(electroless Ni-P at pH 4.5 and 85 °C.)

Sample number	Agitation rate, µm/hr	Deposition rate, µm/hr	SiC bath loading, g/L
39*	3.0	7.19	10
33*	3.0	3.12	20
9+	3.31	.269	10
11+	3.38	.334	30

*Air sparging, t nitrogen sparging

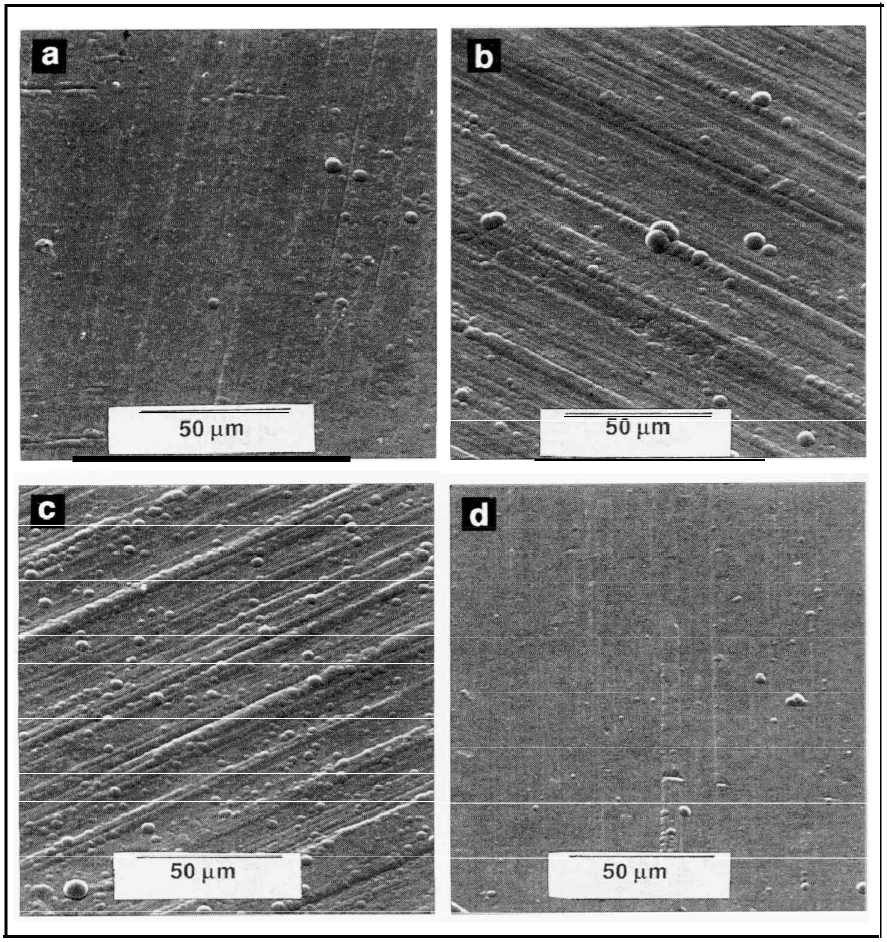

Fig.7—Scanning electron micrographs or electroless nickel-phosphorus coatings under different nitrogen sparging rates; (a) 2.69 L/min, (b) 2.92 L/min, (c) 3.00 L/min, (d) 3.85 L/min. Operating conditions: pH 4.5, 85°C; plating time, one hr.

uni- or hi-directional), 250 to 400 rpm; for aeration, 2.5 to 4.5 L/min. Because this technique is not directly relevant to an electroless system and is based on use of a different solution, these conditions were taken only as a rough guide.

The study of agitation has revealed that magnetic stirring causes the bath to become unstable after some period of plating, as mentioned earlier. This was found to be a result of the rubbing action of the magnetic stirrer bar at the bottom of the vessel, causing plating to commence there. If such an agitation technique were to be used for composite plating, it would reduce the bath life.

Examination of other agitation techniques, such as air and nitrogen sparging, revealed that the plating rate for a particular sparging rate can vary. From the polarization curves, the best plating rate is at the lower agitation rate of about 3.0 L/min. When producing composite coatings containing SiC, it was found that the plating rates using both air and nitrogen sparging were low, compared to rates obtainable without the composite present (Table 5). Because the reduction in rate with air sparging is much less than with nitrogen sparging, and for the reasons mentioned earlier connected with bath stability, sparging with air is considered the better method of agitation.

The scanning electron micrographs of the silicon carbide particles incorporated in the deposited coatings when using nitrogen sparging showed that the adhesion is very poor. This could be simply a result of the low rate of deposition. Agglomeration of the particles was also noticed. The use of aeration for composite plating showed that uniform particle incorporation in the deposit can be obtained, as shown in Fig. 11. From the micrographs and the actual plating, it is concluded that SiC loading **of** the bath should not exceed 35 g/L because the particles make the bath foam, reducing the rate of deposi-

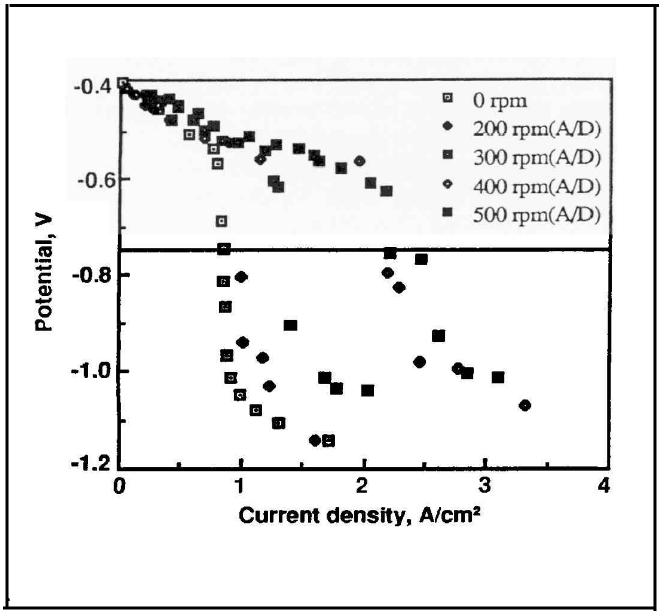

Fig. 8—Polarization curves obtained using an acid copper sulfate electrolyte under different magnetic stirring (clockwise/counter-clockwise) rates.

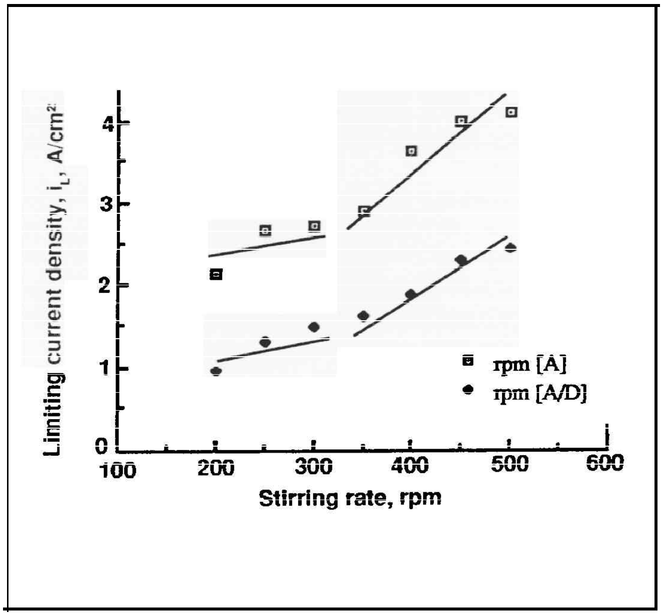

Fig. 9-Limiting current vs. magnetic stirring clockwise [A] and counter-clockwise [D], using an acid copper electrolyte; i_L obtained at E = -0.75 V.

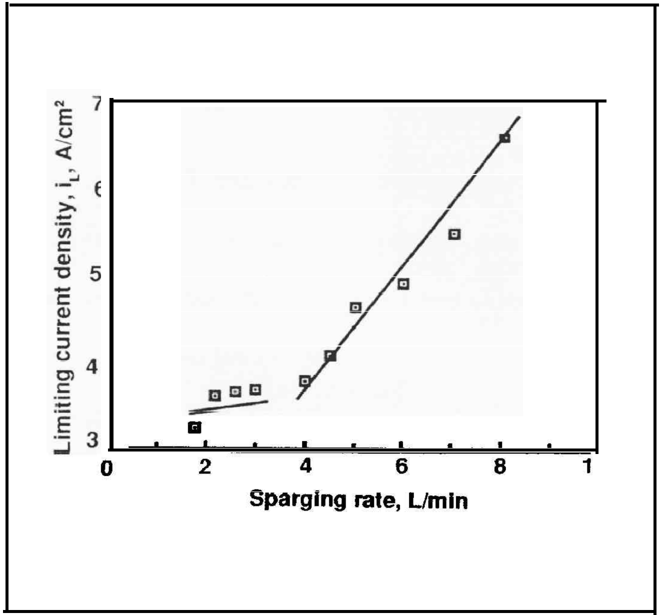

Fig. 10—Limiting current vs. different sparging agitation rates, using an acid copper electrolyte; i_L obtained at E = -0.75 V.

tion. An additional consideration is that too great an agitation rate can be disadvantageous, both practically and economically, because it reduces the rate of deposition. In this study, the ideal rate of aeration was found to be 3.0 L/min.

Summary

The ICP results show that the variation in phosphorus content of the plated deposit under various types of agitation is small.

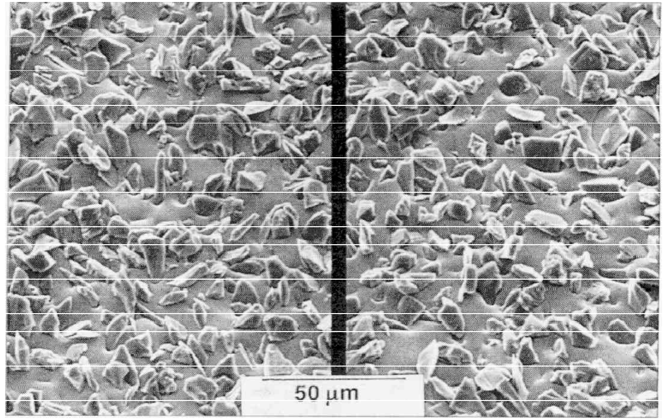

Fig. 11—Scanning electron micrographs of electroless nickel-phosphorus-silicon carbide showing the particle distributions obtained at bath loading of 25g/L and sample in uprjght position. Operating conditions were pH 4.5,85 °C and plating time, two hr.

As for agitation techniques, magnetic stirring and nitrogen sparging cause the bath to become unstable. Moreover, in the presence of silicon carbide particles, the rate of deposition under nitrogen sparging is reduced dramatically, compared to a bath without silicon carbide. The best agitation technique was found to be aeration and, for composite plating, the ideal rate of sparging was about 3.0 L/min.

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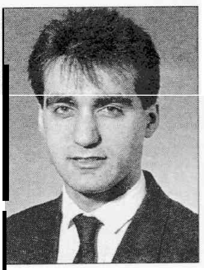
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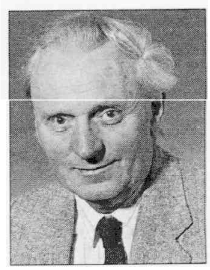
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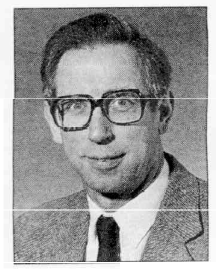
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