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Electrodeposited Ni-P-SiC Composite Coatings

By O. Berkh, A. Bodnevas and J. Zahavi

Electrodeposited Ni-P-SiC composite coatings containing 5 to 7 wt percent P and as much as 6.5 wt percent of SiC were produced with current efficiency of about 80 percent. Powder concentration and dispersion strongly influenced SiC particle incorporation, but not the P content of the deposits. Saccharin additive in the electrolyte considerably reduced the SiC and P content. On the other hand, neither saccharin adsorption on the particle surface, nor any effect on particle size distribution in the composites was revealed. The mechanism of saccharin action in codeposition is discussed in terms of its adsorption on cathode and conversion processes.

Electrodeposited composites based on Ni-P alloys containing different solid particles are very promising as protective coatings. They are characterized by wear and corrosion resistance comparable or superior to electroplated Cr.[1-3] According to limited available data, the level of P in the Ni-P matrix affects particle incorporation, and conversely the particles can considerably influence the process of Ni-P alloy deposition. An extremely important role in codeposition is played by the nature, size and adsorptivity of the particles;[4-6] however, no systematic investigations of these factors were reported. The effect of surface-active organic additives also was not studied, although some sulfur-containing compounds, in particular, saccharin (o-benzoic acid sulfimide), were applied in electrodeposition of Ni-P alloys[7-10] and Ni-P-SiC composites.[11-13] Saccharin was found to convert a tensile internal stress of 29 kgf/mm^2 in a Ni-P alloy into compressive stress[8] and to have a strong effect on the composition, structure and microhardness of Ni-P alloys,[10] as well as on particle codeposition with Ni.[14] Accordingly, it should be expected to play a role in composite deposition and to influence composite properties.

In the current work, the effects of saccharin and SiC powder dispersal on the deposition process of Ni-P-SiC composites were investigated, in some cases in the context of pH, inasmuch as the concentration of H$^+$ ions influences P incorporation,[15-17] as well as saccharin conversion on the cathode.[18,19]

Experimental Procedure

Codeposition of SiC particles with a Ni-P alloy was carried out from sulfate electrolyte. Electrolyte composition and deposition conditions are shown in Table 1.

Three SiC powders: N1, N2 and N3 with mean size values of 3.28, 1.53, and 1.14 µm, respectively, were examined. Powders N2 and N3 were produced from N1 by grinding for 5 and 15 min. at 1500 rpm. The mean size of the powders was determined by a computerized laser inspection system after ultrasonic treatment in ethylene glycol medium for one min. Prior to introduction into the electrolyte, the powder was treated with 1:1 HCl solution and rinsed with water.

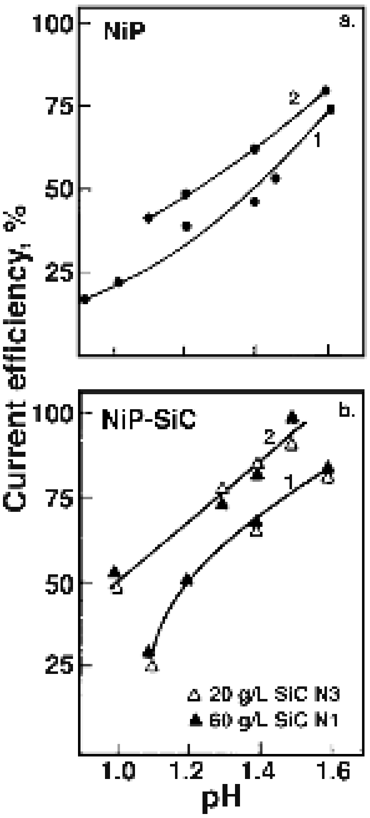

Fig. 1—Effect of pH on current efficiency: (a) in Ni-P alloys; (b) in Ni-P-SiC composites. 1 - deposits produced without saccharin; 2 - in the presence of saccharin, 1.5 g/L.

Particle incorporation in the coatings and their structure were studied by microscopy. The size distribution in the composite coatings was investigated by means of image analysis.[a] Electron Dispersive Spectroscopy (EDS) was used for P determination in the Ni-P alloys and composites.

The SiC content in the composites was determined gravimetrically. The coatings were separated from the stainless steel substrate, weighed and dissolved in 1:1 HNO$_3$; the insoluble SiC precipitate was weighed after washing, drying and annealing at 500 °C. The sulfur content was determined by atomic emission spectroscopy.

Table 1
Bath Composition & Deposition Conditions For Ni-P-SiC Composite Coatings

Bath Composition		Conditions	
Component	**Conc., g/L**	**Parameter**	**Value**
$NiSO_4 \cdot 6H_2O$	250	Temp	50–55 °C
$NiCl_2 \cdot 6H_2O$	50	pH	1.0–1.6
H_3BO_3	30	Current density	10 A/dm
H_3PO_3	10	Air agitation	2mL/L/min
SiC powders N1,N2,N3	0–120	Substrate	Brass & Stainless steel
Saccharin	0–3.0		

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[a] QUANTIMET 970, Cambridge Instruments.

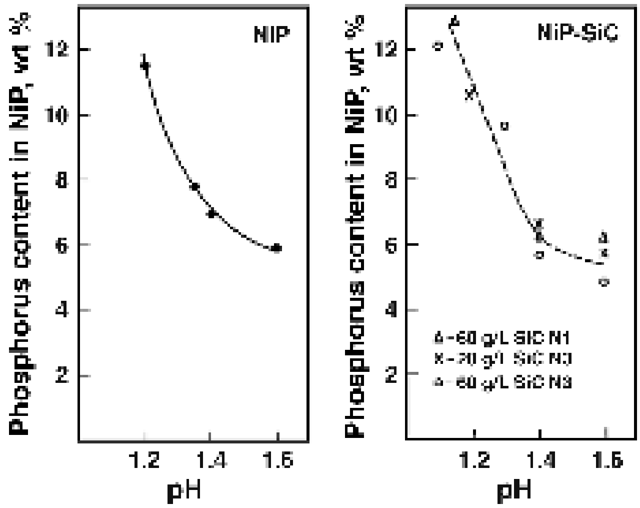

Fig. 2—Effect of pH on phosphorus content: (left) in Ni-P alloys; (right) in Ni-P-SiC composites.

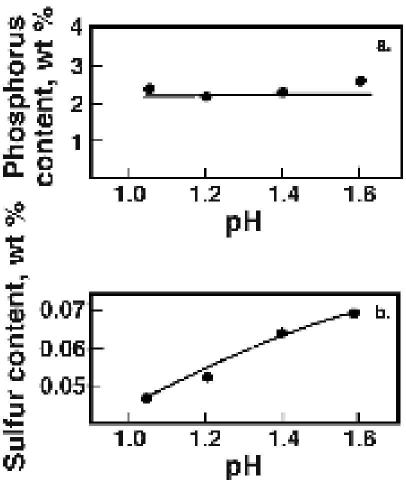

Fig. 3—Effect of pH on composition of Ni-P matrix of composites deposited in the presence of saccharin (1.5 g/L SiC N3): (a) phosphorus content; (b) sulfur content.

Adsorption of saccharin on the SiC particles was investigated by electrolyte spectroscopy in the UV range, as well as by electrophoretic mobility measurements of SiC particles in the electrolytes by zeta meter.

Results

Current Efficiency

Current efficiency as a function of pH is plotted in Figs. 1a and b for deposition of Ni-P alloys and Ni-P-SiC composites, respectively. Its close positive dependence on pH in both cases is evident. The SiC particles in the electrolyte produced a slightly higher efficiency, irrespective of their size and amount. In the presence of saccharin, the current efficiency similarly increased steeply with pH; the values of the efficiency were somewhat higher, both for Ni-P alloys and for Ni-P-SiC composites, the effect of saccharin being more noticeable at low pH.

Phosphorus Content

The phosphorus content of Ni-P and Ni-P-SiC composites decreased sharply with increase of pH, irrespective of the amount and size of the SiC particles (Fig. 2). This pattern was reversed in the composites in the presence of saccharin; the phosphorus level was considerably lower and unaffected by pH (Fig. 3a). The reduction of the P level was more pronounced at low pH, as can be seen by comparing Figs. 2 and 3a. At the same time, sulfur was incorporated in the composites, its amount increasing with pH (Fig. 3b). No effects of SiC powder concentration on the P content in the Ni-P matrix were revealed in codeposition, with or without saccharin (Fig. 4).

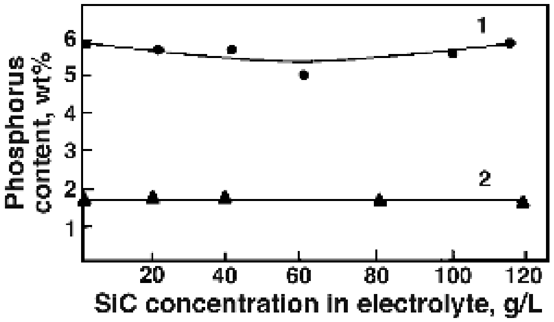

Fig. 4—Effect of SiC powder N2 conc. in electrolyte on phosphorus content in the Ni-P matrix. 1 - deposits produced without saccharin; 2 - deposits produced in the presence of 1.4 g/L saccharin.

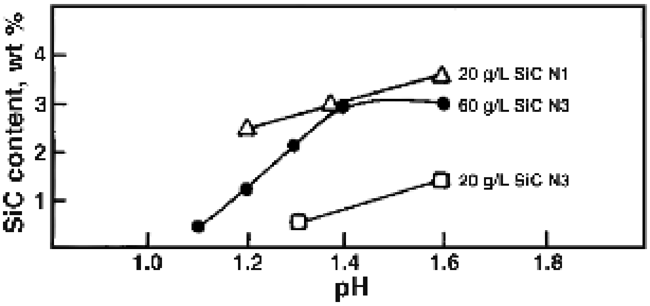

Fig. 5—Effect of pH on SiC content in Ni-P composites.

Effect of SiC Powder Dispersity

The effect of the degree of dispersion of SiC was examined at different values of pH and different SiC powder concentrations in the electrolyte (Figs. 5 and 6). According to the data obtained, increase of pH resulted in increase of SiC content in the composite coatings at low particle concentration (20 g/L), irrespective of the dispersity. At the higher concentration (60 g/L) the particle content increased in the pH range 1.0-1.4 and reached saturation at pH 1.4-1.6 (Fig. 5).

The SiC content in the composites increased with its concentration in the electrolyte, tending to saturation for all powders investigated (Fig. 6).

Decrease of mean particle size in the powder resulted in decrease of the wt percentage of the incorporated SiC throughout the ranges of SiC concentrations and pH investigated (Figs. 5 and 6a), and in increase of the particle count (N) in the composites (Fig. 6b).

Saccharin vs. Coating Composition & Particle Size Distribution

Increase of the saccharin concentration resulted in decrease of the P and SiC contents in the composite coatings while the sulfur content increased (Fig. 7). The decrease in incorporation can also be seen on comparing the data in Figs. 8 and 6a—the SiC content in composites produced with saccharin did not exceed three percent, while without it the values were about 1.8 times higher. The effect of saccharin on SiC particle incorporation is illustrated visually by Fig. 9.

Saccharin concentration did not affect SiC particle distribution in Ni-P-SiC composite coatings (Table 2), or the shape

Table 2
Parameters of Particle Size Distribution in Ni-P-SiC Composites As a Function of Saccharin Concentration
(SiC powder N1, 45 g/L)

Saccharin conc	Parameters of Particle Distribution					
g/L	L	S.D.L.	W	S.D.W.	Shape Factor	$\frac{L + W}{2}$
0	4.59	2.35	2.17	0.96	0.524	3.38
0.3	4.45	2.30	2.17	1.09	0.537	3.31
1.2	4.47	2.40	1.95	0.92	0.481	3.21

L - mean length, µm
W - mean width, µm
S.D.L. & S.D.W. - standard deviations of particle distributions vs. L and W, respectively.
Shape factor - mean W/L
Mean size of particles in SiC powder N1, 3.28 µm
Standard deviation of their distribution, 2.87 µm.

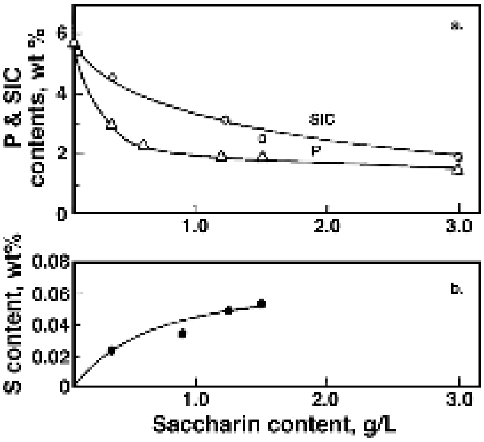

Fig. 7—Composition of Ni-P-SiC composites as a function of saccharin conc. (45 g/L SiC powder N1, pH 1.4): (a) phosphorus and SiC content; (b) sulfur content.

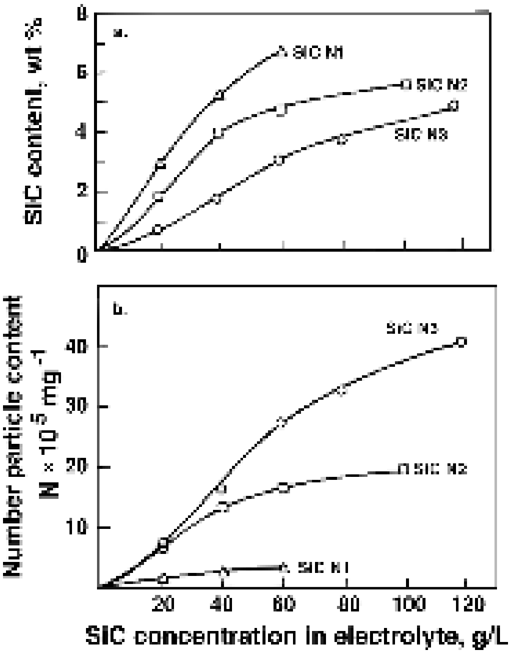

Fig. 6—Effect of SiC powder conc. on SiC contents of powders of different dispersity (pH 1.4): (a) weight content; (b) number particle content (calculated based on mean size of particles and data in (a).

of the incorporated particles—they had the form of plates with thickness about half their diameter (Table 2, Figs. 9 and 10).

Saccharin Adsorption on SiC Particles

The spectrum of the Ni-P electrolyte containing saccharin showed no absorbance decrease in the saccharin analytical bands (226 nm and 270 nm) after SiC particle introduction into the electrolyte, stirring and filtration.

Because saccharin is a weak acid,[20] adsorption of its anion on the SiC particle surface would be expected to increase the negative charge of the latter. Actually, the electrophoretic mobility of the SiC particles with and without saccharin was -1.1 and -1.0 µm/sec/V/cm, respectively, that is, practically the same. The results obtained indicate no adsorption of saccharin on the SiC particles under investigation.

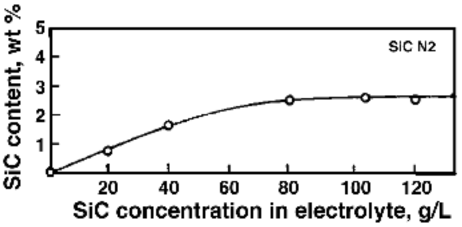

Fig. 8—Effect of SiC powder N2 conc. on SiC content in deposit (Saccharin 1.5 g/L, pH 1.4).

Discussion

Adsorption phenomena were found in previous investigations to be a controlling factor in the particle codeposition process.[21-23] These phenomena play an especially considerable role in particle codeposition with Ni and its alloys, owing to the high adsorption affinity of Ni cathodes for the solid particles and other components of the electrolyte.[22] Most of the data obtained in the present investigation can be explained in terms of the competitive adsorption of phosphorus anions, saccharin and SiC particles on the cathode surface.

The lower phosphorus content in the composites in the presence of saccharin is, among others, the consequence of the occupation of a considerable part of the active centers on the cathode surface by saccharin. The main factor, however, is conversion of the saccharin on the cathode.[18,19] This process, as well as conversion of the phosphite anion and P incorporation in the deposit, proceeds with consumption of active hydrogen on the cathode surface. The result is redistribution of the expendable hydrogen, and reduction in the intensity of phosphorus anion conversion and P incorporation (Fig. 2). The above considerations explain both our own results and the data of Bonino *et al.*,[10] according to which, phosphorus incorporation in Ni-P deposition is inhibited by increasing the saccharin concentration in electrolytes. The saccharin effect is more pronounced at relatively low pH and weakens as pH increases, as a result of the parallel decrease in the surface concentration of the adsorbed hydrogen. As shown by Zhukaite, Matulis *et al.*,[18,19] increase of pH resulted in reduction of the saccharin conversion rate, as well as reduction of accumulation of o-toluenesulfonamide (one of the saccharin conversion products).

Inasmuch as no adsorption of saccharin on the SiC particles was observed, its effect on particle codeposition cannot

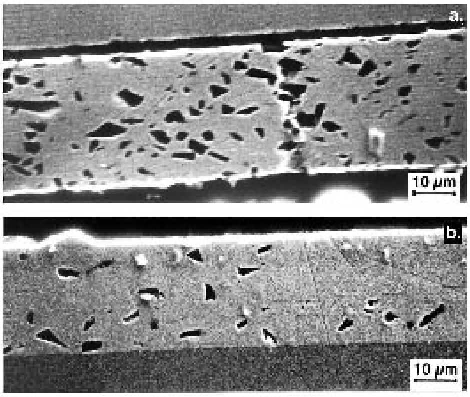

Fig. 9—Effect of saccharin on particle incorporation. Cross sections of Ni-P-SiC composites (20 g/L SiC N2): (top) deposition without saccharin; (bottom) deposition with 1.5 g/L saccharin.

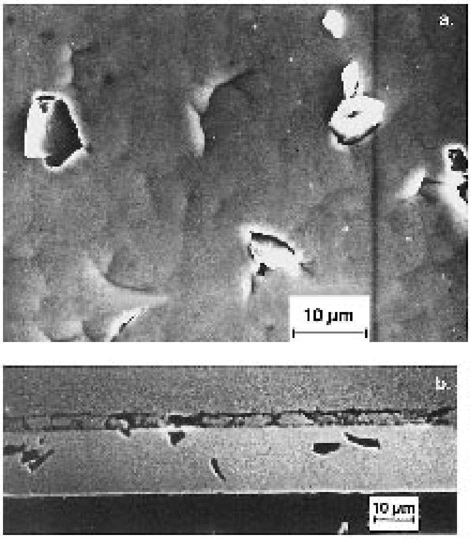

Fig. 10—Structure of Ni-P-SiC composite (SiC powder N1, 20 g/L; H_3PO_3, 25 g/L; saccharin, 1.5 g/L): (top) SEM micrograph of composite surface; (bottom) SEM micrograph of Ni-P-SiC cross-section. 1000X.

be explained by a change in their adsorptivity, but rather by reduction of the active centers, as a result of saccharin adsorption on the cathode. Absence of saccharin adsorption on SiC particles is consistent with the invariance of the particle distribution in the composite with respect to the saccharin concentration in the electrolyte. SiC particle incorporation in the presence of saccharin can also be inhibited by the refining of the growing Ni-P surface. The refining effect of saccharin was observed for both the Ni structure[14] and Ni-P structures.[10] The entrapment intensity of the particles by refined smooth deposits was found to be lower compared to those with a rough surface.[6]

According to our results, the SiC particles did not reduce the P content in the composites. On the other hand, they inhibit sulfur incorporation into Ni deposits by reduction of the active centers and retardation of the saccharin desulfurization.[22,25] The change in cathode surface conditions as a result of SiC particle action was also confirmed by the improved current efficiency (Fig. 1). A similar phenomenon was observed also in studies by Guslienko[5] and Sayfullin[6] for other types of particles.

The effect of particle dispersity on incorporation can also be explained in terms of the adsorption phenomena. Fine particles with high adsorptivity were codeposited at high number concentrations (Fig. 6b). Such preferential incorporation was observed in codeposition of Al_2O_3 with Cr-Ni alloy[23] and of SiC with Ni-P.[24] This phenomenon can be regarded as one of the fundamental features of particle codeposition.

Conclusions

1. Composite coatings of Ni-P-SiC, containing 5-7 wt percent P and as much as 6.5 wt percent SiC were produced with current efficiency of about 80 percent. Decrease of pH leads to decrease of current efficiency and particle incorporation, while phosphorus content sharply increases, reaching 12-13 wt percent.

2. Introduction of saccharin into the electrolyte resulted in enhancement of current efficiency and of sulfur incorporation in the composites, as well as decrease of their SiC and P content. Saccharin was not adsorbed on the particles and did not influence the particle size distribution in composite Ni-P-SiC coatings.

3. Dispersity of the SiC powders considerably influences particle incorporation. The weight percentage of fine SiC particles is lower than that of relatively coarse particles; by contrast, the number content of the former is higher. Phosphorus content in composites was invariant, irrespective of the dispersity and SiC concentration in the electrolyte.

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