Investigation of Electroless Ni-P-SiC Composite Coatings

By Yongjun Li

Electroless Ni-P-SiC composite coatings were investigated from the viewpoint of bath formulation, technology and coating properties. A sound and homogeneous deposit containing 25-30 vol. percent SiC can be produced, using an optimum bath formulation and technology. In comparison with Ni-P coatings, Ni-P-SiC composite coatings possess greater hardness and higher porosity, as well as lower adhesion and corrosion resistance. It is a significant advantage that the wear resistance of the composite coating is considerably increased. Heat treatment at high temperature can improve adhesion and wearability of the composite coating. Structural analysis confirms that a new phase of Ni_3Si compound exists in the Ni-P-SiC deposits annealed at 650 °C for 1 hr. In this paper, formation of the Ni_3Si compound and wear mechanism of the coatings are discussed.

Electroless nickel is an engineering coating normally used because of excellent corrosion and wear resistance, as well as other specific properties.[1] With development of industry demands for improved performance, better surface coatings have become more difficult to attain, such as higher wear and corrosion resistance, self-lubricating properties and better electric and magnetic properties. In the past ten years, therefore, major progress in the field of electroless nickel has been nickel polyalloy deposits and electroless composite coatings[2,3] being tailored more closely to customer and environmental requirements. Electroless nickel composite coatings are usually obtained by codepositing particulate materials, such as silicon, tungsten and chromium carbides, ceramics, diamonds and fluoropolymers. The composite coatings can increase significantly the wearability of the deposits and/or lower coefficient of friction and impart lubricity. Their applications in various industries provide components of higher quality and increase their lifetime. The relevant technology of bath formulation and properties of the deposits for these composite coatings needs to be more deeply understood and improved to keep pace with the demands of end users.

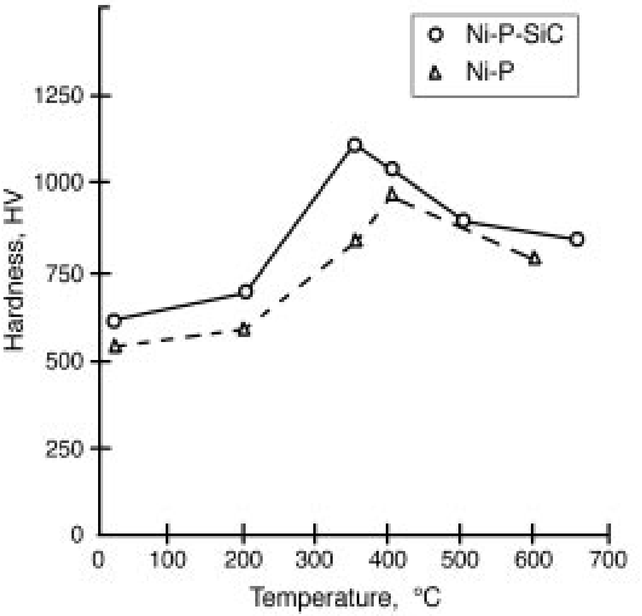


Fig. 1—Effect of heat treatment temperature on hardness of Ni-P and Ni-P-SiC coatings.

The object of this study was to develop a method of producing electroless Ni-P-SiC composite coatings and to evaluate their properties.

Table 1
Plating Solutions for Electroless Ni-P-Sic

Constituent	Bath 1	Bath 2	Bath 3
Nickel sulfate (g/L)	22.4	18	20
Sodium hypophosphite (g/L)	24.6	24.4	22
Complexing agent A (mL/L)	8.5	12	
Complexing agent B (mL/L)	17		12
Complexing agent C (mL/L)		8.0	
Complexing agent D (g/L)			16
Stabilizer 1 (ppm)	1		1
Stabilizer 2 (ppm)		1	1
Surfactant (g/L)	0.01-0.10	0.01-0.10	0.01-0.10

Conditions: pH 4.5-5.5, Temp 80-90 °C, air agitation

Experimental Results & Analyses

Technology & Bath Formulation

The electroless plating tests were carried out in a beaker placed in a thermostatically controlled bath. The substrate was SAE 1010 steel panels, 5 x 10 x 20 mm. Test processes were degrease, soak clean, rinse, dip, rinse, and electroless plating to thickness and after-treatment.

Optimum Bath Formulation

Three types of solution composition were designed in the test, as shown in Table 1. SiC

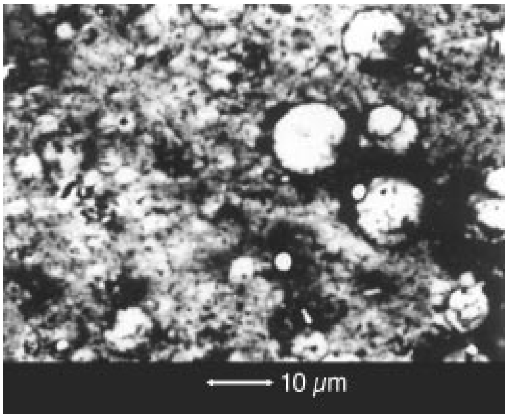


Fig. 2—Distribution of SiC in coating.

Table 2
Test Results of Porosity & Corrosion

Coating	Condition	Porosity	Corrosion Aspect
		(blue point/2.7 cm^2)	
Ni-P	as-plated	0	white
	400 °C	4-8	gray
	650 °C	10-12	dark gray
Ni-P-SiC	as-plated	0	white
	400 °C	8-10	dark gray
	650 °C	12-15	gray-black

(Conc. nitric acid; coating 30 μm)

powder, with particle size of 1-5 μm, was pretreated, then added to a proper solution, followed by a surfactant and sufficient agitation to enable the surfactant to be uniformly absorbed on the SiC particles. The working solution was prepared by adding the concentrated SiC dispersion to the proper electroless solution. The solution was gently stirred for 30-60 min to homogenize the SiC suspension.

The test results show that Bath 3 can produce optimum, sound and homogeneous deposits, containing 25-30 vol. percent SiC with a plating rate of 7-8 μm/hr.

The bath was operated over eight cycles with intermediate maintenance and without any decomposition, indicating its excellent stability. The pH of the plating solution was decreased only about 0.2-0.3 after operating for two hr, indicating its good buffering ability.

Agitation Methods

Because the 1-5 μm SiC particles were significantly denser than the plating solution, they would settle readily to the bottom of the beaker unless efficient agitation was used. To suspend the SiC particles homogeneously in the solution and increase the entrapment probability of the particles on the substrate surface, both continuous and intermittent mechanical and air agitation were adopted. The compressed air intermittent agitation, with off time for 5-10 min in a cycle of 20 min, was found to be the most convenient, resulting in sound and homogeneous deposits, consistent with that reported by Dennis *et al*.[4]

Porosity & Corrosion Resistance

Tests of the porosity and corrosion resistance to concentrated nitric acid were performed on specimens with an area of 2.7 cm^2 and deposit thickness about 30 μm for both Ni-P and Ni-P-SiC. The method of the porosity test was consistent with ISO 4527.6.6. The method of corrosion resistance testing was that specimens were immersed half in concentrated nitric acid solution (d 1.4) for 30 sec. Corrosion aspects of their surfaces were then observed. The test results are shown in Table 2.

The test results reveal that the porosity of Ni-P-SiC coatings is higher and their corrosion resistance weaker by comparison with Ni-P coatings. Whether Ni-P or Ni-P-SiC coatings, porosity is increased and corrosion resistance is lowered with increase in heat treatment temperature. This is relevant to nickel phosphide particle precipitation and cracking in the deposits with tempering at 400 and 650 °C.[1]

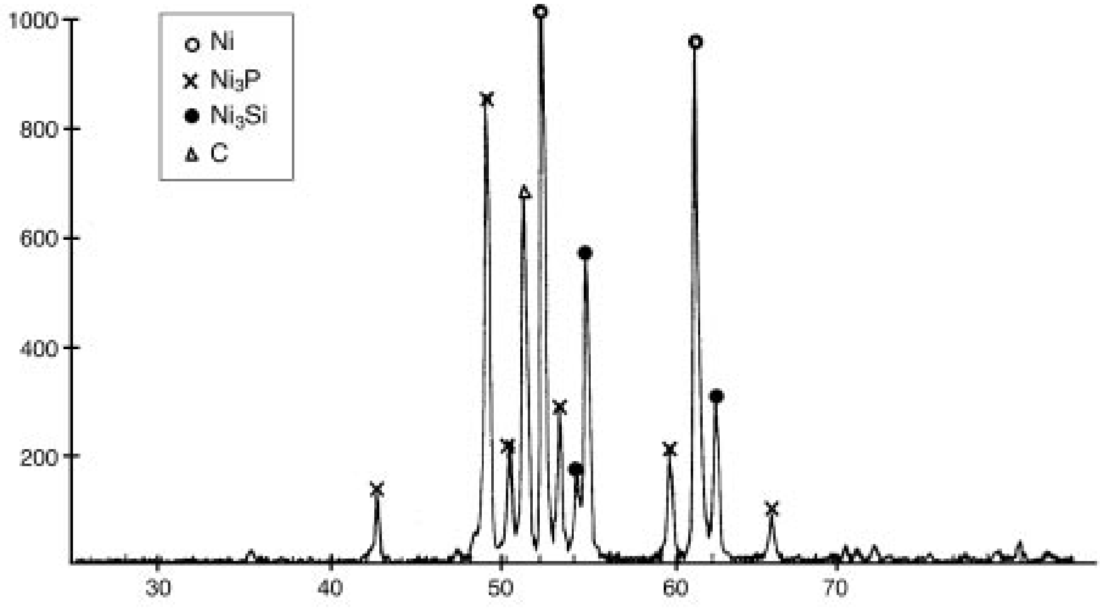


Fig. 3—X-ray diffraction pattern of Ni-P-SiC coating annealed at 650 °C for 1 hr.

Hardness

The hardness of the coatings was examined on a microhardness tester with load of 50 g. From the test results shown in Fig. 1, it can be seen that hardness change in an Ni-P-SiC coating is similar to that of Ni-P with tempering. The maximum hardness is HV 1120 at 350 °C. The hardness of the Ni-P-

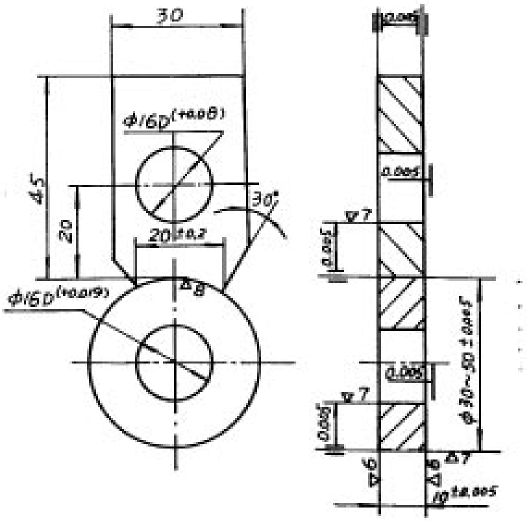


Fig. 4—Wear specimen.

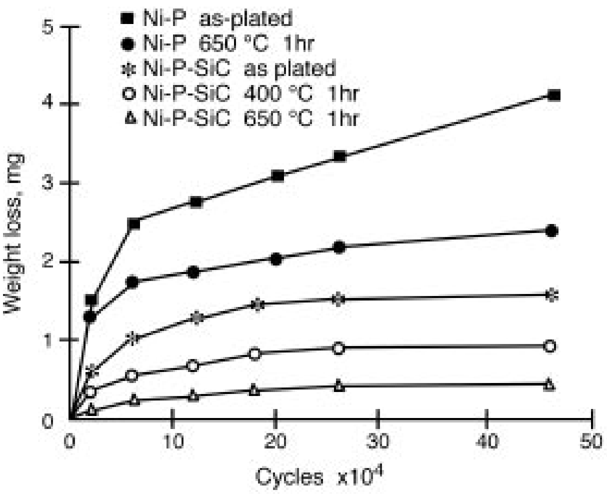


Fig. 5—Wear test results for Ni-P and Ni-P-SiC coatings against GCr15 counterpart.

SiC coating is higher than that of Ni-P under the same heat treatment conditions.The higher hardness is caused by the additive effects of the normal precipitation hardening mechanism and the dispersion hardening effect of the silicon carbide particles, similar to the chromium and tungsten carbides.[4]

Adhesion

The bond strength of the coating was examined by a bending test on the panels of Q235 steel: 1 x 10 x 80 mm. The panels with deposit thickness of 30 µm were bent 180° on a 3 mm dia. mandrel, followed by observation of flaking, peeling and cracking of the coating on the bent areas, using 5X magnification.

From the results shown in Table 3, it can be seen that under as-plated conditions, adhesion of Ni-P-SiC coatings is inferior to that of Ni-P. Heat treatment at 400-600 °C improves adhesion of both coatings, and the difference is not great. It appears that heat treatment at elevated temperature is an important approach to increase adhesion of the composite coating.

Analysis of Deposits

SEM observations show that SiC particles are evenly distributed throughout the matrix of electroless nickel and their amount is about 25-30 vol. percent, measured by linear intersection method (Fig. 2). The composite coating contains 10.68 wt percent P, measured by wave spectrometer. The structural analysis for a Ni-P coating tempered at 650 °C was conducted on D/max-3A mode X-ray diffraction apparatus (Co kα, λ= 1. 7902 Å). The X-ray diffraction pattern shown in Fig. 3 confirms that the coating contains not only Ni and Ni_3P crystals, but contains a new type of phase: Ni_3Si. This new phase has been little reported in previous references.[5]

Takashi OMI *et al.* studied an electroplated Ni-SiC dispersion coating.[6] They found formation of a strong bond on annealing the coating at 600 °C. The bonding reaction was found to have an incubation period of two min and then proceeded to form a bonding layer, which was a composite: SiC/Ni_5Si_2 /Ni_3Si/graphite/Ni. On further annealing at 600 °C, the dispersed particles were transformed into Ni_3Si particles coated with a graphite film. Similar particle-matrix reaction was also observed in electroplated Ni-WC composite at a temperature somewhat above 300 °C.[7] The reaction was found to comprise the dissolution of tungsten at the particle surface into the matrix, with formation of a graphite carbon film that enveloped the WC particles.

For an Ni-P-SiC deposit, tempered at 650 °C, phosphorus in the coating should be fully precipitated in the form of Ni_3P, therefore the interfaces between SiC and the matrix were actually between SiC and nickel crystals. It follows that the particle-matrix reaction in electroless Ni-P-SiC composite is the same as that in electroplated Ni-SiC coating. According to the Ni-Si equilibrium diagram,[8] as a nickel-silicon solid solution accumulates more than 5 wt percent silicon, the compound Ni_3Si would be formed and precipitated from the nickel matrix. The solid solution at the SiC particle/matrix interface may meet the requirement for formation of Ni_3Si as a result of a "bonding reaction" at 650 °C.

It is said that the formation of Ni_3Si promotes ductility of the coatings and doubles the tensile strength of a coating at 400 °C. Further work is needed to reveal the effect of Ni_3Si on other properties of the coating.

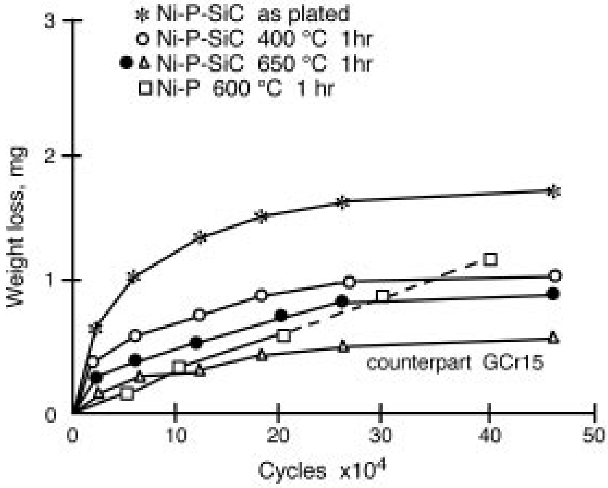


Fig. 6—Wear test results for Ni-P and Ni-P-SiC coatings against themselves.

Wear Test

Wear tests were carried out on an MM-200 machine at 400 rpm, loading of 5O N and oil lubrication. The upper specimens were made of GCr15 steel, quenched and tempered at 200 °C with hardness HRC 64. Lower specimens were made of 2OCr steel, quenched and tempered at 600 °C. Shape and size of the specimens are illustrated in Fig. 4. An electroless nickel composite was generally deposited on the lower specimens to a thickness of 30-40 µm, and deposited also on a set of upper specimens to determine the self-wear effect of the coating.

Table 3
Adhesion Test Results

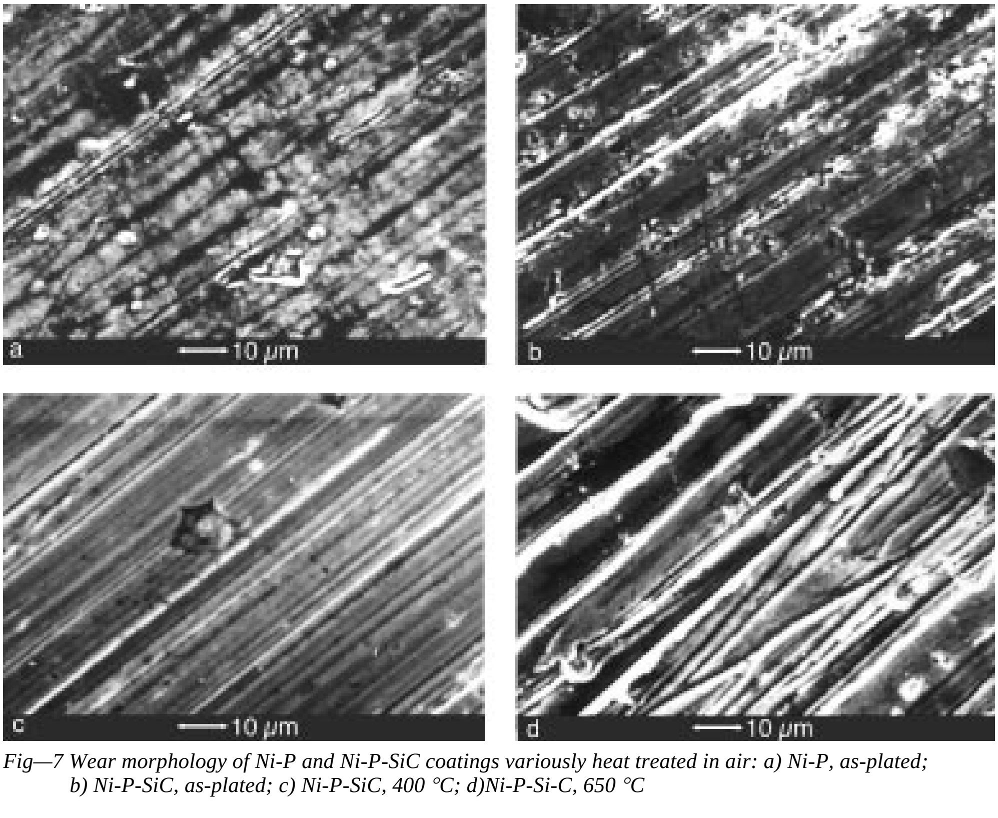
Condition	Ni-P	Ni-P-SiC
As-plated	local scaling & peeling	heavy scaling & peeling
400 °C	no scaling, peeling a few cracks in edge	no scaling, peeling a few cracks
650 °C	no scaling, peeling or cracking	no scaling, peeling or cracking

The test results shown in Fig. 5 indicate that wear resistance of Ni-P-SiC coatings is much higher than that of Ni-P. Under identical conditions, weight loss of the composite coatings is approximately from a quarter to one-fifth that of Ni-P coatings. This suggests that wearability of composite coatings may be increased by a factor of 4 to 5. The wear resistance of the composite coating increases with increase in tempering temperature. Comparing the results of Ni-P-SiC coating against itself with a GCr15 steel counterface (see Fig. 6), it can be seen that the wearability of the composite coating against itself is decreased, which is different from the wearability of an Ni-P coating against itself.[9]

Discussion

SEM observations on wear surfaces show that forms of wear on the coatings are predominantly grooves, peeling and scaling. As illustrated in Fig. 7, heavy peeling in bulk occurred on as-deposited coatings, especially in the edge areas. The grooves on Ni-P coatings are deeper (Fig. 7a), whereas those on Ni-P-SiC are finer and denser (Fig. 7b). For the composite coating tempered at 400 °C, peeling occurs to a greater extent, but its grooves are fine, dense and shallow (Fig. 7c), whereas a coating tempered at 650 °C exhibits wide and shallow grooves with a rolling deformation aspect on their edges without any peeling (Fig. 7d). Obviously, the weight loss of the specimen is greater, with deeper grooves, and heavier peeling. These wear behaviors fully correspond to the wear resistance of various coatings.

In the initial stage of friction and wear, projecting SiC particles in the composite coating first begin the process of wear; therefore, wear resistance of the coating would be very high because of their high hardness. As wear continues, debris is produced and groove wear occurs. Under identical wear conditions, the depth of gouging depends on the hardness of the coating. Because the hardness of an Ni-P-SiC coating is greater than that of Ni-P, grooves in the former are finer and shallower. The hardness is enhanced with increase in tempering temperature, resulting in finer and shallower grooves. For the coating tempered at 650 °C, ductility is improved; accordingly, a plastic deformation layer can be produced by rolling at the edges of grooves.



Fig—7 Wear morphology of Ni-P and Ni-P-SiC coatings variously heat treated in air: a) Ni-P, as-plated; b) Ni-P-SiC, as-plated; c) Ni-P-SiC, 400 °C; d)Ni-P-Si-C, 650 °C

Peeling in bulk is relevant to adhesion and toughness of the coating. Adhesion and toughness of the coating tempered at 650 °C are significantly improved, and it exhibits the best wearability without peeling.

The better wearability of Ni-P-SiC coatings compared with Ni-P can also be related to the fact that voids formed by SiC particles being pulled out have the effect of oil storage, resulting in increased lubrication. This analysis is supported by the fact that weight loss of the counterface made of GCr15 steel against Ni-P-SiC coating is obviously less than that of one against Ni-P deposit under the same conditions.

Conclusions

1. Bath 3 is an excellent solution for electroless Ni-P-SiC composite deposits. SiC content inthe composite coating can reach 25-30 vol. percent.
2. In comparison with Ni-P coatings, Ni-P-SiC composite coatings possess greater hardness, higher porosity, as well as lower adhesion and corrosion resistance. Whether Ni-P-SiC or Ni-P coatings, their porosity is increased andcorrosion resistance decreased with elevated tempering temperature.
3. A new type of compound, Ni_3Si, was found in Ni-P-SiC coating annealed at 650 °C for 1 hr.
4. The wear resistance of an Ni-P-SiC deposit is much higher than that of a Ni-P coating. The wear form of the coatings is predominantly groove and peeling or scaling under given test conditions.

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