

Electrolytic Codeposition Of Submicron Silicon Carbide with Nickel

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Codeposition of submicron SiC powders from different origins with nickel was successfully achieved in laboratory and semi-industrial plating cells. The weight percent of SiC in the coatings depends on the concentration of SiC particles in suspension. The particle distribution was quite uniform across the coating thickness. Several additives were tried to optimize the surface finish of the coatings. The hardness of the Ni-SiC coatings increases with increasing amount of incorporated SiC and the wear resistance in sliding is improved in comparison to pure nickel. A potential application of such wear-resistant composite coatings is given.

Electrolytic synthesis of composite coatings was intensively investigated¹⁻³ with the purpose of creating surfaces with protective, wear-resistant, corrosion-resistant, high-temperature-oxidation resistant and electrocatalytic properties.

Composite coatings such as Ni-SiC have been introduced successfully in the German, French and Japanese automotive industry over the past decade. The first developments were the production of nickel-silicon carbide as wear-resistant coatings in the Wankel motor³ and as cylinder lining in aluminum engines. Control of plating conditions during codeposition is very important, however, for achieving good reproducibility of the amount of particles codeposited⁴ and good uniformity of their distribution within the coating.

In many applications, codeposition of small-sized particles is preferred. In a patent on composite plating,⁵ it is mentioned that particle size should be below 10 μm , preferably not more than 5 μm . Sesame et al.⁶ and Metzger and

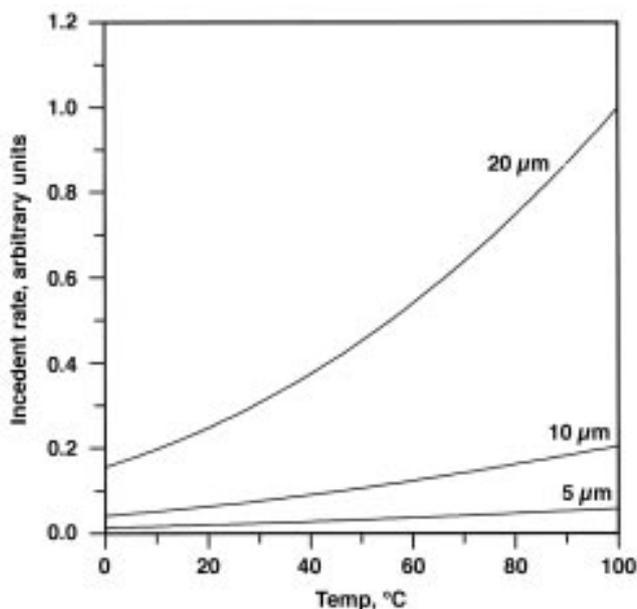


Fig. 1—Calculated dimensionless incident rate of polystyrene particles of different sizes on a disc electrode rotating at 200 rpm as a function of the temperature of an acid copper sulfate solution.¹⁰

Florian⁷ used particles in the range of 1 to 10 μm . When submicron SiC particles are codeposited with nickel, the degree of incorporation is reduced; Maurin and Lavanant⁸ noted that in the case of 0.1 μm SiC powders, incorporation during rotating disc experiments in a nickel sulfate solution never exceeded 0.7 wt pct, which was close to the detection threshold of their analytical technique. On the contrary, they found that with 0.8 μm SiC particles, incorporation of 2 wt pct and with 2.8 μm SiC particles, codeposition of approximately 5 wt pct was obtained. Based on a trajectory analysis, Fransaer et al.^{9,10} predicted quantitatively the dependence of the codeposition of polystyrene particles with copper on a rotating disc electrode under perfect sink conditions. Figure 1 shows their result as a function of mean particle diameter and plating bath temperature. According to their model, codeposition of 5 μm particles is predicted to be 10 times smaller than codeposition of 20 μm particles.

The purpose of this study was to evaluate codeposition of submicron silicon carbide powders of different producers from Watts nickel plating solutions. Tests were done under laboratory and semi-industrial plating conditions. The main parameter investigated was the addition of surfactants used to affect both the plating and the codeposition processes. The microhardness, wear-resistance and corrosion resistance of the composite coatings obtained are briefly discussed.

Experimental Procedure

Codeposition tests were performed in three different cells. A laboratory cell with thermostat, of about 50 mL, was used with a vertical stainless steel cathode of about one cm^2 located at the side wall of the cell. Agitation was by magnetic stirrer. In a laboratory cell with thermostat, of 1 L, the vertical stainless steel cathode was about 25 cm^2 and was located between two larger vertical nickel anodes. Agitation was by an air bubbling system. Finally, a semi-industrial cell of 5 L,



Fig. 2—View of a semi-industrial cell used for the electro-synthesis of Ni-SiC composite coatings. (Photo courtesy of Corroza Engineering, Sofia, Bulgaria)

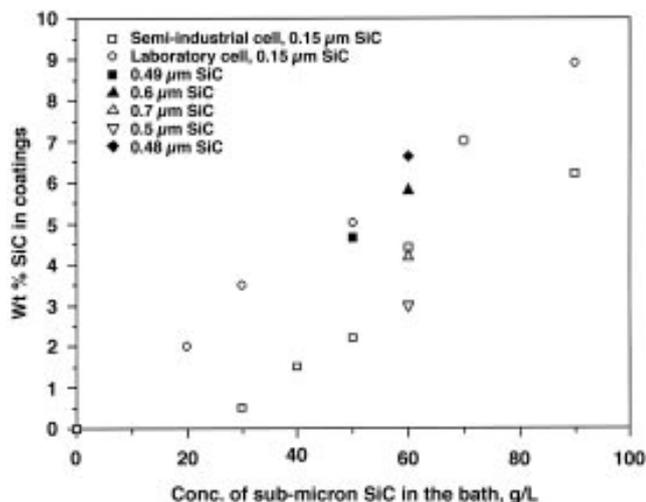


Fig. 3—Weight percentage of silicon carbide powders codeposited from additive-free Watts nickel solutions as a function of the effective concentration of SiC particles in the plating bath.

equipped with an intensive air bubbling system was used (see Fig. 2). A vertical stainless steel cathode of about 100 cm² was moved back and forth horizontally. The air bubbling system was positioned horizontally at the bottom of the cell and provided a homogeneous bubble distribution in the bulk of the plating solution. The cell contained a PTFE heater and a thermosensor for automatic temperature control. Nickel rounds 6–12 mm and containing 0.025 percent sulfur were put in titanium baskets and used as counter electrodes. The baskets were covered by bags to prevent contamination of the plating baths.

Coatings were deposited on stainless steel cathodes,^a which allow coatings to be stripped off for testing. The substrate pretreatment consisted of a cathodic degreasing at 65 °C, done at 5 to 10 A/dm² for 3 min. The cathode-to-anode surface ratio was 1:2. The cathodic degreasing was followed by anodic degreasing at 55 °C and 5 A/dm², a hot rinse at 75 °C, a cold rinse, de-tarnishing at 18 to 30 °C for 30 to 60 sec, and finally by another rinse. After pretreatment of the cathode, the composite plating was performed at pH 4.5, 55 °C, and 5 A/dm². The Watts plating solution contained 300 g/L NiSO₄ · 6H₂O, 35 g/L NiCl₂ · 6H₂O and 40 g/L H₃BO₃. In

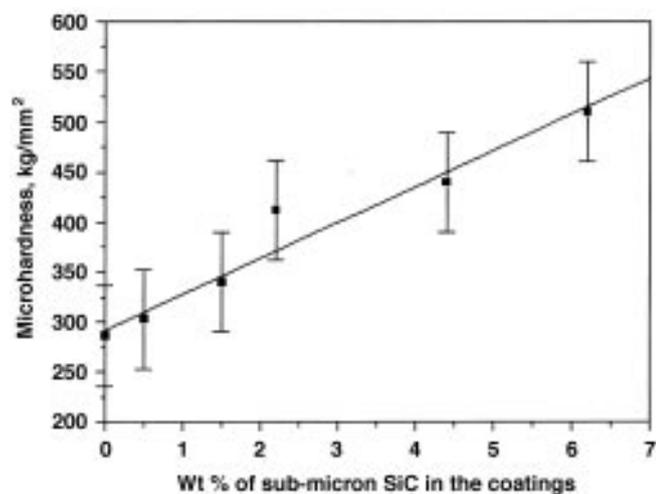


Fig. 5—Microhardness of Ni-SiC composite coatings as a function of the wt pct of SiC in the coatings. The coatings were obtained from Watts nickel solutions containing β BSC-21 C SiC particles.

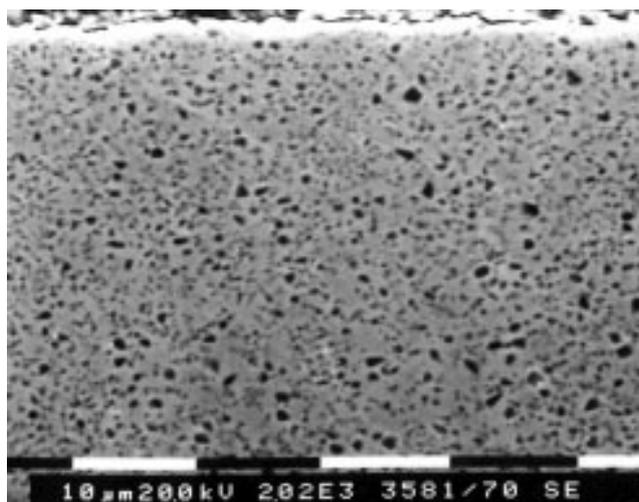


Fig. 4—SEM cross sectional microstructure of a Ni-SiC composite coating electrodeposited from a Watts bath containing 90 g/L β BSC-21C SiC particles, 1.5 g/L saccharine, and 0.2 g/L butyne diol.

some experiments, the following additives were used: 1.5 g/L saccharin, 0.2 g/L 2-butyne-1,4-diol, and 0.2 g/L 2-butyne-1,4-diol in combination with 0.7 to 3 g/L saccharin.

The weight percentage of SiC particles embedded in the nickel composites was determined by dissolving the nickel matrix in 20-percent hot nitric acid. After centrifuging, multiple washings in distilled water and separation of the supernatant solution by pipette, the SiC sediment was dried at 110 °C and weighed. The effective concentration of SiC suspended in the electrolyte was checked, especially in the semi-industrial cell, because part of the SiC particles may become sediment at the bottom of the cell during operation.

Coatings were investigated by SEM^b with secondary electron emission at 20 kV and by X-ray microanalyses^c of the coatings. Microhardness was determined on polished cross sections^d.

^a Thyssen 4301

^b Philips 515

^c HNU System-5000

^d Leiz-Duramet-2.



Fig. 6—Punches coated with composite nickel coatings containing β BSC21 C SiC particles (Photo courtesy of Corroza Engineering, Sofia, Bulgaria). These punches were successfully used for forming PVC foils inserted into metal cups of bottles of non-alcoholic drinks.

Table 1
Properties of SiC Powders Used*

Type of SiC	Mean diameter	Specific area	Free SiO ₂	Al content	Fe content
	μm	m ² /g	%	% or ppm	% or ppm
α ASC-25 [†]	0.49	14	0.45	0.02	0.005
β BSC-21C [†]	0.15	20.7	0.11	50	141
Green α FCP-15-NLC [§]	0.6	15	0.80	200	100
Black α FCP-13-NLC [§]	0.7	13	0.80	600	100
Green α E-110 #10000 [§]	0.5	-	1.40	0.01% as Al ₂ O ₃	0.25% as Fe ₂ O ₃
β HSC 059 [‡]	0.48	16.8	0.62 as O ₂	160	162
α Black hexagonal #1200-W [‡]	5.5	-	0.5	0.1%	0.08%

* as reported by the respective suppliers.

[†] Performance Ceramics Co.

[§] Norton A/S

[‡] Superior Graphite Co.

[‡] Electro Abrasives Corp.

The wear behavior of pure nickel and composite Ni-SiC coatings was investigated via bi-directional sliding tests. The set-up used has been described earlier.¹¹ In such fretting tests (ball-on-flat), balls (φ 10 mm) made either of corundum or chromium steel were used as counterbody. The displacement amplitude was 100 μm, the normal load was 2 N, the frequency 10 Hz. Tests were performed for 10,000 cycles. The wear loss was derived from wear track measurements by laser profilometry.^e

Results & Discussion

The SiC powders investigated in codeposition tests are listed in Table 1. SEM observations of these powders confirmed that the beta silicon carbide BSC-21C powder is the finest and consists of small, rounded submicron size particles. For comparison, codeposition experiments were also performed with micron-sized SiC (α-black hexagonal #1200-W in Table 1). Results of the codeposition of SiC with nickel are summarized in Fig. 3. The effective concentration of particles held in suspension is reported in Fig. 3 for tests performed in the semi-industrial plating cell.

The concentration of suspended particles has a large influence on the degree of codeposition. In the semi-industrial plating cell (see curve *a* in Fig. 3), incorporation of β BSC-21C SiC reaches 6.2 wt pct at a concentration of 90 g/L SiC

^e Rodenstock RM600

Table 2
Roughness of Ni-SiC Coatings
Produced in Different Watts Baths
Containing 90 g/L β BSC-21C SiC

Bath	Roughness Parameters	
	R _z	R _{sk}
Without additives	4.62 ± 1.38	0.02
With saccharin	5.40 ± 0.31	0.38
With saccharin & 2-butyne-1,4-diol	3.00 ± 0.20	-0.12

particles in the bath. In the laboratory cells, the codeposition rate achieved was even higher (see curve *b* in Fig. 3). The difference in the rate of codeposition between different cells can be linked to different fluid flow conditions along the cathode. The incorporation of other types of submicron SiC powders is in the same range as for β BSC-21 C SiC. It was noticed that the codeposition of submicron SiC decreased with time. Such an aging effect in composite nickel plating with micron-sized SiC particles has been reported earlier.⁴

A SEM topographical analysis showed that the surfaces of Ni composite coatings containing either α SiC Crystolon FTP-1 5-NLC or β BSC-21C SiC and deposited from additive free nickel baths are rough (see Table 2). Notwithstanding that, the investigation of cross sections

of composite coatings showed that, for example, for β BSC-21C SiC particles, a fairly uniform distribution of particles throughout the coating was achieved (Fig. 4). It appeared also, however, that the mean size of the particles codeposited is larger than the one mentioned by the producer (see Table 1). A possible cause can be an agglomeration of particles in contact with the plating solution. No significant effect on the percentage of incorporated SiC was noticed when the current density was changed between 1 and 20 A/dm². In many practical applications, as for example on a weaver's loom, a smooth and wear-resistant surface is required. For that purpose, 2-butyne-1,4-diol and saccharin were added separately and in combination to the Watts nickel bath. The compound 2-butyne-1,4-diol increases the hardness of the coatings and enhances the leveling power of the Watts nickel bath. It also increases the internal stresses in nickel coatings and must, therefore, be added in limited amounts to prevent cracking and delamination. Our experiments showed that saccharin and 2-butyne-1,4-diol, when used separately, do not lead to the production of coatings with a smooth surface finish (see Table 2). Also, the addition of these agents separately or in combination does not decrease the amount of submicron SiC codeposited, as observed from chemical analysis and SEM investigations. The particle distribution is comparable to the one shown in Fig. 4. The roughness of Ni-SiC composite coatings obtained from a Watts plating solution containing both 1.5 g/L saccharin and 0.2 g/L butyne diol is smoother, however, (Table 2) and their appearance is brighter in comparison to the dull Ni-SiC coatings obtained from additive-free baths.

Concerning the mechanical properties of the Ni-SiC coatings, an increase of β BSC-21C SiC in the coatings leads to increased microhardness (Fig. 5). The microhardness of Ni-SiC composite coatings containing 6.2 wt pct SiC is 510 kg/mm² compared to one of pure Watts nickel coating, which is only 286 kg/mm².

Unlubricated fretting wear tests on composite nickel coatings containing β BSC-21C SiC indicated the good wear resistance of these coatings. The coefficient of friction of such coatings produced in a bath containing 90 g/L β BSC-

21C SiC particles, butyne diol and saccharin is slightly lower than the coefficient of friction of pure nickel coatings produced from a Watts nickel plating bath containing the same additives, but no SiC particles. Examination of the wear tracks of these two coatings after 10,000 fretting cycles revealed that the wear resistance of the composite Ni/SiC coating is twice that of pure nickel coatings obtained from a Watts bath with the same additives. A wear loss of $1.76 \times 10^{-11} \text{ m}^3$ was determined on pure nickel, compared with 0.88×10^{-11} for the Ni-SiC composite coating. The depth of the wear track is the same on pure Ni and composite Ni/SiC coatings when only saccharin is added to the Watts nickel plating bath.

Nickel composite coatings containing β BSC-21C SiC particles were electrodeposited in the semi-industrial cell in the presence of butyne diol and saccharin on 100 punches (Fig. 6) used for forming the PVC foil inserts in metal cups of bottles of non-alcoholic drinks. The requirements for their physical characteristics (hardness, roughness, thickness distribution, wt pct SiC...) were achieved and an attractive field performance was obtained in terms of wear resistance.

Conclusions

These experiments show that submicron SiC particles can be codeposited from a Watts nickel plating solution in semi-industrial plating cells. A high percentage of uniformly distributed submicron SiC particles in the coatings was obtained. The weight percent of incorporated fine SiC particles can be varied by varying the amount of particles suspended in the plating solution. Composite nickel coatings containing submicron SiC particles exhibit high microhardness and good wear resistance. Optimization of such coatings requires the use of additives to suppress extensive roughening of the surface of coated parts and requires selection of plating parameters suitable for achieving the desired wt pct of codeposited particles.

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References

1. J.-P. Celis, J. Roos & J. Fransaer, *Proc. Interfinish 92*, Sao Paolo, **1**, 442 (1992).
2. J.-P. Celis & J. Fransaer, *Galvanotechnik*, **88**(7), 2229 (1997).
3. W. Metzger, R. Oft, G. Laux & H. Harst, *Galvanotechnik*, **61**, 998 (1970).
4. J. Roos & J.-P. Celis, *Proc. AESF SURF/FIN '84*, Session O, New York, (1984).
5. UK patent 1 421 975 issued to Elektroschmelzwerk Kempten GmbH (1976).
6. T. Sesame, T. Shigeta & T. Yamada, U.S. patent 3,929,596 (1975).
7. W. Metzger & Th. Florian, *Galvano-Organo-Traitements de Surface*, **532**, 67 (1983).
8. G. Maurin & A. Lavanant, *J. Appl. Electrochem.*, **25**, 1113 (1995).
9. J. Fransaer, J.-P. Celis & J. Roos, *J. Electrochem. Soc.*, **139**, 413 (1992).
10. J. Fransaer and J.-P. Celis, in "Electrochemical Synthesis and Modification of Materials", Proc. MRS, Pittsburgh, ed. P. Andriacos, **451** (1997)475.
11. H. Mohrbacher, J.-P. Celis, and J. Roos, *Tribology International*, **28** (5), (1995)269.



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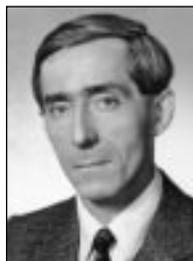
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