Influence of the Pretreatment of Silicon Powder by Electroless Nickel Coating on Its Codeposition with Nickel

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The influence of the pretreatment of silicon powders by electroless nickel or copper coating on its codeposition with nickel was investigated. It was found that the pretreatment allows to increase the content of silicon in the coating up to 15 mass % while without this procedure, the content of silicon in the layer was lower than 1 mass % under the same conditions. The influence of current density and mass concentration of silicon powder in suspension on the composition of the composite layer was studied in detail. The results are compared with codeposition of nonpretreated Si and α-SiC particles.

Composite coatings consisting of a metal matrix with fine particles or fibres have been studied extensively and have been used for a number of industrial applications [1—4]. The purpose of composite coating is to give various function properties, such as wear resistance, high temperature corrosion protection or oxidation resistance, self-lubricating, etc. to the plated surface.

Properties of composite coatings with electrolytically deposited matrix depend remarkably on the concentration of dispersed particles. In the literature [1—7] the influence of many parameters like concentration of solid particles in the suspension, current density, hydrodynamic conditions, etc. on composition of the composite has been investigated. Although the composite coatings are used in many industrial processes, the mechanism of codeposition of dispersoid is not fully known. Three possible mechanisms are usually considered as most probable:

i) mechanical entrapment of the particles to the cathode,

ii) adsorption of the particles on the cathode,

iii) electrostatic interaction of the particle with the cathode.

In this work we will discuss the influence of the electroless coating of codeposited particles of silicon on the formation of the composite layer Si—Ni.

EXPERIMENTAL

The nickel matrix was prepared from the sulfate—chloride electrolyte of the composition 300—330 g dm^{-3} $NiSO_4 \cdot 7H_2O$ + 50—60 g dm^{-3} $NiCl_2 \cdot 6H_2O$ + 40 g dm^{-3} H_3BO_3. Content of silicon particles in the suspension ranged from 0 to 150 g dm^{-3}.

Silicon powder was prepared by grinding silicon of purity "for semi-conductors". Size distribution of silicon particles was as follows:

$d/\mu m$	<1.07	1.07—2.11	2.11—4.13	4.13—9.56	> 9.56
%	50.2	18.9	19.8	11.0	0.1

(Preparation and characterization of the silicon powder was done at the Institute of Mining, Slovak Academy of Sciences.)

Prior to use the powders were treated with diluted nitric acid (φ_r = 1 : 3) and thoroughly washed in distilled water in order to clean their surface from impurities which could be introduced by grinding.

Electroless nickel coating of Si powders was carried out in the bath of composition 30 g dm^{-3} $NiCl_2 \cdot 6H_2O$ + 10 g dm^{-3} $Na_2PH_2O_2 \cdot 2H_2O$ + 80 g dm^{-3} sodium citrate + 50 g dm^{-3} NH_4Cl. pH of the solution was in the range 9—10, temperature was kept at 95 °C, time of electroless nickel coating was 30 min. Micrographs of noncoated and nickel-coated silicon particles are shown in Fig. 1a, 1b. It was found that the amount of nickel in the samples of silicon powder covered with electroless nickel coating ranged from 7 to 12 mass %. X-Ray microanalysis of the composite layers showed that the deposited layer did not contain particles bigger than 3 μm.

In some experiments copper-coated particles were used. Copper was deposited from the solution of the following composition: 15 g dm^{-3} $CuSO_4 \cdot 5H_2O$ + 30 g dm^{-3} $KNaC_4H_4O_6 \cdot 4H_2O$ + 15 g dm^{-3} NaOH + 15 cm^3 formaldehyde (37 %). Coating was carried out for 30 min at the temperature of 40 °C under in-
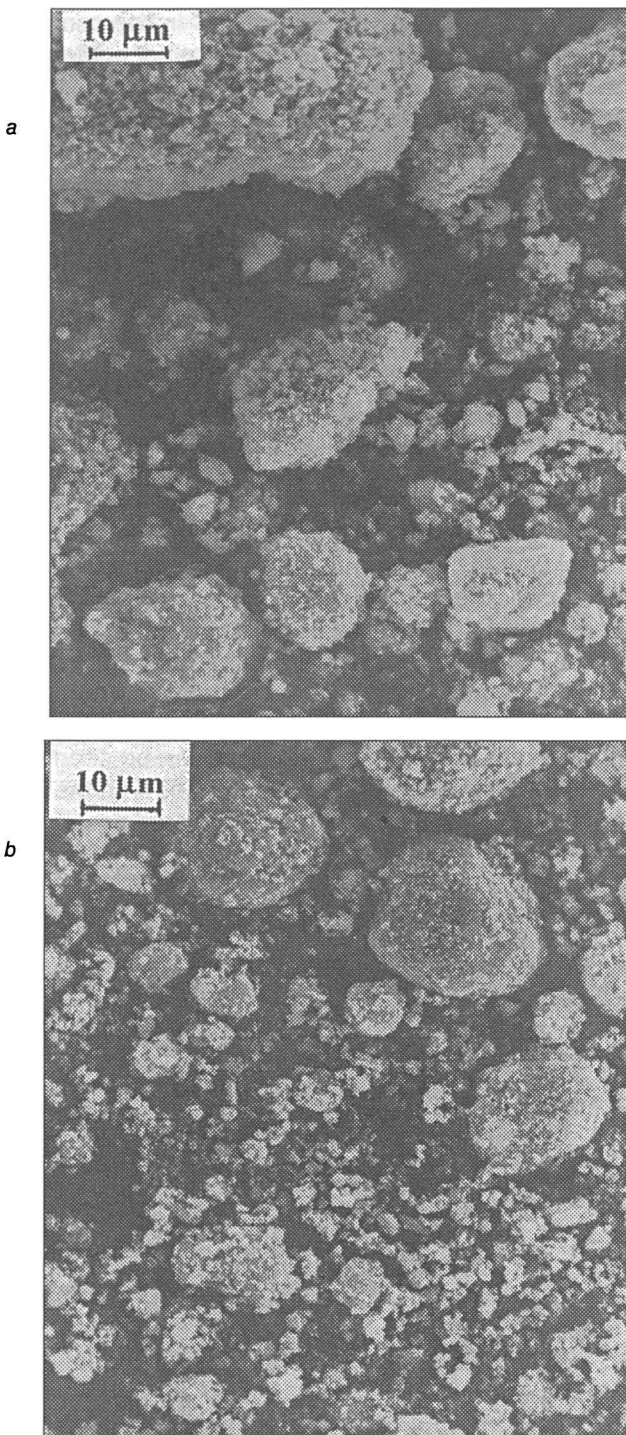
Fig. 1. a) Micrograph of silicon powder. b) Micrograph of silicon powder covered with nickel.

tense stirring. Coating is stopped by lowering pH of solution by the addition of H_2SO_4.

Size of particles of α-SiC (pure) was in the range 0.3—3 μm.

Apparatus

Volume of cylindrical cell (diameter 70 mm, height 90 mm) used for electrodeposition of composite coatings was 250 cm^3. The suspension was agitated with a magnetic stirrer. The temperature of the bath was kept constant using an ultrathermostat. The composite layer was deposited on mild steel base of dimensions 40 mm × 5 mm × 0.25 mm placed vertically in the cell. Nickel anode (99.99 %) was placed parallelly to the cathode, the interpolar distance being 35 mm.

Revolution of the stirrer was kept constant at 200 min^{-1}, which was sufficient for preventing the suspension from sedimentation of particles bigger than 3 μm. Temperature of the bath was (50 ± 2) °C, time of deposition was 60 min. According to the used current density, the thickness of obtained composite layer was 30—60 μm.

Analysis of the Samples

The content of silicon in the composite layer was determined both by X-ray microanalysis (Jeol JXA 840 analyzer) of polished cross-sections of samples and by the chemical analysis. The principle of the chemical analysis consists in dissolution of the composite layer in warm diluted nitric acid (φ_r = 1 : 3). The content of particles of silicon was determined by weighing. Content of nickel was determined by titration with Chelaton III. Comparison of both these methods is discussed in the next section.

The amount of electroless nickel deposited on silicon particles was determined in similar way, *i.e.* by dissolution of nickel in diluted nitric acid.

RESULTS AND DISCUSSION

In Table 1 the contents of silicon in the composite Ni—Si layer determined by X-ray microanalysis and by chemical analysis are compared. The data were obtained with nickel-coated silicon powder. Concentration of particles was 100 g dm^{-3}. Used current densities are given in Table 1.

It can be seen that the values determined by the chemical analysis are lower than those obtained by X-ray analysis. This discrepancy cannot be explained only by the inaccuracy of the used methods. The true concentration of silicon in composite layer is that determined by the chemical analysis. X-Ray microanalysis determines rather surface concentra-

Table 1. Content of Silicon (Mass %) in the Composite Layer Determined by X-Ray Microanalysis and Chemical Analysis

$j_c/$(A dm^{-2})	1	2	3	5	7
w(Si, X-ray)	9.23	9.76	10.70	12.10	13.03
w(Si, chem.)	3.45	6.10	7.13	8.35	11.53
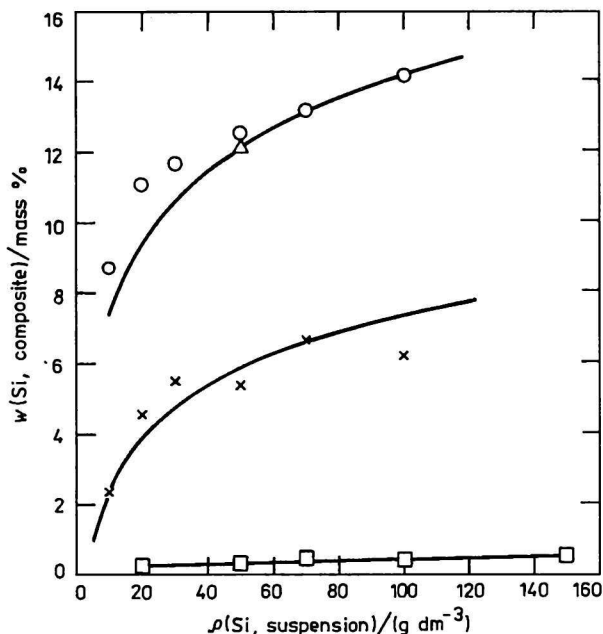
Fig. 2. Content of silicon in nickel matrix vs. mass concentration of particles in the suspension. □ Nontreated Si powder, ○ electroless nickel-coated Si powder, △ electroless copper-coated Si powder, x α-SiC powder, — eqn (1).

tion of silicon on the cross-section of the layer than the bulk concentration. Penetration of electron beam into the sample can also play a role. Nevertheless, in this work, the data obtained by X-ray microanalysis are reported because this method allows a more detailed study of distribution of silicon in the layer. Moreover, the X-ray analysis is a nondestructive method and the samples could be used for further investigation.

In Fig. 2 the content of silicon and SiC in the metal matrix is plotted as a function of the content of particles of these substances in the solution. Cathodic current density was 3 A dm^{-2}. From this figure it follows that the content of codeposited silicon depends remarkably on the covering of silicon particles by electroless nickel. A similar effect was observed when the silicon particles were covered with copper. As the nature of these two metals is different it seems that it is the surface electrical conductivity of the particles which may influence their ability for incorporation into the composite layer. This parameter, however, is not explicitly included in the models describing formation of the composite layers [1—7].

In Fig. 2 the results obtained for codeposition of α-SiC particles are included. Conductivity of α-SiC is 770 S m^{-1}. This is a lower value than that of nickel (12.8 MS m^{-1}) but much higher than the electrical conductivity of silicon (4 × 10^{-3} S m^{-1}). The α-SiC particles are different from the silicon particles in the size distribution, so the comparison with silicon is only qualitative. Nevertheless, it can be seen that

also in this case the content of SiC in the composite layer is remarkably higher than that of nontreated silicon.

The conductive particles influence distribution of the electric field and transport of electroactive species to the electrode. It can be assumed that this effect will be similar as in the case of metal deposition on small-scale profiles [8]. The levelling effect, i.e. covering of electrically conductive particles by electrodeposited nickel, is qualitatively described in literature [2].

The assumption of the influence of the surface electrical conductivity of codeposited particles made in this work is supported by the effect of current density on composition of the composite layers. These results are summarized in Fig. 3 and Table 2. The cathodic current density in this series of experiments was changed in the range 1—7 A dm^{-2}. The upper limit of the current density is given by the quality of deposited nickel matrix. It follows that current density had no influence on composition of the composite layer when nonconductive particles were used.

In Fig. 3 the influence of the cathodic current density on the content of Si particles covered with nickel in the composite layer is shown. It can be seen that in this case the content of Si increases with the current density and concentration of particles in the suspension.
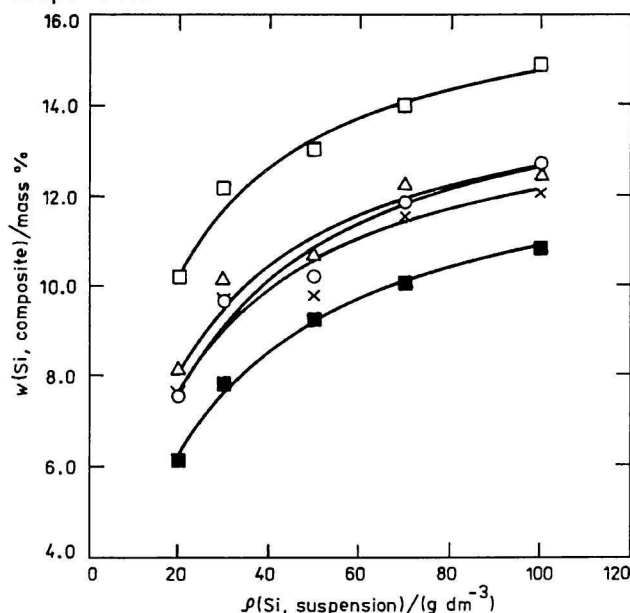
Fig. 3. Content of silicon in the Ni—Si composite layer as a function of current density and mass concentration of particles in the suspension. j_c/(A dm^{-2}): ■ 1, x 2, ○ 3, △ 5, □ 7, —eqn (1).

Table 2. Content of Si Particles Uncovered with Electroless Nickel in the Composite Layer

j_c/(A dm^{-2})	1	2	3	5	7
w(Si)/%	0.51	0.37	0.62	0.44	0.53

Concentration of particles in suspension was 100 g dm^{-3}.

The curves shown in Figs. 2 and 3 can be described by the equation

$$w = w_{max} \frac{k \cdot \rho}{1 + k \cdot \rho} \qquad (1)$$

w_{max} denotes the maximum content of silicon in the layer and k is a constant. ρ is the concentration of silicon particles in the suspension. Eqn (1) follows from the adsorption theory of codeposition of solid particles proposed by *Guglielmi* [5]. The curves plotted in Figs. 2 and 3 were obtained using this equation. Values of the constants w_{max} and k obtained for codeposition of silicon particles covered with nickel are given in Table 3.

Table 3. Values of the Parameters w_{max} and k and Their Standard Deviations Obtained from Eqn (1) for Codeposition of Si Particles Covered with Nickel

$j_c/(A\ dm^{-2})$	1	2	3	5	7
w_{max} mass %	13.4 ± 0.4	15.2 ± 1.0	14.3 ± 1.2	14.8 ± 0.8	16.6 ± 0.5
k $dm^{-3}\ g^{-1}$	0.044 ± ± 0.003	0.055 ± ± 0.009	0.057 ± ± 0.015	0.060 ± ± 0.010	0.080 ± ± 0.010

The results presented in this work suggest that the electrical conductivity of the codeposited particles plays an important role in the process of entrapment of particles into the composite layer and in their covering with metal matrix.

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