Adsorption of Hydrogen Ions on the Surface of SiC Powder in Solution of Nickel Sulfate During Composite Coating

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In codeposition of inert particles with a metal, two processes are involved—adsorption of ions on inert particles and on the cathode. For the first of these processes, for the Ni-SiC system, the pH changes of NiSO₄ and Watts solutions resulting from addition of SiC particles were measured. The influence on the character of pH changes as a function of time was determined for nickel ions, initial pH, SiC particle concentration, dimensions and type, and for preliminary purification in HNO₃.

Codeposition of solid particles with a metal to obtain composite coats involves two adsorption processes. First, the metal ions are adsorbed on the surface of the particles; second, solid particles, after reaching the cathode, undergo adsorption. The metal ions are commonly considered to be adsorbed on a solid particle to enable its codeposition with a metal. Observations of the incorporation of particles that are negatively charged in solution into galvanic coatings do not change this opinion.

Investigations carried out for various baths confirm the variability of metal ion adsorption on solid particles, depending on concentration of the bath components, and type and concentration of the powder added. Adsorption of the deposited metal ions is changed considerably in the presence, in suspension, of other ions that can cause significant changes in the composition of the deposit.

The number of Ni⁺² ions adsorbed on TiO₂ and Al₂O₃ is reduced by several times by addition of 0.01 M of Al⁺³ or Mg⁺² ions to ammonium sulfate baths used for nickel plating.¹ The surface properties of TiO₂ are changed also after treatment in a solution containing Al⁺³ or Mg⁺² ions,² (*e.g.* the powder was intensively agitated for 30 min in solution of Al⁺³ ions, conc. 0.01 mol/L). SiC particles were subsequently deposited with a metal in an amount five times less than before. The TiO₂ content in a nickel coating was 30 to 50 percent greater after treating the powder in solution with Mg⁺² ions. Another example, found in the literature, is the function of thallium ions that raise the content of Al₂O₃ and TiO₂ in copper deposited from CuSO₄ solution.³⁻⁷

The presence of Cl⁻ ions, acting as an inhibitor of codeposition, is a significant danger for obtaining dispersion copper coatings. It can be masked by adding Tl⁺, Rb⁺, or Cs⁺ ions.^{1,8}

The most substantial conflict in adsorption of basic metal ions on solid particles comes from hydrogen ions that impede adsorption of other ions in a strongly acidic environment (pH \leq 2). For instance, adsorption of Ni⁺² or Cu⁺² ions on Al₂O₃ from Watts and CuSO₄ solutions (200 g/L) respectively, reached a minimum at pH < 2, then increased steeply up to pH 4, then remained unchanged or decreased.⁹⁻¹² The contribution of H⁺ or OH⁻ ions to adsorption is increased also in the case of very dilute solutions with a concentration of metal ions less than 10⁻⁴ mol/L.¹²

Range of Studies

To determine adsorption of H⁺ ions on the surface of SiC particles, pH changes of NiSO₄ solution were measured that occurred after addition of silicon carbide particles. The influence of nickel ion concentration, initial pH (pH₀), SiC particle concentration, dispersion, type and purification in HNO₃, on the character of pH changes with time was investigated. The measurements were made in NiSO₄ solution of about 1 mol/L (280 g/L NiSO₄ · 7H₂O) as well as in solutions diluted by factors of 10 and 100. Some of the experiments were run in a Watts bath consisting of (g/L): NiSO₄ · 7H₂O, 300; NiCl₂ · 6H₂O, 35; H₃BO₃, 35.

Measurements were made to determine the influence of various factors on the change of pH of a solution after introduction of SiC. For reference, these measurements were also made without SiC. Two kinds of SiC were used—in a major part of this study, SiC made in Austria and named "N" and another "S" powder produced in the Korund plant in Koło, Poland. Both types were ground and split into fractions in a mill. In both cases, the SiC was obtained by reduction of SiO, with carbon from 2,000 to 2,500 °C. The fraction between 0 and 4 μ m in size (according to granulometric analysis, 93 percent of SiC was in this range), and from 3 to 6 μ m (84 percent) was used in our investigations. Silicon carbide was applied either as powder without preliminary purification ("no") or as purified in HNO₃ (1:1) at 70 °C for 15 min ("o").

The specific area of SiC surface was determined by means of nitrogen thermodesorption. The results are collected in Table 1. A great difference (more than one order of magnitude) in specific surface area can be seen for both applied powders. Because the distribution of granulation is similar for both "N" and "S" types, the results obtained can be explained on the basis of distinction in their porosity.

The presence of metallic elements in HNO₃ used for preliminary treatment of SiC powder was analyzed with a plasmic spectroscope to determine impurities contained in the SiC and the difference between purified and unpurified powders. A similar analysis was carried out for NiSO₄ solution (pH 4) before and after introducing silicon carbide. The content of Al, Ba, Ca, Cd, Cr, and Fe, as well as Ti, V, Sc, Sr, Pt, Si, P, Pb, Na, Mn, Mo, La, Mg, Cu, Co, B, Ag, and Zn was determined. The results are shown in Table 2.

It can be seen that the SiC powder "N" contains much more admixture than does "S." Some departure from this principle appears in the case of cadmium. Results of the experiments performed with NiSO₄ solution at pH₄ revealed that unpurified silicon carbide was the source of a rather small amount of bath impurities; because of their quantity, only the presence of Ca and Fe may influence adsorption on the SiC surface as well as the process of composite coating formation.

Table 1 Specific Surface Area of SiC Powders

Туре	Part Size µm	icle	Specific Area m²/g	
		BET Multipoint	BET Single	Langmuir
S no (S o)	0-4	4.8 (7.9)	4.6 (7.7)	7.3 (11.1)
	3-6	1.9 (3.5)	1.8 (3.4)	3.0 (4.9)
N no (N o)	0-4	72.4 (78.7)	71.1 (77.8)	108.6 (110.0)
	3-6	34.9 (31.0)	34.3 (30.5)	52.4 (48.7)

Table 2Content of Selected Metals in HNO3Used for SiC Powder Purificationand in NiSO4Solution

Analyzed Sample		Metal Content					
	Al	Ba	Ca	Cd	Cr	Fe	
HNO_3 (1:1) after 10 times dilution (background)	0.26	0.03	0.48	0.00	0.02	0.21	
HNO ₃ (1:1) in which 1 g SiC ("N", the 0-4 µm fraction) was purified, diluted to 50 mL	18.7	1.04	114.7	0.00	1.41	223.7	
HNO ₃ (1:1) in which 1 g SiC ("S", the 0-4 µm fraction) was purified, diluted to 50 mL	5.11	0.22	11.50	0.44	0.25	57.13	
NiSO ₄ solution, pH 4, background	0.00	0.01	0.04	0.00	0.00	0.00	
NiSO ₄ solution, pH 4, containing SiC for 24 hr ("N no" $C_{siC} = 10$ g/L, the 0-4 µm fraction)	0.38	0.19	8.98	0.00	0.01	0.96	

Experimental Procedure

Measurements were made according to the following scheme:

- Preparation of electrolyte solution by dissolving nickel salt in water (for a Watts bath, components were added as follows: H₃BO₃, NiSO₄, NiCl₂)
- Introductory working of the bath (D_k , 0.2-0.3 A/dm²; time, 3-5 hr; corrugated iron cathode)
- Adjustment of pH to the required value, using H_2SO_4
- Stirring to obtain stable initial pH (pH₀)
- Adding slurry consisting of specific amount of SiC and solution to a bath, agitated and kept at constant temperature, with simultaneous monitoring of pH (pH after 0.5 hr from the moment of powder addition = pH_1)
- Allowing sediment to settle
- Measurement of pH after 2 hr from the moment of SiC addition in both upper clear and lower, just above the carbide sediment, layers of solution (mean value, pH₂)
- pH measurements after 24 hr (mean value, pH₃).

Results

The most visible changes in pH of the solution occurred immediately after SiC powder addition, during the 0.5 hr interval and during intensive stirring of the suspension. The pH changed only slightly over the next 1.5 hr while the silicon carbide settled. The values of the pH measured in the upper clear and lower, enriched in SiC, parts of the bath were similar. Substantial differences occurred occasionally. The pH changes in solutions without SiC during the 24 hr of the experiment for all concentrations of Ni⁺² [$C_{Ni(II)}$] and pH₀ were small and did not influence interpretation of the results. Accordingly, the results of "blind tests" are presented only at random in selected figures. Analysis of the results obtained enables some conclusions concerning the influence of various factors on the character of pH changes in NiSO₄ solution caused by SiC powder and on adsorption of H⁺ ions on SiC.

Influence of pH

The direction and magnitude of pH changes in NiSO₄ solution after silicon carbide addition depend on pH₀ and are different for SiC powder without preliminary treatment and SiC purified in HNO₃. In the first case, the increase in pH up to 6.5-7.0 could be observed for all pH₀ values in the range 3-6 (Fig. 1a). Adsorption of H⁺ ions on the SiC surface may be the reason; it may also result from transfer of impurities from powder to solution. Different results have been obtained for SiC purified in HNO₃ ("o"). For pH₀ between 2 and 4 there was no substantial shift in value during a period of 24 hr. For pH₀ of 5 or 6, however, a pH₃ value of about 5.5 was obtained (Fig. 1b).

When applying the powder "So" with $pH_0 = 5$, an increase in pH_3 was seen up to 5.34, whereas for pH_0 5.6, a drop was observed to $pH_3 = 5.39$. The pH values after 24 hr from the moment of SiC addition were higher for the "S" carbide than for "N".

Influence of Concentration $C_{Ni(II)}$ of $NiSO_4$

The influence of solution concentration on shift of pH observed after SiC addition is shown in Figs. 2 and 3. Experiments carried out at various values of pH_0 for the "N o"



Fig. 1—Changes in pH of NiSO₄ solution (1 mol/L) as a function of time, caused by SiC powder ($C_{sic} = 10 \text{ g/L}$, fraction 0-4 µm at various pH₀ values). (a) SiC: "N no;" (b) SiC: "N o."

powder showed very similar dependence on time for 1, 0.1, and 0.01 mol/L solutions (Fig. 2). All three solutions had converging pH changes in the 24-hr period (pH_3-pH_0) (Fig.3).

Effect of Purification of SiC

The purification process of carbide affects markedly the direction and quantity of pH changes with time. The purified "N" form has been found to weigh more than the "S" form, which can be easily understood because the SiC "S" contains a lesser amount of admixtures. The relations between pH_0 and pH_3 for SiC of "N o" and "N no" types are shown in Fig. 4. The essential influence of purification of powder on the pH_3 value of a solution has been confirmed in all measurements and, therefore, is of significance during the deposition of dispersion coatings.

Influence of Type of SiC

Selected properties of both powders "N" and "S" used are collected in Tables 1 and 2. The largest difference in behavior of solutions containing either "N" or "S" silicon carbide appeared at pH 5, where directions of pH changes were opposite ("N o" and "S o"; Fig. 5). In a major part of the experiments, the influence of the type of powder was less than that of other factors.

Effect of SiC Particle Size

Higher pH values were observed at $pH_0 = 5$ in solutions containing powder of larger grains when using purified carbide (Fig. 5). Higher pH_3 values were observed for the "n o" SiC in baths with a finer fraction, irrespective of the type of powder.

Effect of SiC Concentration in Suspension

The results of studies made to determine the influence of SiC powder concentration in suspension on magnitude of pH changes with time are shown in Fig. 6. Silicon carbide in amounts of 10, 20, and 50 g/L was used.



Fig. 2—Examples of pH changes of NiSO₄ solution at various nickel ion concentrations as a function of time, caused by SiC powder (SiC: "N o," $C_{\rm SiC} = 10$ g/L, fraction 0-4 μ m; (a) pH₀ \approx 4; (b) pH₀ \approx 5.

When using the "N o" SiC in NiSO₄ solution of 1 mol/L and $pH_0 = 5$, lower and lower pH values were obtained as SiC concentration increased. This is a result of a larger number of adsorbed H⁺ ions because of the larger surface of powder in suspension. A similar tendency was observed for solutions where $C_{Ni(II)} = 0.1$ and 0.01 mol/L and pH = 4.

In a portion of the investigations, $NiSO_4$ solution was replaced with the Watts electrolyte. In that case, the pH value was not corrected with H_2SO_4 . The value of pH_0 was about 3.95 in all such experiments.

After introducing the "N no" SiC powder to the Watts solution, an increase in pH occurred, much less, however, than in the case of the same powder added to $NiSO_4$ solution ($C_{Ni(II)} = 1 \text{ mol/L}$) at pH 4 (Fig. 7). Such behavior results certainly from the presence of buffering species in the Watts solution.

A small decrease in pH could be seen after adding the "N o" SiC powder to a Watts solution. As SiC concentration increased, pH₃ reached lower and lower values (Fig. 7). For NiSO₄ solution ($C_{Ni(II)} = 1 \text{ mol/L}$), the pH₃ change for the function of C_{SiC} was of the same tendency, but the drop in pH was somewhat larger, especially for $C_{SiC} = 10$ and 20 g/L.

Discussion

Adsorption of H⁺ ions occurring on the surface of solid particles codeposited with a metal was evaluated from measurements of decrease of the concentration of those ions. In the literature, there are many reports concerning the mechanism of the formation of dispersion coatings, focusing, however, on the step of adsorption on solid particles and describing definite systems (*e.g.* Ni-Al₂O₃).^{1,12} There are some advantages and disadvantages in considering that problem from



Fig. 3—Changes in pH ($\Delta pH = pH_3 - pH_0$) of NiSO₄ solution at various concentrations after 24 hr from the moment of SiC powder addition (SiC: "N o," $C_{SiC} = 10$ g/L, fraction 0-4 μ m).



Fig. 4—Dependence of NiSO₄ solution (1 mol/L) between pH_0 and pH_3 obtained for both purified and unpurified SiC powders (10 g/L, fraction 0-4 μ m).



Fig. 5—Dependence of pH_3 value of NiSO4 solution (1 mol/L, $pH_0 = 5$) on the powder fraction for different types of SiC powder ($C_{syc} = 10 \text{ g/L}$).



Fig. 6—Changes in pH of NiSO₄ solution (1 mol/L) as a function of time caused by various SiC concentrations (SiC: "N o," fraction 0-4 μ m).



Fig. 7—Comparison of pH changes with time for Watts and NiSO₄ solutions (conc. 1 mol/L, pH₀ = 4) caused by SiC powder added (fraction 0-4 μ m, C_{siC} = 10 g/L): #100 - Watts solution, SiC "N no," 10 g/L; #101 - Watts solution, SiC "N o," 10 g/L; #102 - Watts solution, SiC "N o," 20 g/L; #108 - Watts solution, SiC "N o," 50 g/L; #57 - NiSO₄ solution, SiC "N no," 10 g/L; #70 - NiSO₄ solution, SiC "N no," 10 g/L; #70



Fig. 8—Dependence between $\Delta pH(pH_3 - pH_0)$ of suspension ($C_{Ni(H)} = 1 \text{ mol/} L$; $pH_0 = 5$) and the surface area of the SiC powder contained.

the aspect of changes, either of H⁺ ions or metal ion concentrations; both these approaches are partly complementary. When estimating adsorption on solid particles from the analysis of metal ion concentration, very dilute solutions are used, compared with those applied in a galvanic process. This is necessary to determine concentration changes within permissible error. In turn, when based on measurements of hydrogen ion concentration, electrolyte solutions of simple composition are commonly used. The buffering additions applied as standard in practice make pH measurements not fully suitable as the measure of adsorption.

Some conclusions can be drawn from the measurements of pH changes of NiSO₄ solution after introduction of SiC powder, concerning processes occurring on the surface of silicon carbide. The direction and magnitude of pH changes depend to a high degree on the purity of the applied powder. In this study, the pH increase to 6.5-6.9 was observed for NiSO₄ concentration of 1 mol/L in the pH₀ range between 2.8 and 6.0 when adding SiC powder without earlier purification ("no") at $C_{siC} = 10$ g/L. The main change in pH was observed about 0.5 hr after addition of SiC during intensive agitation of the solution, but equilibrium was not reached in many cases even after 24 hr.

The pH increases to a great extent because of adsorption of H⁺ions on the powder surface and because contamination can constitute centers of adsorption. On the other hand, analysis of the NiSO₄ solution (pH 4) containing 10 g/L of the "N no" SiC showed the presence of about 9 ppm of Ca⁺² ion and significantly less of other cations; the SiC powder was their source. If there is calcium in the powder in the form of oxide or hydroxide, its transition to the bath causes slight alkalization of the solution.

In general, an increase in the pH of a bath was observed after addition of either of the powders-the "S" not purified previously ("no") or the powder treated with HNO₂ ("o") (Fig.5). An increase in pH after use of the "N no" powder was higher still (Figs. 1b, 4, 5, 7). Such an effect should be expected when trying to relate the amount of adsorbed H⁺ ions to the magnitude of the surface of the powder placed in the solution. The results for the SiC "N o" powder do not fit that model. This powder introduced to the solution does not cause any increase in pH. There occurs even a slight lowering of pH (Figs. 1a, 2a, 2b, 3-7). It should be recalled, when interpreting results, that powders can contain a great amount of impurities that can constitute adsorption centers and that these can be destroyed during purification of the powder in nitric acid. To determine the number of active centers on the surface, the acid-base properties of the powder were tested by use of a solution of n-butyl amine and benzoic acid in benzene.13,14 Adsorption of n-butyl amine and of benzoic acid on the surface of the powder (0-4 µm fraction) was investigated and the results collected in Table 3. It can be seen that purification of the "N" powder results in an increase of its acidic function and a decrease in its basic function (the "S" powder changes are insignificant). Accordingly, the lowering of adsorption of H⁺ ions and the rise in adsorption of a basic agent (e.g. $OH^{-}ion$), should be an effect of purification.

Adsorption of OH⁻ ions on the surface of powder particles contained in an electrolyte used for plating with nickel, is only slightly probable, especially in the range of acidic baths. Nevertheless, reports exist in the literature about the role of OH⁻ ions in processes occurring on the surface of dispersion substances.

Dispersion particles applied to obtain composite coatings can be negatively charged in an electrolyte for plating with nickel. The region where a particle has a negative charge depends on many factors, among them the pH. According to Sajfullin et al.,¹ reactions taking place on the surface of particles and connected with transition of cations to solution are a possible reason for formation of the negative charge. As a result, some excess of O⁻² and OH⁻ ions appears on the surface. Ions of powdered metal, or metals appearing as impurities, can also constitute cations. Additionally, Bhagwat et al.,¹² write of the role of hydroxide ions in formation of dispersion coatings and assert that protons and hydroxide ions, depending on pH, determine ion exchange on the powder surface in dilute water solutions. If there are multivalent metal ions in solution, they can undergo hydrolysis to the first hydroxy-complex (e.g., $Fe^{+3} \longrightarrow FeOH^{+2}$). These hydroxy-complexes are so active that they can be adsorbed even on the positively charged surface of powders.

When analyzing results, the possibility was also considered that the lowering of pH of the $NiSO_4$ solution after introduction of the "N o" SiC was caused by a small amount of nitric acid remaining in pores after the purification process. Even though the powder was rinsed thoroughly and many additional tests were made with different amounts of rinsewater, such a possibility, although not very probable, cannot be excluded.

Acidification of the $NiSO_4$ solution as a result of dissolution of impurities from the "o" powder is also not very likely. Analysis of a solution with the "N o" SiC showed that at pH 4 there were no metal ions other than Ni⁺².

The same amount of SiC added to $NiSO_4$ solution and to distilled water at pH_0 6 causes pH increase to 6.8 and 9.8, respectively. This may be evidence that competition exists between Ni(II) and H⁺ ions on the SiC surface.

Table 3
Acidic and Basic Functions of SiC Powder
$0-4\mu m fraction$

Туре	Acidic adsorption o mmol/g	Function f n-butyl amine mmol/m²	Basic Function adsorption of benzoic acid mmol/g mmol/m ²			
So	0.06	7.59 • 10 ⁻³	0.02	2.53 • 10 ⁻³		
N o	0.41	5.21 • 10 ⁻³	0.11	$1.40 \bullet 10^{-3}$		
S no	0.07	14.58 • 10 ⁻³	0.00	—		
N no	0.31	4.28 • 10 ⁻³	0.23	3.18 • 10 ⁻³		

Table 4
pH_3 Values for NiSO $_4$ Solution and
Corresponding Surface Area of SiC Powder
$1 \text{ mol/L}, \text{ pH}_0 = 5$

Туре	Fraction	Conc.	Р	log P	pH ₃	$\Delta \mathbf{pH}$	
SiC	μm	SiC, g/L	m²/L		pH ₃ - pH ₀		
N o	0-4	10	787	2.90	4.59	-0.42	
S o	0-4	10	79	1.9	5.34	0.33	
N o	0-4	20	1574	3.20	4.32	-0.70	
N o	0-4	50	3935	3.59	4.02	-0.99	
N o	3-6	10	310	2.94	4.99	-0.05	
S o	3-6	10	35	1.54	5.83	0.80	

Findings

Studies of the dispersion coating process with use of solid substances containing a great deal of impurities are very important for the description of phenomena appearing in processes operating on a technical and industrial scale. In such cases, the use of low purity substrates should be expected, considering the economy of the process. Without question, however, it makes the system, which is complex itself, even more complicated from the scientific point of view and causes significant difficulties in the interpretation of obtained results.

Among factors analyzed, there are three that determine the surface magnitude of SiC placed in a bath, namely, the type of powder, its fraction and concentration. The trial to establish the relationship between pH values reached after 24 hr of powder inclusion in a bath, and the magnitude of the surface (P) of SiC in suspension, shows a linear dependence: pH vs. $\log P \text{ or } \Delta pH (pH_2 - pH_0) \text{ vs. } \log P$, as can be seen in Table 4 and Fig. 8. The larger the area of SiC surface in suspension, the lower the established final value of $pH(pH_2)$. The results indicate that pH₂ is changed in a linear way as a function of SiC surface with the slope depending on the value of pH_0 . At $pH_0 = 2$ and 3, the pH changes of NiSO₄ solution after addition of SiC are small, which does not mean that the change of H⁺ ion concentration is small. It must be emphasized that in logarithmic coordinates, the change of H⁺ ion concentration is less noticeable. Starting from $pH_0 = 4$, a decrease in pH of a bath is observed while measuring, whereas $\Delta pH(pH_3 - pH_0)$ increases with the pH_o increase.

When applying less concentrated solutions (*i.e.*, below 1 mol/L), greater changes of pH occur, so the influence of Ni(II) ions is diminished. When replacing NiSO₄ solution with a Watts solution, $(pH_0 = 3.95)$, the pH increase after an unpurified SiC powder addition is decidedly less. It can be explained by the presence of a buffering substance. For the "N o" powder, the results are comparable for both baths.

Editor's note: Manuscript received, September 1994; revision received, August 1996.

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