

# Ni-P/SiC Composite Coatings Obtained by Chemical Methods

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## ABSTRACT

Nickel can be deposited chemically from water solution on a solid support, under the action of a reduction agent like natrium hypophosphite. Thus, a Ni + P deposition is obtained, with a P content between 3 – 25 %, depending on the solution pH. In this paper the possibility is studied of fabricating composite coatings, by including in the Ni + P matrix SiC particles with average size of 3  $\mu\text{m}$  *during deposition*. The weight percentage of disperse particles *in the coating* could be brought up to 10%, depending on the SiC concentration *in solution*, on its chemical composition and on the stirring conditions. A technological flux for deposition was established. Properties like corrosion or wear resistance were determined and found superior to those of normal coatings.

## 1. INTRODUCTION

Today's advanced technology requires new materials with special properties /1/. Among these, the composite coatings are of major interest /2,3,4,6,10/. Thin films of composite materials can be obtained by metal chemical deposition and include dispersed particles that do not participate in the reactions taking place during the deposition process /2,6/.

The chemical deposition of the thin films implies a number of advantages as compared with the electrochemical method, like:

- excellent uniformity of the thin film independent of the object's shape and size;
- it can be performed on dielectrics (e.g., plastics,

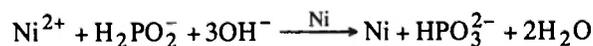
glass, ceramics, etc.), semiconductors and metallic substrates;

- coatings are generally denser, thus providing the layer underneath with higher resistance to corrosion even for small thicknesses;
- no electric power is necessary;
- selective coatings can be made, since only certain surfaces can act as catalysts.

## 2. NICKEL-PHOSPHORUS FILM DEPOSITION IN HYPOPHOSPHITE SOLUTIONS

A number of papers have focused on composite coatings in a matrix of Ni-P, Cu and Ag /5-10/, etc. Nickel can be deposited from aqueous solutions under the action of the hypophosphite, boron hydrate, hydrazine and chromium /2,4/.

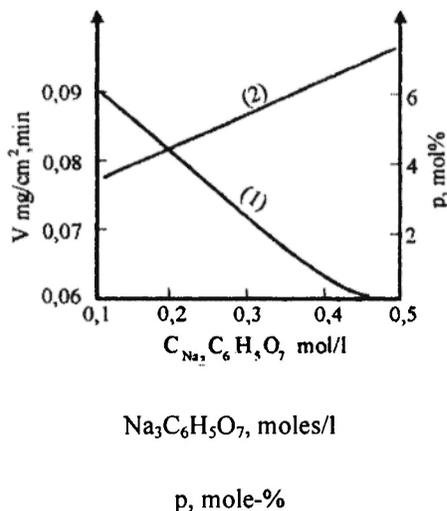
Nickel reduction can take place in acid and base media. Nickel chemical deposition on the metal catalyst surface involves chemical reactions and film formation. In highly basic ethylene-diaminic solutions, the catalyst decomposition of the hypophosphite is slowed down and practically stops at  $\text{pH} > 10$ . Under these circumstances, the nickel deposition process changes and no hydrogen is released:



With nickel, phosphorus is deposited and the percentage of phosphorus depends on the solution acidity. The film deposited from the acid solutions ( $\text{pH} = 3-4$ ) contains up to 25 mole-%, while that obtained

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from basic solutions (pH = 8-9) contains 8 to 10 mole-% phosphorus. Thus, as a function of pH, there are three regions: in acid solutions (pH = 2.5-6) the phosphorus percentage increases with pH, within the neutral and basic range (pH = 6-10) it slowly increases and at pH > 10 it decreases considerably.



**Fig. 1:** Dependence of the Ni(1) and P(2) deposition speed on the sodium citrate concentration at T=20 degrees

The alkaline solutions of acid ligands are characterized by high stability, but low deposition speed, significantly limiting their applications. For practical applications, solutions of two ligands are used (citrate and ammonia, citrate and triethanolamine). Changing the citrate concentration in a wide range changes the reaction speed of Ni and P deposition (Fig. 1). The solution composition: NiCl<sub>2</sub> – 0.13 moles/l; NaH<sub>2</sub>PO<sub>2</sub> – 0.1 moles/l; NH<sub>4</sub>Cl – 1 moles/l (pH = 8.5).

### 3. KINETICS OF THE NI-P CHEMICAL COATINGS

The Ni deposition speed on reduction with hypophosphite depends on the concentration of the components in the solution. The pH and the nature of the surface apparently affect the reaction orders. The kinetic equation showing the dependence of the Ni deposition speed on the concentrations in solution (with

citric acid as ligand) is:

$$V = K C_{M^{n+}}^a \cdot C_{Red}^b \cdot C_{OH^-}^c \cdot C_L^d$$

where: K - reaction speed constant

a, b, c, d - apparent partial reaction orders, which account for the influence of each solution component on the reaction speed..

### 4. TECHNOLOGY OF CHEMICAL COATINGS FABRICATION

The technological operations used to obtain chemical composite coatings are as follows:

- preparation of surface
- preparation of electrolyte suspension
- chemical deposition
- neutralization and hot water rinsing of the surface

The preparation of the metal surface involves the following steps:

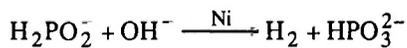
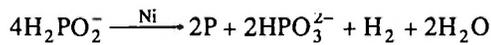
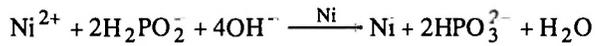
- a) mechanical polishing;
- b) pre-degreasing with organic solutions, by immersion and stirring;
- c) alkaline-chemical degreasing with sodium hydroxide (15 g/l at t = 60°C);
- d) electrochemical degreasing in electrolyte consisting of: Na<sub>2</sub>CO<sub>3</sub> = 30-50 g/l; Na<sub>3</sub>PO<sub>4</sub> = 30-50 g/l; NaOH = 15-20 g/l; Na<sub>2</sub>SiO<sub>3</sub> = 2-5 g/l; the anodic degreasing takes place under the following conditions: temperature 70-75; current density 700 A/dm, stirring for 6-9 min;
- e) hot water rinsing for 1 min at t = 50-70 °C;
- f) anodic cleaning in solution of: FeSO<sub>4</sub> · 7H<sub>2</sub>O = 250-300 g/l; H<sub>3</sub>PO<sub>4</sub> = 100-150 g/l; Na<sub>3</sub>PO<sub>4</sub> = 20-50 g/l, current density 60 A/dm<sup>2</sup>; solution temperature 20°C, stirring for 1 min.
- g) cold water rinsing at 20°C;
- h) chemical activation with HCl - 125 g/l or electrochemical (cathodic) activation in the nickel-phosphite electrolyte.

To obtain the composite Ni-P/SiC, the following solution was used: NiSO<sub>4</sub> – 0.09 moles/l; CH<sub>3</sub>COONa –

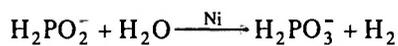
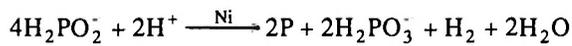
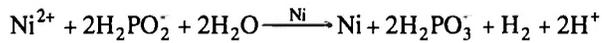
0.12 moles/l;  $\text{NaH}_2\text{PO}_2$  – 0.24 moles/l to which silicon carbide powder, with an average particle size of  $3 \mu\text{m}$ , was added; the stabilizer was maleic anhydride,  $1.2 \cdot 10^{-1}$  moles/l. The deposition parameters were: pH 5.2, temperature  $90^\circ\text{C}$  and deposition speed  $12 \mu\text{m/h}$ . Activated carbon steel was used as underlying substrate. The solution was vigorously stirred.

The following reactions take place when the Ni-P/SiC composite film is formed:

*In basic medium:*



*In acid medium:*



The speed of the Ni-P/SiC chemical deposition is lower than in the case of solutions with no dispersed particles. The inclusion process of the particles begins immediately and their position in the Ni-P matrix is random (Fig. 2).

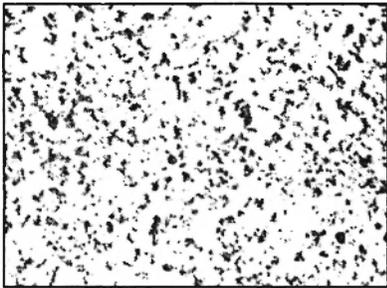


Fig. 2: Microstructure of the composite film Ni-P-SiC coating on steel base

Within the concentration interval 0.025-0.2 moles/l SiC, the coating includes 1 to 10% particles by weight (Fig. 3).

The small particles are more likely to be incorporated in the thin film, while the large ones settle at the bottom of the vessel, without taking part in the

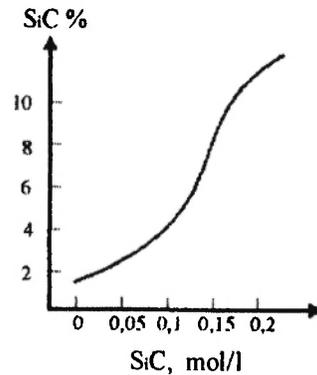


Fig. 3: Dependence of the silicon carbide weight percentage in Ni-P/SiC on the SiC concentration in solution, with citrate-hypophosphite

coating formation. With steel samples, where the activation stage of the process flow was not performed, the layer is discontinuous and thin.

The quality of the composite coatings was analyzed and compared with a pure nickel layer. The composite film has a compact uniform aspect. The coating adherence was tested by thermal shock, i.e. by heating at  $300^\circ\text{C}$  for one hour and sudden cooling in cold water and was found to be very good.

The microscopic study of the cross section through the composite coating shows a good distribution of the SiC particles in the nickel matrix. It features good adherence with no micro-fissures (Fig. 2).

The corrosion resistance was tested with chemical agents: HCl 15%,  $\text{H}_2\text{SO}_4$  – 0,5 moles/l, mixture HCl +  $\text{H}_2\text{SO}_4$  (1:1), estimating the sample weight loss. A very low corrosion speed was found (0.01 mm/year). This is explained by the fact that the active centers leading to metal dissolution are blocked. We also heated the sample to  $700^\circ\text{C}$  for one hour in an oxidizing atmosphere in order to test the resistance to high temperatures. After testing, the composite coat showed no modifications. Stability to friction was found to increase as the amount of silicon carbide particles increased. The wear resistance increases four-fold when the silicon carbide inclusion increases from 1 to 10%. The wear stability of the composite layer is 3 to 4.5 times higher than that of the electrochemically made composites.

## 5. CONCLUSIONS

The research carried out in the laboratory demonstrated the production of composite layers Ni-P/SiC by chemical methods. The composite has much better properties than the base metal and, therefore, this type of material can be employed in a variety of applications.

## 6. REFERENCES

1. P.S. Sidky and H.G. Hoking, *British Corrosion Journal*, **34** (3), 171-183 (1999).
2. V.V. Suimidov and T.N. Vorobieva, *Chemical Deposition of Metals in Water Solution*, University Publishing House, Minsk, Belarus, 1987.
3. S.R. Saifulin, *Physical Chemistry of Inorganic, Polymeric and Composite Materials*, H. Ellis Ltd., London, 1992.
4. S. Steinhäuser, *Mat-wiss. u. Werkstofftech.*, **26**, 608-614 (1995).
5. S.H. Yeh and C.C. Won, *Plating and Surface Finishing*, 1997, (March), 54-59.
6. L. Mitoseriu, O. Mitoseriu, C. Iticescu and A. Preda, *EUROMAT 2001*, Rimini, Italy, June 2001, 123-127 (in conference proceedings).
7. R.J. Roos, J.P. Celis and J.P. Chonglun, *J. Electrochem. Soc.*, **137** (4), 1096-1099 (1990).
8. P. Nowak, R.P. Socha, M. Kaisheva, J. Fransaer, J.P. Celis and Z. Stoinov, *J. Applied Electroch.*, **30**, 429-437 (2000).
9. U. Berger, *Galvanotechnik*, **53** (2), 34-35 (1999).
10. L. Benea, O. Mitoseriu, J. Galland, F. Wenger and P. Ponthiaux, *Werkstoffe und Korrosion*, **51** (7), 491-495 (2000).