

ELECTROLESS DEPOSITION OF NI-P/SiO₂ COMPOSITE COATING

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Abstract

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Electroless deposit Ni-P/SiO₂ composite coating was performed on the steel substrate, DIN EN 10130. The preparation of nickel coating included two main steps. In the first step, the fraction of SiO₂ particles sized the tens of nanometres was obtained by sedimentation. In the second step, the composite coating was plated on the steel substrate. The actual deposition process contains the deposition of plain Ni-P interlayer which served as the nucleation center for the deposition of Ni-P/SiO₂ composite coating with co-deposited SiO₂ particles. The morphology of deposited composite coating was studied by scanning electron microscope (SEM). Amount of individual elements in deposited coatings was determined by EDS analysis. The microhardness of deposited composite coating was subsequently compared with microhardness value of the plain Ni-P coating.

Keywords: EDS analysis, electroless deposition, Ni-P coating, Ni-P/SiO₂ composite coating, steel substrate DIN EN 10130.

INTRODUCTION

Electroless deposition of Ni-P coatings is still a very requested surface treatment in the industry. These Ni-P coatings are characterized by their equally deposited coating and their deep effectiveness. Electroless Ni-P deposition is used due to the created layer high hardness, good abrasion and corrosion resistance (Riedel, 1991; Buchtík, 2014). The considerable increase of the mentioned mechanical properties is reached by co-deposition of inorganic particles as SiO₂ (De Hazan *et al.*, 2010; Rabizadeh *et al.*, 2011; Dong *et al.*, 2009), Al₂O₃ (Li *et al.*, 2013), ZrO₂, TiO₂ (Georzig *et al.*, 2013), SiC (Farzaneh *et al.*, 2013) or diamond into the Ni-P matrix (Mallory *et al.*, 1990).

Ni-P composite coatings can be used in aviation, automotive industry or as the platings for cutting tools, sliding bearings or shafts with high abrasion resistance (Hu *et al.*, 2013; Shao *et al.*, 2014).

However there exist some disadvantages of electroless deposition of composite coating when compared to the electroplated nickel coatings

as lower low deposition rate and low stability of the coating bath (ELCHEMCo, 2016).

The plain electroless deposition of Ni-P coating generally run as a redox reaction. Nickel is reduced on the surface of a substrate. Using the hypophosphite, two atoms of hydrogen bonded to the central atom of phosphorus are in oxidation number –I, not in oxidation number I. So the hydrogen atoms have the hydride character. If there is no reduction to elemental phosphorus, the phosphorus atom is still in oxidation number V (Riedel, 1991). The donor-acceptor mechanism describing both, the reduction of nickel and the reduction of elemental phosphorus, is analyzed in Cavallotti *et al.*, 1968; Bielinski, 1984.

Adding inorganic particles to the coating bath makes the mechanism of the deposition more difficult. The process of deposition of Ni-P composite coating is divided into four steps: I) Ejection of the particles from the coagulants, II) Transport of the particles to the deposited surface, III) Adsorption of the particles to the deposited

surface, IV) Growth of the Ni-P matrix around the particles (Riedel, 1991; Rabizadeh *et al.*, 2011).

The other possibility how to increase the microhardness of Ni-P coatings is the heat treatment of this coatings. This application is often used for increasing the wear resistance. Anyway, it is necessary to notify that the deposited heat-treated Ni-P coatings become more brittle. The highest values of microhardness of Ni-P coatings are reached after the heat treatment at the temperature of 400 °C for 1 hour, (Riedel, 1991; Mallory *et al.*, 1990). Heat treatment decomposes the amorphous Ni-P phase, and the Ni₃P – nickel (III) phosphide particles in the form of hardening precipitates are formed in the coating layer structure.

The present paper deals with an electroless deposition of Ni-P composite coating from a nickel bath with co-deposited inorganic SiO₂ particles on a DIN EN 10130 steel substrate. The usage of inorganic particles should result in improvement of microhardness of coated layer and following improvement of wear resistance of the coating and treated engineering part.

EXPERIMENTAL MATERIALS AND METHODS

The unalloyed cold rolled steel substrate DIN EN 10130 (Brhel, 2016) was used for the coating application. The chemical composition of used steel substrate according to the DIN EN 10130 standard is given in Table 1.

Preparation of suspension containing SiO₂ particles

Inorganic particles of SiO₂ from Grace Davison company in the form of microsilica with the specific surface of 171 m²·g⁻¹ were used in this experiment.

SiO₂ particles were mixed with water to prepare a mixture of a volume of 1000 ml with a holding time of 168 hrs. and concentration of 200 g·l⁻¹. After the holding time (168 h), 200 ml of the suspension from the top was removed after sedimentation. The concentration of SiO₂ particles in taken upper fraction of suspension, determined by gravimetric method, was of 16.02 g·l⁻¹.

Electroless deposition of Ni-P composite coating on the steel substrate

Technological process of Ni-P coating processing mentioned in De Hazan *et al.*, 2010, and nickel bath with the chemical composition according to Kosár, 2013, were used for electroless deposition of Ni-P composite coating containing SiO₂ particles. Continuous Ni-P/SiO₂ composite layer was

deposited on steel substrate with interlayer using the nickel bath of the same composition.

Surface pre-treatment

Steel substrate DIN EN 10130 was firstly degreased in industrial ecologic degreaser STAR 75PN in ultrasonic bath for 1 min. After cleaning the sample was insert into alkaline bath which contained 10 g·l⁻¹ NaOH with the addition of 100 ml·l⁻¹ of liquid surfactant, heated to 60 °C for 4 min. The surfactants in the bath decrease the surface tension so it makes easy to remove the impurities. The last part of pre-treatment included deposition of zinc layer from zinc bath for duration of 45 minutes. The used zinc bath contained 42 g·l⁻¹ of ZnO and 458 g·l⁻¹ of NaOH. Thin compact zinc layer will be dissolved during the Ni-P coating process and Ni-P layer will be created directly on the steel surface.

Electroless deposition of Ni-P/SiO₂ composite coating

Electroless deposition of Ni-P/SiO₂ composite coating consisted of two steps. In the first step, the thin continuous layer of plain Ni-P coating was deposited on the steel substrate with zinc layer which served as the nucleation center for deposition of Ni-P coating containing SiO₂ particles. Nickel bath contained 30 g·l⁻¹ of NiSO₄·7H₂O, 25 g·l⁻¹ of NaH₂PO₂·H₂O, 15 g·l⁻¹ of C₂H₅NO₂ (glycine) and 15 g·l⁻¹ of NH₄HF₂ (Kosár, 2013). Deposition of Ni-P interlayer was performed at 60 °C in a bath with pH of 5.7 ± 0.2 for 5 min. The exact pH value was corrected by NaOH solution added to the nickel bath. The Ni-P composite coating containing inorganic particles was deposited on this interlayer. Composite layer was coated from nickel bath under the same conditions as it was in the case of basic Ni-P layer. This nickel bath contained extra 2.2 g·l⁻¹ of SiO₂ particles. Time of deposition was of 120 min.

Sample was rinsed among each step in the distilled water and in the ethanol to remove the rests of salts from used coating baths and impurities.

Element analysis – EDS

Using the EDS analysis with Oxfrod Instruments Xmax 80 mm² detector and AZtec software, the chemical composition of deposited layers was analyzed (Fig. 3). The element analysis was performed using accelerating voltage 15 kV, work distance 12 mm, dead time was 50 %, counts/s 32,000, live time was 50 sec. and current volume was 500 pA.

Microhardness testing

The microhardness of deposited Ni-P/SiO₂ composite coating was compared with

I: Chemical composition of steel substrate DIN EN 10130

Element	C	Mn	P	S	Fe
max. wt. %	0.10	0.45	0.03	0.03	Balance

the microhardness of plain Ni-P coating deposited under the same conditions. Using the Vickers method (Ludvík *et al.*, 2010), the microhardness was measured on microhardness tester LECO AMH43. Measurement was performed at the load of 5 g for 10 sec. The results of testing were analyzed using the light optical microscope according to ASTM International, 2007.

RESULTS

Morphology and chemical composition of the nickel based layers

The Ni-P layer was deposited on the pre-treated steel substrate using the methodology from De Hazan *et al.*, 2010, described in part 2.2. This layer served as the nucleation center for deposition of composite coating containing SiO₂ particles obtained by sedimentation.

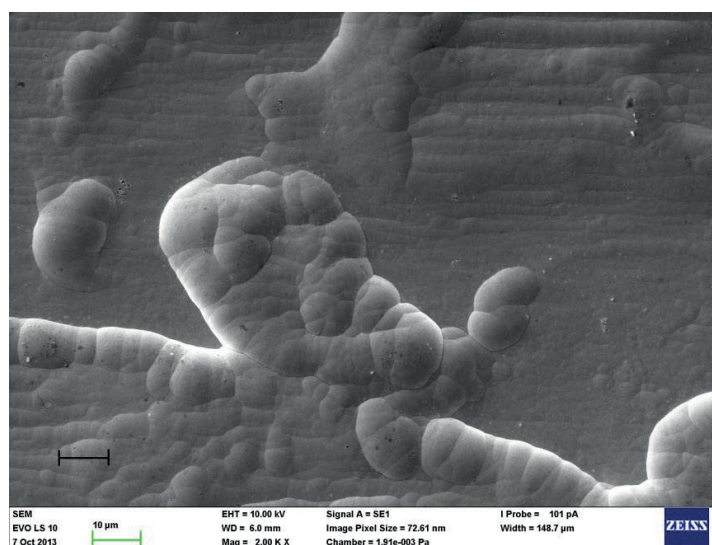
The morphology and thickness of Ni-P/SiO₂ composite coating (Figure 1) was analyzed on scanning electron microscope (SEM) ZEISS EVO

LS10. It could be seen that the surface of Ni-P composite coating was relatively smooth, however it's coarser when compared to the plain Ni-P coatings. There were possible to see many nodular cusps, typical for deposited nickel. Using the EDS analysis, it was determined that the Ni-P matrix contains equally co-deposited SiO₂ particles, which is obvious from the figure representing the content of Si in the examined area (Fig. 3).

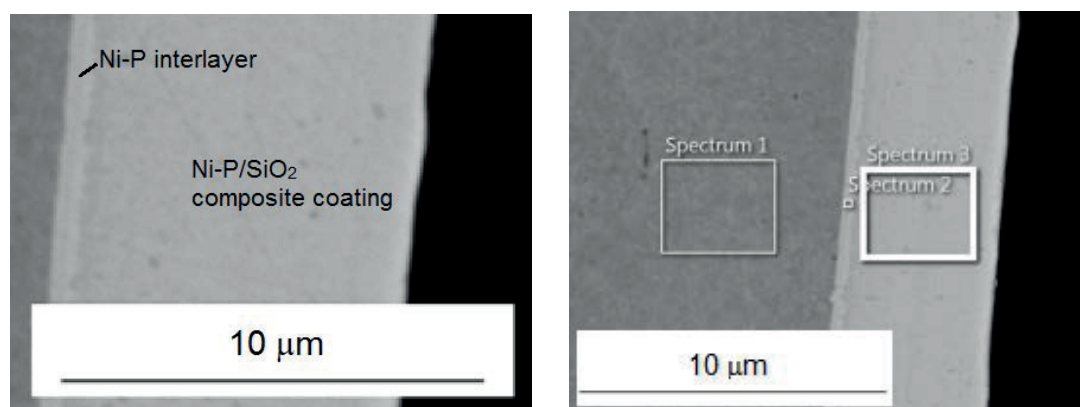
The average thickness of the deposited coating layer was of $8.7 \pm 0.3 \mu\text{m}$. The thickness of Ni-P interlayer was of $0.63 \mu\text{m}$.

By the EDS analysis the volume content of individual chemical elements in the deposited layers and the used steel substrate was analyzed. The results are shown in Fig. 3.

From the element analysis, Figure 3, it was found that the concentration of SiO₂ particles was the highest at the interface of Ni-P interlayer/composite coating. The amount of SiO₂ particles was relatively homogenous in the composite coating (Figure 3).



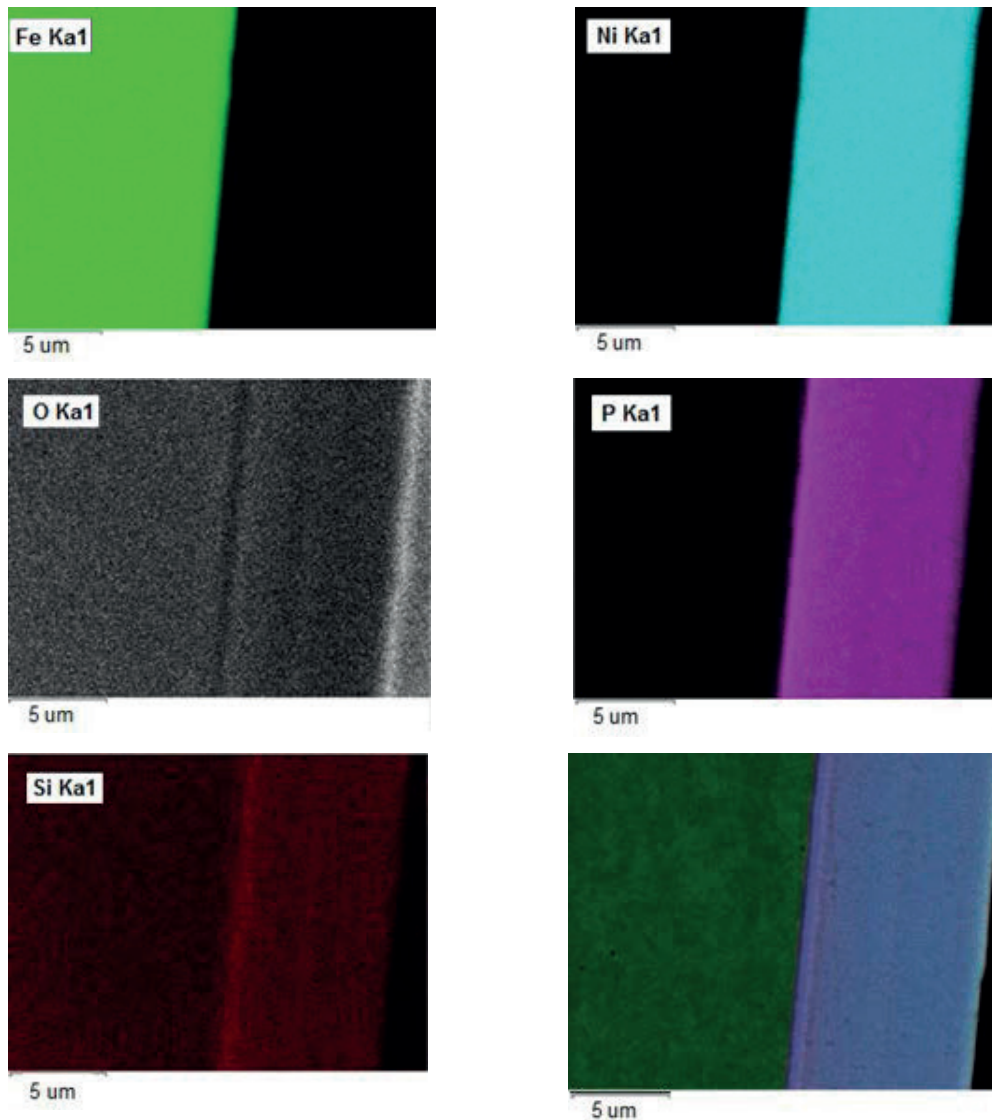
1: Surface of deposited composite coating



2: a) Perpendicular cut through the deposited layers, SEM, b) Chemical composition analysis places of the deposited layers

II: The average value of elements contained in the individual spectra (see Fig. 2b) (wt. %)

Spectrum	Fe	Ni	P	Si
1	100	-	-	-
2	13	81	6	0.1
3	3	92	5	0.3



3: The element analysis showing the representation on individual elements in coatings and substrate.

Microhardness testing

The microhardness was performed on 5 specimens, 10 indents on each specimen. The average value of microhardness for plain Ni-P coating was of 550 ± 30 HV 0.005 and the average value of microhardness for Ni-P/SiO₂ composite coating was of 670 ± 40 HV 0.005. The microhardness value of composite coating was increased by 21 % when compared to plain Ni-P coating.

DISCUSSION

Technological process mentioned in De Hazan *et al.*, 2010, and nickel bath with the chemical composition according to Kosár, 2013 were used in this study for electroless deposition of Ni-P composite coating containing SiO₂ particles. Continuous Ni-P/SiO₂ composite layer was deposited on steel substrate using the nickel bath.

The average thickness of electroless deposited Ni-P/SiO₂ composite coating presented in this work was of 8.7 ± 0.3 µm. As shown in the Fig. 1, the surface of this coating was highly compact

and uniform. Hazan in De Hazan *et al.*, 2010 prepared the highly homogenous Ni-P/SiO₂ composite coating from composite bath. The bath used in this study contained also dispersed SiO₂ particles while the compactness and uniformity of the coating remained stable. It was observed that the concentration of SiO₂ particles in coating increases gradually with the concentration in the bath. The Ni-P coating according to De Hazan *et al.*, 2010 and Ni-P/SiO₂, presented in this study, composite coating were deposited on substrates from the same material and under the same conditions for the comparison of qualitative and hardness properties. The microhardness of plain Ni-P coating was $550 \pm 30 \text{ HV}_{0.005}$. However, the microhardness of Ni-P/SiO₂ composite coating was $670 \pm 40 \text{ HV}_{0.005}$. The microhardness of composite coating increased by 21 % was observed comparing to the plain Ni-P coating. This supposed effect was observed in article Novakovic, *et al.*, 2006, where were compared the particle-free Ni-P and

Ni-P/TiO₂ composite heat-treated coatings. Using the heat treatment, the microhardness of Ni-P/SiO₂ composite coating would increase over 1000 HV (Riedel, 1991; Mallory *et al.*, 1990) while in De Hazan *et al.*, the heat treatment led to the composite coating microhardness decrease when compared to the non-treated state.

In this experiment, using the EDS analysis it was determined that the deposited composite coating contained co-deposited SiO₂ particles (Fig. 3, SiK α 1). There was seen that the highest concentration of SiO₂ particles is in the interface of Ni-P interlayer/composite coating. In the coating cross section the concentration of particles was lower, but very homogeneously represented. This effect is possible to explain by deposited Ni-P interlayer and following immersion of the sample into the bath containing SiO₂ particles. It immediately came to saturate SiO₂ particles from the bath and began incorporate to the coating.

CONCLUSION

The aim of the study was the examination of deposition of Ni-P composite coating with co-deposited inorganic SiO₂ particles using electroless nickel bath on a DIN EN 10130 steel substrate. From the performed experimental deposition following conclusions can be concluded:

- Ni-P interlayer was deposited on steel substrate for better the Ni-P/SiO₂ composite coating deposition,
- the thickness of double coating was of $8.7 \pm 0.3 \text{ }\mu\text{m}$,
- the highest concentration of SiO₂ particles was observed at the interface of Ni-P interlayer/ Ni-P/ SiO₂ composite coating,
- microhardness of Ni-P/SiO₂ composite coating was of $670 \pm 40 \text{ HV}_{0.005}$ which means the increase by 21 % when compared to plain Ni-P coating interlayer ($550 \pm 30 \text{ HV}_{0.005}$).

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