



DETERMINATION OF ELECTROLESS DEPOSITION BY CHEMICAL NICKELING

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Abstract:

Increasing of technical level and reliability of machine products in compliance with the economic and ecological terms belongs to the main trends of the industrial development. During the utilisation of these products there arise their each other contacts and the interaction with the environment. That is the reason for their surface degradation by wear effect, corrosion and other influences. The deficient of surface protection, respectively the effort for surface protection, can also destroy the excellent technical product.

The development of surface finishing technologies, decreasing of energy and increasing of requirements on technologies brought about demand for new, progressive and highly stable nickel baths. The chemical nickel-plating is a kind of surface finishing, which allows autocatalytic deposition of nickel from water solutions in the form of coherent, technically very profitable coating without usage of external source of electric current. The research was aimed at evaluating the surface changes after chemical nickel-plating at various changes of technological parameters.

Keywords:

Deposition, chemical nickeling, layer thickness

INTRODUCTION

The surface finishing technologies play an important role in the finishing quality of technical equipment. It influences its life-service, service dependability and it is related to utilisation, preparedness and requirements on services. The surface protection depends on the function of the machine products and furthermore it influences both its function and appearance. The surface coating protects the parts against the corrosive environment. It guarantees better physical properties, wear-resistance and it has a decorative function, too. The successful solution of material protection is dependent upon economical, ecological criteria and parameters, which characterize the particular problem.

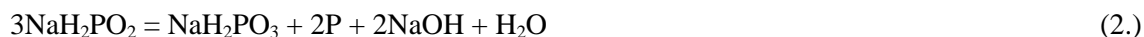
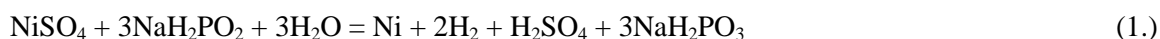
The solution of surface finishing requires a broad range of basic knowledge from electrochemistry, metallurgy, physics, chemistry, material properties and also the knowledge –based theory and technology of surface finishing [1], [2]. The long term aims of both surface finishing and machinery can be formulated as follows:

- increasing of life-service and life of surface finishing,
- increasing of technical parameters of surface finishing,
- decreasing of product costs, mainly power and material saving ,
- product humanisation, automation and robot- technology,

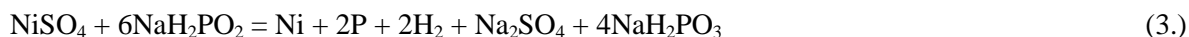
- delimitation of environment pollution [8].

The technology of chemical nickeling is a type of surface finishing, which enables to exclude nickel from water solution auto-catalytically in the form of coherent, hold-on contact and technically sufficient, favourable coating without using the outdoor source of electric current [9]. The most determined advantage of this technology is the possibility to apply electro-less deposition nickeling on the shaped complicated parts, blind holes and edges, whereby chemically separated nickel layer shows regular layer thickness on the whole surface of the part. The following machining is not necessary due to the technological requirements of chromizing. The coating after nickeling segregation has the hardness around 550HV. As it is a nickel-phosphor alloy coating, it is possible to harden it by a following heat treatment (350°C/2 hours) to achieve the hardness of hard chrome, i.e. 1000HV. The chemical nickel coating is a universal one, which due to its properties currently delivers the coated part the following attributes such as anticorrosion resistance, wear resistance and good sliding property and moreover it provides an attractive appearance. Due to these priorities it can be always utilized in different fields of electrochemical and machinery industries, mainly in the area of production of precise parts for auto-body panel industry, aerial industry, nuclear industry, etc. [8], [14], [15].

The chemical nickeling does not belong to widespread technologies. This technological process is characterized by high demand for energy as it works at the temperature around 90°C and moreover there is a high requirement on cleanness and accuracy of own nickeling. The principle can be expressed by the following equations:



Both equations can be summed into the following form:



Solutions used for real chemical deposition of nickel are more complex and contain a wide range of important components such as:

- complex tanner,
- catalyst,
- stabilizer,
- working component,
- regulator pH,
- detergents.

The following reducers are used: sodium hypophosphite, sodium borohydride or dimethylamine borane. The nickel coating is not segregated as pure nickel, but in the form of binary or ternary alloys, i.e. Ni - P, Ni - B, Ni - Co - P, Ni - W - P alloys, etc. The most widespread and technically used alloy is Ni-P which creates 98% of chemically segregated nickel coatings. Metallisation by current-less nickel is the process, in which the nickel coating on the part is produced by chemical oxidation and reduction. This type of metallisation belongs to common ones and has the following advantages in comparison with conventional electro-metallisation of nickeling [11], [12]:

- (1) uniform coating is created on the parts also with more complicated shapes,
- (2) the coatings are characterized by lower porosity, excellent resistance against wearing and corrosion,
- (3) non-conducting surface can be coated by nickel and the deposition can be simplified.

No contact is required between the parts and the coating layers.

The main components of the bath are nickel ions, hypophosphite, buffers and others. The nickel ions, in the form of nickel sulphide, are often added into the bath and coalescence with hypophosphite occurs during the metallisation and consequently the nickel coating is created. The hypophosphite, usually in the form of sodium hypophosphite, is a reducer, which catalyzes the chemical reduction of nickel ions. The buffers maintain the bath pH and the other components maintain the nickel ions in soluble form. Both parts stabilise the bath and help maintain the metallisation speed [13].

The aim of this research was to perform the model of non- electrolytic reaction of metallisation on a large number of sample experiments. This model enables to calculate the dynamic concentration of types (nickel, hydrogen, hypo – and orthophosphate) from the substance equilibrium of the metallisation bath. The speed of nickel coat deposition and phosphor is calculated according to immediate density of particular reaction. The mixing potential is the only necessary external input calculation. The other parameters (e.g. concentration of nickel ions, pH, metallisation time, bath temperature, supply and delivery current) are the parts of current inspection process of metallised system. According to these measurements, the model calculates the thickness of the created coating and phosphor volume in Ni-P alloy. Moreover these critical parameters together with reagent concentration and accessory products can be estimated within non- observed processes. This is the way how to obtain important information about the process, which can be used for process control, Fig.1 [15]

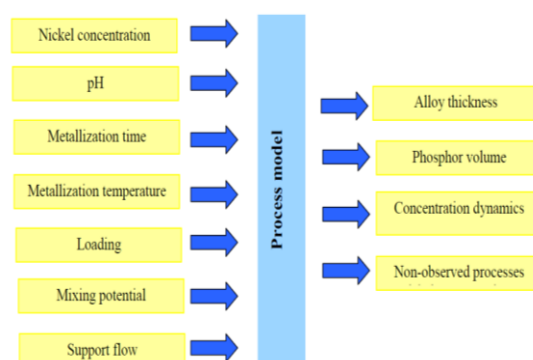


Figure 1: The model of chemical nickeling [15]

MATERIAL AND EXPERIMENTAL METHODS

The material, ISO Fe 590 (W. Nr. 1.0542), plain carbon steel with higher content of carbon was used for experimental research. The chemical composition of tested material is shown in Table1. Acquirement and mastering of a particular field of knowledge and the method known as DOE- Design of Experiments are the prerequisites of providing a good-quality preparation, realization and analysis of laboratory research experiments.

Table 1: Chemical properties of the material

Material	Ni	P	S
ISO Fe 590, W.Nr. 1.0542	max 0,009	max 0,045	max 0,040

The determination of relations and bonds between determined values of investigated process are the parts of experiments of technological-technical practice. Especially, there are the cases, when the process is very complicated and there does not exist convenient mathematic-physical and chemical models [3]. The most commonly stated aim of the experiment is to determine how the particular parameters influence the monitored ones. This process is called a respond. The required data for model formation can be obtained by observation of parameters of the investigated process.

Table 2 : Matrix of planned experiment

Number	x ₁	x ₂	x ₃	x ₄	x ₅	x ₆
1	1	1	1	1	1	1
2	1	2	2	2	2	2
3	1	3	3	3	3	3
4	1	4	4	4	4	4
5	1	5	5	5	5	5
6	2	1	2	3	4	5
7	2	2	3	4	5	1
8	2	3	4	5	1	2
9	2	4	5	1	2	3
10	2	5	1	2	3	4
11	3	1	3	5	2	4
12	3	2	4	1	3	5
13	3	3	5	2	4	1
14	3	4	1	3	5	2
15	3	5	2	4	1	3
16	4	1	4	2	5	3
17	4	2	5	3	1	4
18	4	3	1	4	2	5
19	4	4	2	5	3	1
20	4	5	3	1	4	2
21	5	1	5	4	3	2
22	5	2	1	5	4	3
23	5	3	2	1	5	4
24	5	4	3	2	1	5
25	5	5	4	3	2	1

x_1 - nickel chloride, x_2 - nickel sulphide, x_3 - natrium phosphate, x_4 -.natrium citrate, x_5 - time, x_6 – temperature

The experiment is identified as the system of tests, which is suitably arranged in the planned experiment. The planned experiment is aimed at creating such conditions which would lead to achievement of the smallest volume of experiments and more qualitative extent and form of information. [4], [5], [6]. In this case the Taguchi experimental design was proposed, which matrix for six independent variables is introduced and shown in Table 2.

The real conditions (the matrix) of experiments are shown in **Table 3**.

Table 3: Real conditions of experiment

Coded parameter	Parameter	Unit	Level of parameter in natural scale				
			1	2	3	4	5
x_1	Nickel chloride	g.l ⁻¹	40	50	60	70	80
x_2	Nickel sulphide	g.l ⁻¹	50	60	70	80	90
x_3	Natrium phosphate	g.l ⁻¹	4	7	10	13	16
x_4	Natrium citrate	g.l ⁻¹	20	25	30	35	40
x_5	Time	min	10	20	30	40	50
x_6	Temperature	°C	75	85	95	105	115

ANALYSIS AND EVALUATION OF RESEARCH RESULTS

In Table 4 the summary results of experiments are shown.

According to the obtained results, shown in Table 4, it is possible to make a statement that the index of determination between the technological parameters and observed parameter (R²) is 57,59%. The modified determination index is often used in the practice for the evaluation of percentage explanation of variability of experimentally obtained data. According to input data of independent variables and parameters the determination index is modified, which presents the second power of multiple correlation coefficient, modified due to the influence of parameter numbers (Adj.R² – number of factors), which means in our case 43,45%. This lower number is caused predominantly by using basic component of solution designed for chemical nickeling, furthermore by selection of each independent variable, respectively by neglecting the effecting influence.

Technical properties of nickel coating used in experiment are as follows:

- (1) structure and composition of layer: nickel - phosphorus alloy, content of phosphorus: from 8,5% to 10%, structure: amorphous, after heat treatment above 300°C crystalline nickel phosphide is in nickel,
- (2) coating appearance: light and bright, magnetic properties: weak magnetism
melting point: 800°C - 900°C,
- (3) density: 8 g/cm³,
- (4) linear technical expansion coefficient : 12- 12 µm/m for 0°C,

(5) hardness: 550-600 HV(0.1), after 1 hour at temperature 400⁰C: 1000 HV (0.1), corrosion resistance (It depends on the basic material, therefore only approximated values can be presented.): coating thickness: >25 µm in salt spray according to DIN 50021 ESS: ≥ 400 hours.

Table 4: Summary results of experiments

Parameter	Value	Parameter	Value
Dependent variable	h	Rows processed	25
Number independent variables	6	Rows filtered out	0
Weight variable	None	Rows with X's missing	0
R2- observed parameter	0,5759	Rows with weight missing	0
Adj R2 – number of factors	0,4345	Rows with Y missing	0
Coefficient of variation	0,0689	Rows used in estimation	25
Mean square error	3,58E-03	Sum of weights	25
Square root of MSE	5,98E-02	Completion status	Normal completion
Ave Abs Pct Error	4,383		

In Fig.2 and Fig.3 there are shown the samples after chemical nickeling of the planned experiment.



Figure 2: Samples after chemical nickeling of the planned experiment

The magnitude of shown tested coated samples was 60 x 100 mm. The typical detail of nickel coating was prepared on scanning electron microscopy BS 301, where 1200 multiple magnification of tested

sample was made. The shown surface presents the compact integral layer of precipitate Ni – P, whereby there were not presented any errors or cracks.

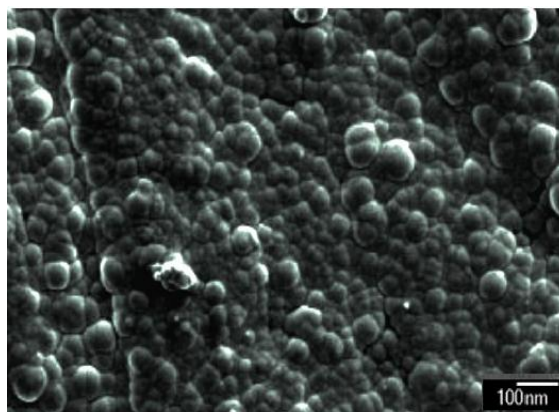


Figure 3: Detail of nickel coating

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In Table 5 the results of regression analysis are demonstrated. According to Table 5 the regressive coefficients for particular parameters can be determined and simultaneously reached the significance level of Student test criterion (p) showing [7], [17] in accordance with Pareto diagram, presented in Fig.4, the significant parameters, which influenced the final thickness of coating on the selected level of significance $\alpha = 5\%$.

Table 5: Results of regression analysis

Regression independent variable	Standard coefficient b(i)	T-Value error Sb(i)	T-Value $H_0: b(i)=0$	Probably level	Reject H_0 at 5%	Power of test at 5%
Intercept	0,7987	0,0508	15,733	0	Yes	1
x_1	-0,1410	0,0484	-2,911	0,0093	Yes	0,786
x_2	-0,0364	0,0484	-0,751	0,4624	No	0,1097
x_3	0,0377	0,0484	0,779	0,446	No	0,1144
x_4	0,0524	0,0484	1,082	0,2938	No	0,1762
x_5	0,1365	0,0484	2,818	0,0114	Yes	0,7598
x_6	0,1155	0,0484	2,385	0,0283	Yes	0,6165

We can conclude due to the experiment and chosen independent variables that the final thickness of chemical nickeling is the function of quantity of nickel chloride, temperature and time, which is possible to demonstrate as

$$h = f(\text{NiCl}_2, T, t) \quad (4)$$

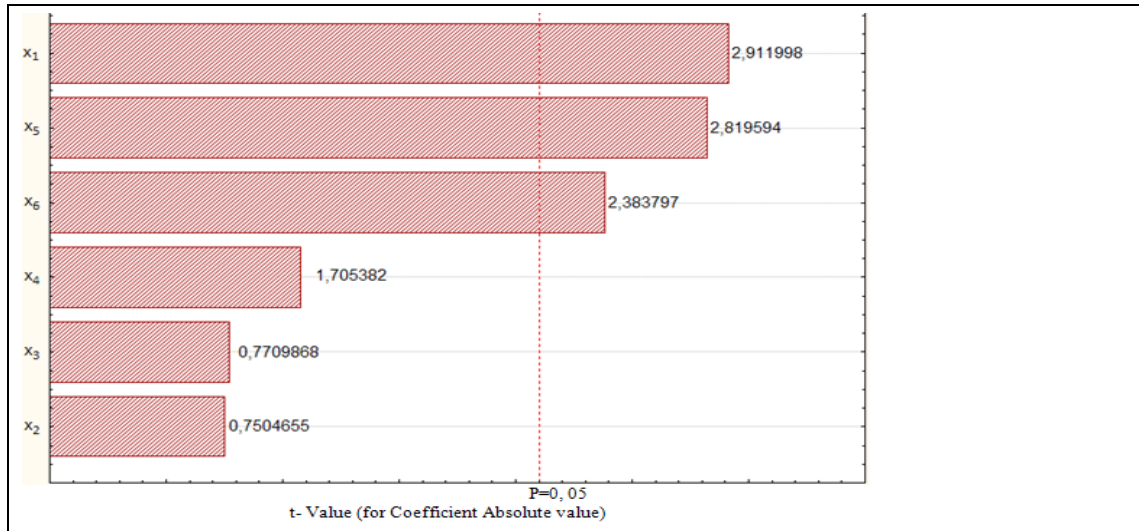


Figure 4: The detail of nickel coating

We can conclude that while the quantity of nickel chloride (x₁) and nickel sulphate (x₂), is increasing, the final coating thickness is decreasing and there features more significant influence of nickel chloride. In the experiments the following parameters were applied such as sodium hypophosphite (x₃), sodium citrate (x₄), time (x₅) and temperature (x₆), whereby the positive independence was recorded according to coating thickness. We can conclude that due to increasing level of above mentioned parameters the final thickness is expanding mainly in dependence on time and temperature.

The general equation of mathematical model (4) can be expressed by logarithmic transformation taking into consideration only the significant parameters influencing the response, it means the investigated parameter, based on Table 5 the expression will be as follows:

$$\log \hat{y}(h) = b_0 \cdot \log x_0 + b_1 \cdot \log x_1 (\text{NiCl}_2) + b_5 \cdot \log x_5 + b_6 \cdot \log x_6 (T) \quad (5)$$

considering the regressive coefficients, the equation will be (5) :

$$\log \hat{y}(h) = 0,7987 \cdot \log x_0 - 0,1410 \cdot \log x_1 (\text{NiCl}_2) + 0,1365 \cdot \log x_5 (t) + 0,1155 \cdot \log x_6 (T) \quad (6)$$

The equation (6) can be written into the final mathematic – statistic model by applying transformation into the natural scale factor and modification:

$$h = \frac{0,152 \cdot t^{0,352} \cdot T^{1,239}}{\text{NiCl}_2^{1,023}} \quad (7)$$

It is important to remember that the equation (7), which describes the dependence of significant parameters and thickness of created coating, applies only in the range of used levels of parameters. For its generalisation it is necessary to derive this equation for expanded intervals of used values in the process of autocatalysis secretion of nickel coating.

DISCUSSION

From the diagrams, Fig.5, Fig.6 and Fig.7, it follows that the thickness of coating is increasing with time and decreasing with the quantity of NiCl_2 . On the other hand the thickness of coating is reduced by decreasing of time and increasing of the quantity of NiCl_2 . This is not a linear dependence in the scale of utilized values.

The thickness of coating is reduced with increasing of the quantity of NiCl_2 and with the decreasing temperature T and on the other hand the thickness of created coating is growing with decreasing of the quantity of NiCl_2 and increasing of the temperature T .

We can observe the other conditions such as the thickness of coating which is growing with increasing of the temperature T and time t . The smallest thickness $3 \mu\text{m}$ is created at the temperature 70°C and time 10 minutes. We can suppose that the maximal thickness of coating will be created at the temperature 115°C and at time 50 minutes.

In Fig.5, Fig.6 and Fig.7 there are shown the results of experiments at various technological parameters and their influence on thickness of coating.

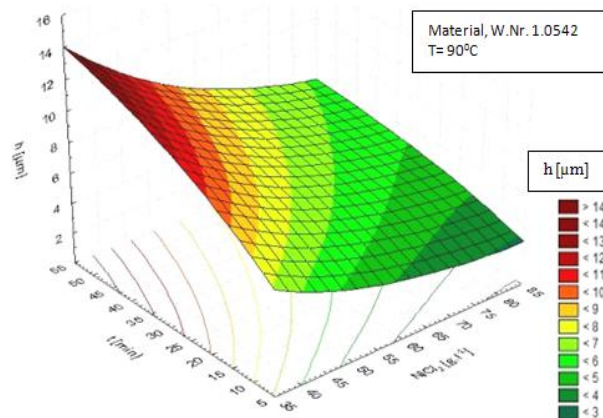


Figure 5: The space dependence of significant parameters (x_1, x_5) on the material thickness

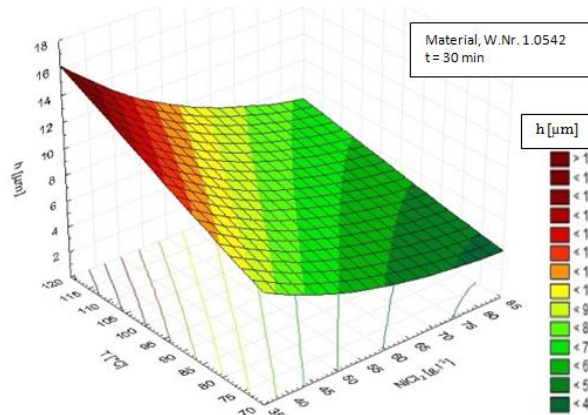


Figure 6: The space dependence of significant parameters (x_1, x_5) on the material thickness

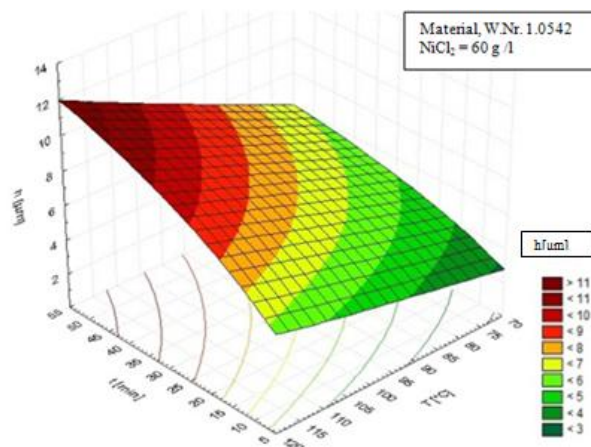


Figure 7: The space dependence of significant parameters (x_1, x_5) on the material thickness

CONCLUSIONS

The great advantage of nickeling is the simplicity of its service. It works under simple and poor conditions. Both the electricity power electrodes and other electric components are not needed compared with galvanic metallisation.

If we compare this process with other galvanic processes, one of the great advantages is the depth efficiency of bath, which is very important for example in metallisation of various caves and rugged topography of surfaces. The de energized separated coatings have more advantageous and special properties and they are appropriate for special applications compared with galvanic coatings.

This type of surface finishing has a number of advantages therefore the further industrial research has to focus on the utilisation of technology which would lead to decrease of used temperature to minimal values of metalising temperature and increase of separating speed of chemical coating. This is the way how to decrease service costs as well. The target of further research will be the application of catalysers in this area, respectively the chemical agents, which increase the determined process, respectively which increase the glitter of the final coating.

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