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DETERMINATION OF ELECTRO LESS DEPOSITION BY CHEMICAL NICKELING

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Increasing of technical level and reliability of machine products in compliance with the economical 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 chemical nickel-plating 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.

Key words: deposition, chemical nickeling, layer thickness, surface protection

INTRODUCTION

The surface finishing technologies play an important role in the finishing quality of technical equipments. It influences on its life-service requirements on services. The surface protection depends on the function of the machine products and appearance. 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 by increasing of:

- life-service and life of surface finishing,
- technical parameters of surface finishing,
- decreasing of product costs, mainly power and material saving,
- product humanisation, automation and robot- technology,
- delimitation of environment pollution [3].

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:

$$NiSO_4 + 3NaH_2PO_2 + 3H_2O = Ni + 2H_2 + H_2SO_4 + 3NaH_2PO_3 \quad (1)$$

$$3NaH_2PO = NaH_2PO_3 + 2P + 2NaOH + H_2O \quad (2)$$

Both equations can be summed into the following form:

$$NiSO_4 + 6NaH_2PO_2 = Ni + 2P + 2H_2 + Na_2SO_4 + 4NaH_2PO_3 \quad (3)$$

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 [3]:

- uniform coating is created on the parts with more complicated shapes,
- the coatings have lower porosity, resistance against wearing and corrosion,
- non-conducting surface can be coated by nickel and 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

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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 [4].

MATERIAL AND EXPERIMENTAL METHODS

The material, ISO Fe 590 (W.Nr. 1.0542, where Ni-max 0,009, P-max 0,045, S-max 0,040), plain carbon steel with higher content of carbon was used for experimental research. 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.

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 [4]. 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. 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]. In this case the Taguch experimental design L16 was proposed. The real conditions (the matrix) of experiments are shown in Table 1.

Table 1 **Real conditions of experiment**

C. pr.	Parameter	Un.	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 phosph.	$g.l^{-1}$	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	Tempe-rature	°C	75	85	95	105	115

C.pr.- code parameter, un.- unit

RESULTS AND DISCUSSION

According to the obtained results, shown in Table 2, 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, 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. In Figure 1 there are shown the samples after chemical nickeling of the planned experiment.

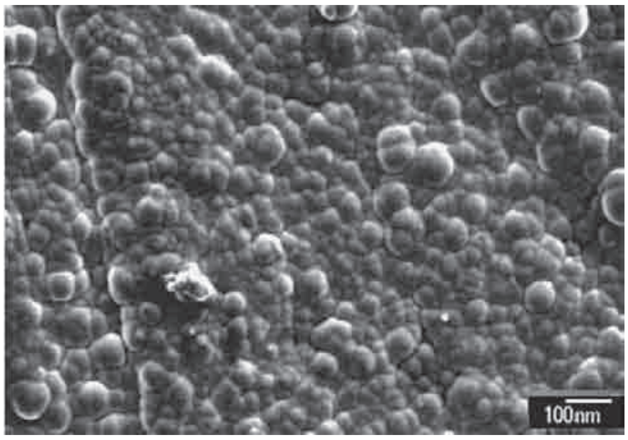

Figure 1 Detail of nickel coating

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 1 200 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. In Table 2 the results of regression analysis are demonstrated. According to Table 2 the regressive coefficients for particular parameters can be determined and simultaneously reached the significance level of Student test criterion (p) showing [5] in accordance with Pareto diagram, presented in Figure 2, the significant parameters, which influenced the final thickness of coating on the selected level of significance a = 5 %.

Table 2 **Results of regression analysis**

Reg-res. indp-var.	Stand. coef. b(i)	T-Value error Sb(i)	T-Value H_0: b(i)=0	Prob. level	Rej. H_0 at 5%	Power of test at 5 %
Int.	0,7987	0,0508	15,733	0	Y	1
x_1	-0,1410	0,0484	-2,911	0,0093	Y	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	Y	0,7598
x_6	0,1155	0,0484	2,385	0,0283	Y	0,6165

We can conclude that while the quantity of nickel chloride (x_1) and nickel sulphate (x_2), is increasing, the final coating thickness is decreasing and there features more significant influence of nickel chloride. In the ex-

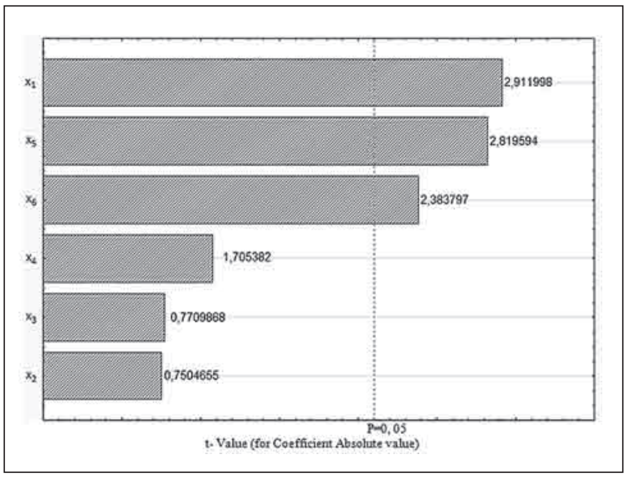

Figure 2 The detail of nickel coating

periments the following parameters were applied such as sodium hypophosphite (x_3), sodium citrate (x_4), time (x_5) and temperature (x_6), 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, the expression will be as follows:

$$h = f(NiCl_2, T, t) \tag{4}$$

$$\log \hat{y}(h) = b_0 \cdot \log x_0 + b_1 \cdot \log x_1 (NiCl_2) + b_5 \cdot \log x_5 + b_6 \cdot \log x_6 (T) \tag{5}$$

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

$$\log \hat{y}(h) = 0{,}7987 \cdot \log x_0 - 0{,}1410 \cdot \log x_1 (NiCl_2) + 0{,}1365 \cdot \log x_5 (t) + 0{,}1155 \cdot \log x_6 (T) \tag{6}$$

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

$$h = \frac{0{,}152 \cdot t^{0,352} \cdot T^{1,239}}{NiCl_2^{1,023}} \tag{7}$$

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.

From diagrams Figures 3, 4, 5 follow that the thickness of coating is increasing with time and decreasing with the quantity of $NiCl_2$.

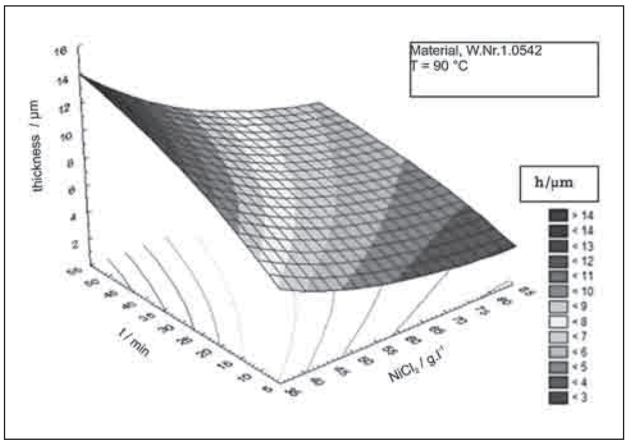

Figure 3 The space dependence of significant factors (x_1, x_5) on the material thickness

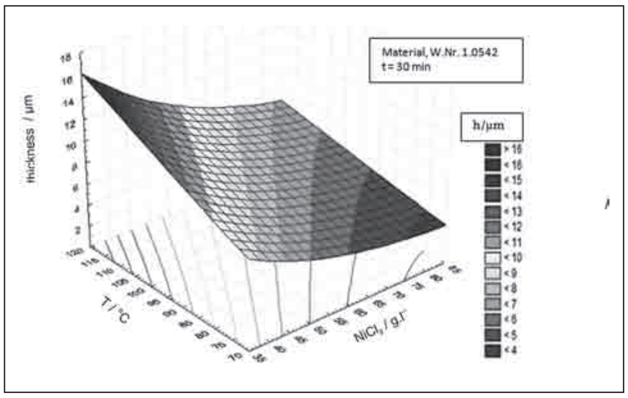

Figure 4 The space dependence of significant factors (x_1, x_6) on the material thickness

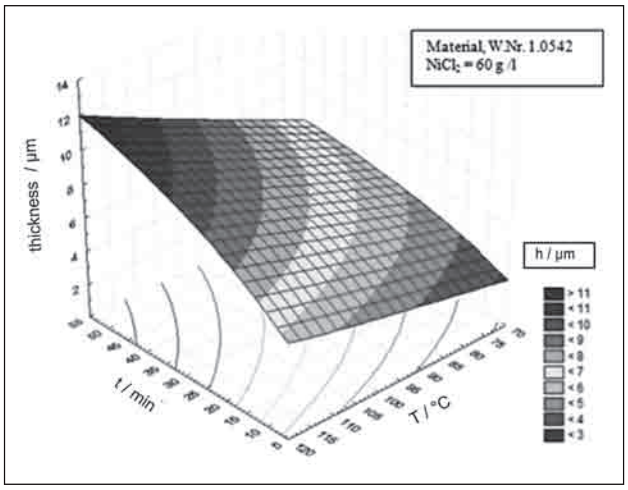

Figure 5 The space dependence of significant parameters (x_5, x_6) on the material thickness

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 [6].

In Figures 3, 4, 5 there are shown the results of experiments at various technological parameters and their influence on thickness of coating.

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 metalizing 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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