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CONSIDERATIONS ABOUT ELECTRODEPOSITION OF TITANIUM IN A NICKEL MATRIX

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ABSTRACT: This paper deals with the obtaining of a composite layer based on a nickel matrix with embedded titanium grains. The Ti embedding into the layer is based on the adsorption phenomenon and migration of the charged particles towards the cathode. The result of this process is the obtaining of some composite layers with considerable thickness and good adhesive properties that protects against corrosion.

KEY WORDS: electrodeposition, nickel matrix, adsorption, regression analysis, titanium powder

1. INTRODUCTION

For protection against corrosion in aggressive environment good results have been obtained with alloys based on nickel. Electrolytic nickel layers with crystalline structure are mostly applied as decorative and protection coatings and electrolytic amorphous layers containing phosphorous have a good corrosion resistance. Nickel layers have been improved by adding of some oxides (TiO_2, NiO) and were characterized by special properties: good resistance at corrosion, great hardness and resistance to high temperature [4], [5].

Among composite layers of special importances are the layers containing the following metals: Ti,W, Al or Mo. By incorporating of these metal particles as composite led to obtain after thermal and chemical treatment a new kind of composite material.

In this case was studied the obtaining of composite layers containing Ti in a nickel matrix, the presence of the titanium grains improving the nickel resistance.

2. DESIGN AND REALISATION OF THE EXPERIMENT

The electrodeposition process was achieved in an electrolytic bath based on nickel sulphate in which were added increasing quantities of titanium powder 6, 12, 20, 28, 40 [g/dm^3].

The experimental conditions were the following:

- the current density was chosen 0,1 A/cm^2;
- the deposition time was 30 minutes;
- the cathodes were made from steel;
- the anode was made from lead.

The steel plate substrates were mechanically polished on abrasive paper and treated with dilute HNO_3 solution in order to remove impurities and then the substrate surface was chemically treated in a dilute HCl solution.

The mass increment of the layer was measured and estimated on the basis of the mass difference before and after layer electrodeposition.

The steel plate area (S) was 8 cm^2 and the distance between the plates and the surface of the solution was 5 cm.

The electrolyte solution consists from nickel sulphate $NiSO_4 \cdot 7H_2O$, sodium acetate, ammonium chloride, in which were gradually introduced certain quantities of titanium.

Nickel from the eletrolyte together with titanium will migrate toward cathode and will be deposited on the steel surface. The obtained layer has a composite structure with Ti and Ni embedded.

Electrodeposition was conducted in an electrolytic cell containing 500 cm^3 of solution that was permanently mixed in order to obtain a homogenous suspension and to assure the titanium transportation toward cathode. It was observed that the presence of titanium powder in the solution activates the electrodeposition of nickel.

The obtained surface was rough with visible titanium grains that have been evidenced with a specific reactive. By increasing of the titanium powder content increases also the layers thickness and its adherence on the steel substrate.

3. PROCESSING OF THE EXPERIMENTAL DATA

In this experiment the purpose was to study the influence of the increasing of the titanium powder in bath on the layers thickness, founded on basis of the mass difference, determined before and after layer electrodeposition.

Table 1 Experimental dependence between the Ni-Ti layer thickness δ and the Ti content

Number of experimental points	**Ti content** $x \equiv t$ **[g/dm^3]**	**Mass difference Δm [g]**	**Layer thickness Ni+ Ti** $y \equiv \delta$ **[µm]**	**Density of coating, ρ [g/dm^3]**
1	6	0,020	43,78	5,710
2	10	0,056	103,32	6,775
3	14	0,070	113,00	7,742
4	19	0,094	138,65	8,473
5	25	0,135	177,41	9,511
6	30	0,152	193,08	9,841
7	38	0,171	206,00	10,375

Table 1 presents this mass difference Δm experimentally obtained, as well as the titanium layer thickness δ, calculated with the relationship (1), with respect to the titanium powder content t in the bath:

$$\delta = \frac{\Delta m}{\rho S} \quad , \qquad (1)$$

where S is the area of the adsorbed layer .

Increasing content of Ti in the bath results in the increase of the weight of the deposited Ni+Ti layer. The presence of Ti powder in the bath activates the layer forming process (Fig.1).

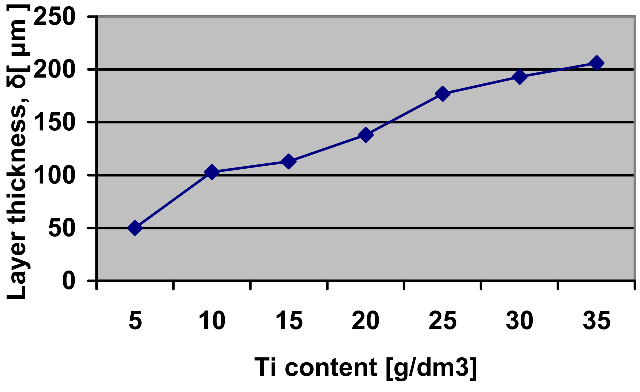

Figure 1. Dependence of the Ni+Ti layer thickness on the amount of Ti powder in the bath

There is also a relation between the weight linear increase of deposited layer and the increase of Ti powder content in the bath (Fig.2).
For mathematical modelling of the relation between the dependent variable y and the independent variable x, i.e. between the titanium layer thickness δ and the titanium powder content t in the bath, the regression analysis method was carried out [1], [2], [3], [6]. Since there is no preliminary sufficient information concerning the function type of the dependences, four alternatives were chosen for ulterior developing and analysis.

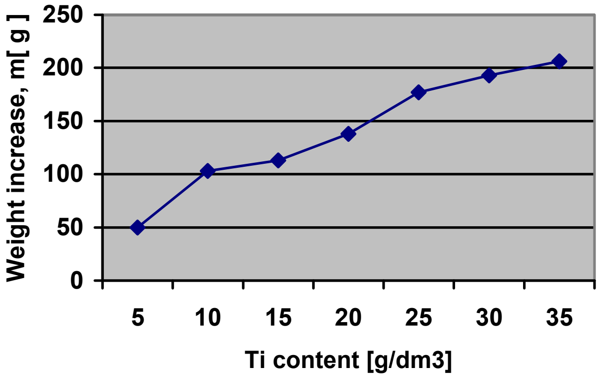

Figure 2. Dependence of the weight increase of the layers Ni+Ti, on the amount of Ti powder in the bath

For determining the regression coefficients, the Least Squares Method is utilized, which consists of imposing minimum values for the variance of conformity between the estimated and experimental values.
The establishing of the coefficient value is deducted from the minimizing condition, for the experimental points, of the deviation between the measured values and the estimated ones of the objective function.
On a finite domain, an assemble of points resulted by measuring can be analytically described by some types of functions:

$$y = f\left(x_i, b_j\right), i = 1,\dots n, \; j = 1,\dots d \qquad (2)$$

In which f(x$_i$,b$_j$) represents the estimation of the real dependence:

$$y = \varphi\left(x_1, x_2 \dots x_k, z_1, z_2 \dots z_m, \beta_1, \beta_2 \dots \beta_d\right) \qquad (3)$$

And:

$x_1, x_2 ..., x_k \Rightarrow$ controllable influence parameters

$z_1, z_2 ...., z_m \Rightarrow$ uncontrollable influence parameters, that provokes random errors

$\beta_1, \beta_2 ..., \beta_d \Rightarrow$ statistic parameters, unknown, called influence coefficients or regression coefficients

$b_1, b_2 ... b_d \Rightarrow$ statistic estimations obtained from experiments, of parameters β_j

The Least Square Calculation Method doesn't indicate the best shape of the regression function $\varphi(x_i,b_j)$ for data representation. It permits the estimation of the regression coefficients values, b_j so that the analytical relation to assure the particularization of function $\varphi(x_i,b_j)$ that belongs to a chosen functions family (referring to the studied object, phenomenon or process), which will assure the best analytically approximation of the tests results.

For exemplifying the application of this method, it will be analysed the case of an objective function y dependent on a single influence parameter, x.

It is considered a process for which were established by measurements values y_i of an objective function of a variable, corresponding to values x_i of the influence parameter, i=1,…n and it will be obtained the functional dependence (2) in which βj are unknown parameters which will be estimated from the obtained tests results. The chosen estimation has to be the best (for the Least Square Calculation Method) among all the possible estimations. It is considered that the number of tests, n, can be always greater than the number of unknown parameters, d.

If values y_i wouldn't be affected by the measurements errors, the equation systems:

$$\begin{aligned} y_1 &= \varphi(x_1, \beta_1, \beta_2 ... \beta_d) \\ y_2 &= \varphi(x_2, \beta_1, \beta_2 ... \beta_d) \\ &\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ y_n &= \varphi(x_m, \beta_1, \beta_2 ... \beta_d) \end{aligned} \qquad (4)$$

resulted from the measurements results, would be compatible towards the unknowns β_j and the supplementary equations n-d would be simple consequences of the first d equations. In reality, values y_i are affected by random errors ε_I so that system (4) have to be replaced by the equation systems:

$$\begin{aligned} &\varphi(x_1, \beta_1, \beta_2 ... \beta_d) - y_1 = \varepsilon_1 \\ &\varphi(x_1, \beta_1, \beta_2 ... \beta_d) - y_1 = \varepsilon_1 \\ &\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ &\varphi(x_n, \beta_1, \beta_2 ... \beta_d) - y_n = \varepsilon_n \end{aligned} \qquad (5)$$

In accordance with the Least Square Calculation Method results that for obtaining the best estimation of values y_i, is necessary that the sum of errors squares ε_I to be minimized. Passing from the real dependence of its, are substituted the errors ε_I with the rests e_i and coefficients β_j with theirs estimations, b_j, and the equations systems (4) will become:

$$\begin{aligned} &f(x_1, b_1, b_2 .... b_d) - y_1 = e_1 \\ &f(x_2, b_1, b_2 .... b_d) - y_2 = e_2 \\ &\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\ &f(x_n, b_1, b_2 .... b_d) - y_n = e_n \end{aligned} \qquad (6)$$

And it is called the system of condition equations because the establishing of parameters b_j is made considering the minimum condition for the sum of square rests:

$$e^2{}_1 + e^2{}_2 + ... e^2{}_i = \sum_{i=1}^{n} e^2{}_i \Rightarrow \text{minimum} \qquad (7)$$

With system (5) and relation (6) results:

$$S = \sum_{i=1}^{n} [f(x_i, b_1, b_2 .... b_j) - y_i]^2 \Rightarrow \text{minimum} \qquad (8)$$

The minimum value of expression S is obtained for parameters values b_j resulted as solutions of the equations system obtained by equalizing with the partial derivates of toward the unknowns b_j.

$$\begin{aligned} &\frac{\partial S}{\partial b_1} = 0 \\ &\frac{\partial S}{\partial b_2} = 0 \\ &\dots\dots\dots \\ &\frac{\partial S}{\partial b_d} = 0 \end{aligned} \qquad (9)$$

This system is called normal equations system.

From the above data resulted that for resolving a problem using the Least Square Calculation Method is necessary the random choosing of the function $f(x, b_1, b_2, ... b_d)$.

If the function is linear towards unknowns b_j then the most convenient values of these unknowns are obtained by resolving the normal equations system (9).

If the function isn't linear towards unknown b_j is necessary to know or to choose some initial values b_j^* for parameters b_j that will respect the relation:

$$b_j = b^*{}_j + \Psi_j \qquad (10)$$

In which quantities Ψ_j are values that permits the approximation of coefficients b_j and which have smaller values than b_j^*.In this conditions the system of normal equations is resolved by substituting b_j towards the ratio of unknown Ψ_j.

The regression models obtained are represented together with the experimental points in figure 3 for linear function and figure 4 for power regression;

In the same figure, there are presented labels with the founded regression functions and the values of R^2 coefficient, which indicates the percentage the model explains the scattering of the experimental data. It can be observed that, in all cases, values greater than 90% were obtained. Thus, any of the models corresponds, from the precision of estimation point of view. The statistical analysis of the regression functions was realized by means of STATGRAPHICS software [6], [7]. For estimating the variance of reproducibility, one of the experimental points was replicated (c = 3). The conformity of the mathematical models with the experimental data was checked using Fisher criterion. All the obtained models were founded to be conforming to the process studied. Also, after testing with the Student criterion, all the regression coefficients were certified to be significant.

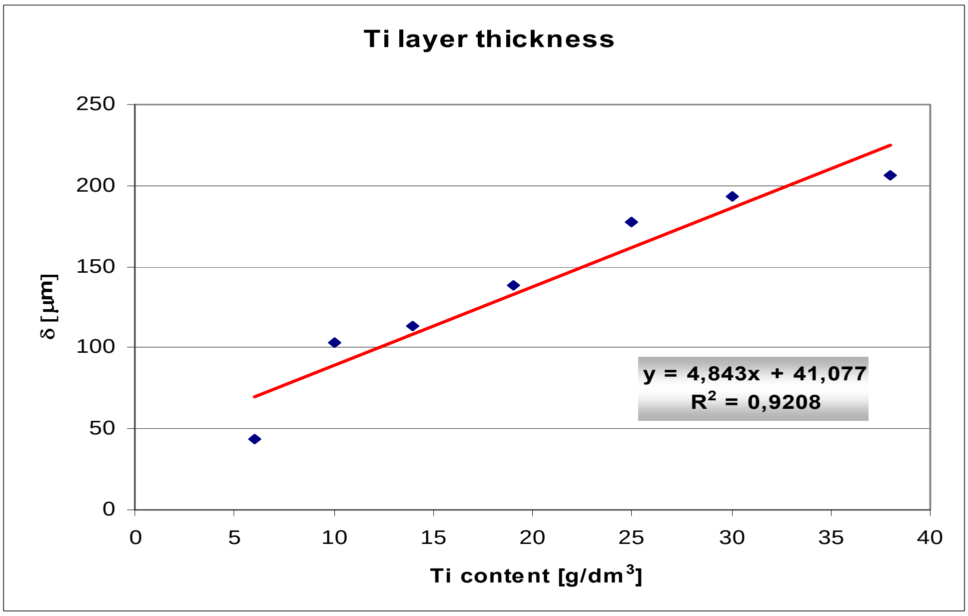

Figure. 3. Modelling of the dependence between the Ti layer thickness and the Ti powder content using linear regression

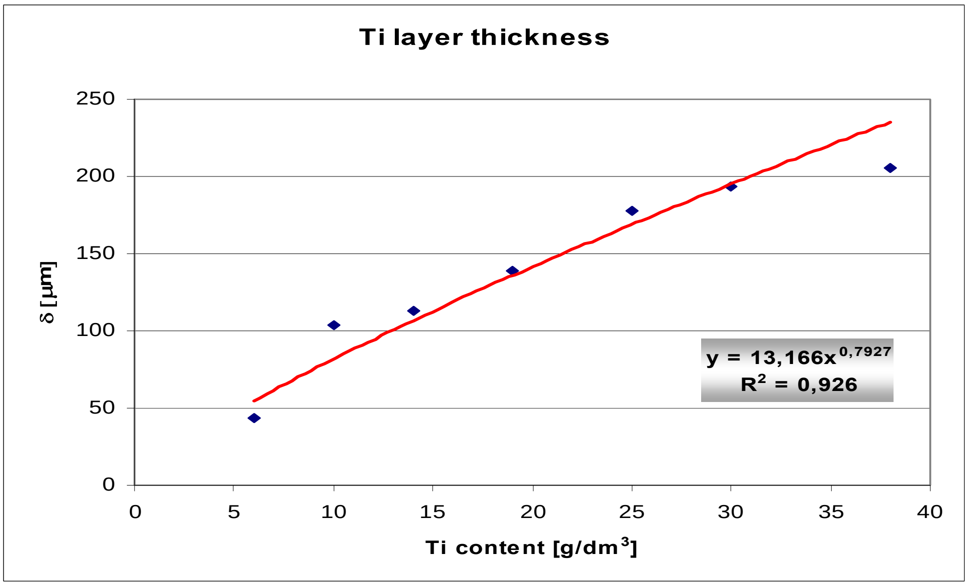

Figure. 4. Modelling of the dependence between the Ti layer thickness and the Ti powder content using power regression

4. CONCLUSIONS

The increase of the titanium powder in the bath increases the titanium embedded in the composite layers.

After processing the experimental data by means of the regression analysis method, proved that the presence of Ti powder in the bath activates the nickel electro deposition process. The increase of efficiency of the nickel electro deposition process is caused by the rise of titanium powder content in the bath.

The presence of Ti powder activates the nickel electro deposition process and between the weight linear increase of deposited layer and the Ti powder content in the bath is a linear relation (figure 4).

The higher Ti content in the bath, the bigger the amount of adsorbed nickel ions on Ti powder moved toward the cathode.

The thickness of the Ni +Ti layers was evaluated from cross-section using the microscopic method.

Proportionally, the increase of Ti powder content in the bath, the thickness of the composite layer increases to about 193-206 μm. This layer has a good adhesiveness to the steel substrate, endures with good results the thermal shock and does not separate from the steel plate after multiple bending and breaking of the substrate with the layer.

The mechanism of Ti embedding into the layer is based on adsorption phenomena and migration of the charged suspension micelles towards the cathode that will create the possibility of obtaining a considerable thickness and good adhesive properties of the composite layer.

The process of Ti embedding in the Ni matrix is based on the ability to absorb Ni^{+2} ions on Ti powder surface.

This suspension of Ni-Ti moves towards the cathode and by applying considerable current densities will increase the number of adsorbed Ni^{+2} ions than the ones hydrated in the bath. It also causes embedding of a greater quantity of Ti in the composite layer.

According to the linear regression model, an increase of the Ti content with 2 [g/dm^3] determines, in case of similar conditions, an augmentation of thickness δ of over 10 [μm]. Moreover, since the correlation coefficient is 95,95%, the intensity of the relation between the variables is very strong, being a relative determinist relation.

This study was done with the purpose to obtain the galvanic composite layers on a nickel substrate containing embedded titanium grains. By incorporating into a metallic substrate particles of Ti, is obtaining after thermal and chemical treatment a new kind of composite material.

5. REFERENCES

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