



STUDIES AND RESEARCHES ON OBTAINING ELECTROCHEMICAL COMPOSITE COATINGS IN NICHEL - Ni / KAOLIN MATRIX

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ABSTRACT

The paper presents the electrochemical obtaining of nickel matrix composite coatings using kaolin particles as dispersed phases. Watts electrolytes were used, with a pH = 4.5 current densities of 6, 9, 12 A/dm², a dispersed phase concentration of 20 g/L, shaking speeds of 500, 700 and 900 rpm, deposition time of 60 minutes. Their characterization has been achieved both from a microstructural point of view and from the point of view of layer thickness, microhardness and behaviour in salt mist corrosion. The presence of dispersed phase particles, which acted as nucleation centres, led to the reduction of the nickel crystallites, which further decreased the roughness of the coatings while increasing hardness. By correlating the current density with the rate of stirring, respectively the increase their, thicker layers were obtained.

KEYWORDS: Ni composite coatings, electrodeposition, kaolin, microhardness

1. Introduction

The field of composite materials is in a rapid and continuous expansion due to the large number of possible combinations between two or more components and the advantage of obtaining a wide range of materials the use of which can be expanded in almost all technical fields (aerospace, naval, automotive, electrical and electronics industries) as a result of the possibility of modelling their structure and properties. In this respect, the following properties are to be improved: hardness, wear resistance, high temperature resistance, dimensional stability, corrosion resistance, vibration damping capacity, lubrication [1, 2, 4, 5].

ACE electrochemical composite coatings have a number of advantages such as high deposition velocity (rate), simple automation equipment, easy control of microstructure and thickness deposition (from nanometer to micrometric level), uniform coverage capability of both complicated geometry surfaces and large ones [1, 2, 4, 5].

Ni - kaolin composite materials are used in the aerospace, automotive industry, in applications requiring good behavior to wear, abrasion, fatigue, corrosion [3].

The properties of the composite materials depend on the type, structure, shape, size,

morphology and content of the complementary phase particles, as well as their distribution in the metal matrix.

The functional properties of composite coatings are strongly influenced by their structure, tensions developed in the layer as well as by the orientation of the complementary phases which can determine the anisotropy of the properties.

Nickel was chosen as a coating material because it is one of the most common industrial coatings used for decorative and functional applications [4].

Kaolin - $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ - is a very fine grain, white 2.65 g/cm³ density clay (mineral) of low-plasticity, high temperature resistance and by burning it turns solid and very compact. A mineral layer has a triclinic crystalline symmetry made up of octahedral Al_2O_3 and tetrahedral formations of SiO_2 that share a common plan formed by oxygen atoms. The layers thus formed are linked together by hydrogen atoms [bonds] [3]. The mechanical properties of the composite materials depend on their microstructure (nanocrystalline, microcrystalline), correlating with dislocation theory, strength and ductility. The addition of dispersed phase particles in order to obtain composite materials acts as a barrier against the displacement of dislocations followed by blocking them at the grain boundary which results in increased resistance to deformation and hardness [6].

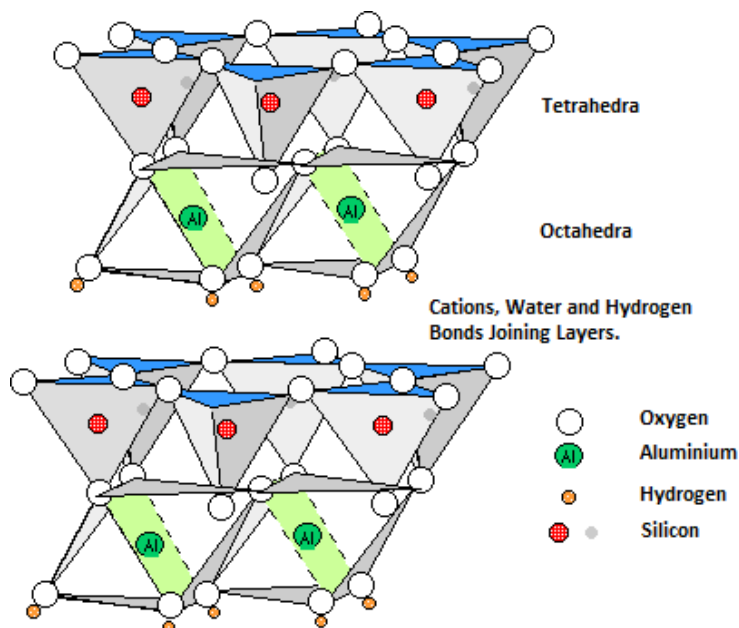


Fig. 1. Crystalline structure of kaolin [3]

The research carried out in this paper has as a general objective the development of a technology for the electrochemical production of composite coatings in nickel matrix using as dispersed phase kaolin particles with dimensions of approx. 2 μm and their characterization in terms of microstructure, layer thickness, microhardness and behaviour in salt mist corrosion.

2. Experimental research

To obtain nickel coatings and composite coatings in a nickel matrix, a DC source, a device provided with a magnetic stirrer and a bath temperature control system with an electrolyte receptacle were employed. A volume of 300 ml solution was used and the experiments were carried out at 50 °C.

Watts electrolytes consisting of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ – 300 g/L, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ – 50 g/L and H_3BO_3 – 40 g/L, pH = 4.5 current densities of 6, 9, 12 A/dm^2 , a dispersion phase concentration of 20 g/L, stirring speeds of 500, 700 and 900 rpm, with a 60 minutes deposition time.

The electrodeposition was achieved by vertical alignment of the electrodes at a distance of 14 mm from each other. As anode, high purity nickel (99%) was used, the cathode being copper strip, representing the support material for 76 x 20 x 1 mm coatings.

The copper band used was prepared by degreasing (organic solvents - trichlorethylene), pickled (HNO_3 + HCl at room temperature for 1-2 minutes) followed by washing with distilled water.

The metallographic analysis of the samples was carried out on a Neophot 2 microscope, with the acquisition of data on the computer and revealed the appearance of the nickel deposition surface compared to the composite coatings, their adhesion, the way electrodes have grown, as well as the presence of defects such as pores, cracks, exfoliations. The EDS analysis was performed with a SEM Quanta 200 electronic scanning microscope provided with an energy dispersion spectrometer.

To determine the microhardness, the PMT-3 micro-hardness durimeter was used with a load of 50 g.

The corrosion behavior in salt mist of the composite layers was performed according to ISO 9227/2012 for a period of 96 hours. For the test, the sodium chloride solution was prepared by dissolving in distilled water with a conductivity of less than or equal to 20 $\mu\text{S}/\text{cm}^2$ at 25 ± 2 °C, of a quantity of sodium chloride to give a concentration of 50 ± 5 g/L.

The relative density of a solution with this concentration is between 1.00255 and 1.0400. The pH of the saline solution was adjusted so that the pH of the solution collected in the spraying chamber ranged between 6.5 and 7.2. This was measured with a pH meter HI 991001, produced by "Hanna Instruments", also provided with a temperature indicator.

3. Experimental Results

Characterization of composite coatings in nickel matrix with dispersed phase

Al₂O₃*2SiO₂*2H₂O kaolin obtained electrochemically

Characterization of ACE composite coatings was performed compared to pure nickel coatings and consisted of macro and microstructural analysis, layer thickness and micro hardness determinations.

Fig. 1 shows the appearance of pure nickel coatings for different current densities and different agitation/stirring rates. It can be seen that the deposited layers are homogeneous, without cracked and have good adhesion to the copper supports. It can also be seen that increasing the density of the current increases the thickness of the obtained layer, keeping the temperature and deposition time constant. Increasing the current density leads to the formation of finer structures as a result of the multiplication of the crystallization germs on the cathode.

This influence of the current density can be explained by increasing the active surface of the cathode, the crystalline germs being formed on the inactive parts of the less active cathode [5].

As to the influence of the stirring speed (correlated with the current density), it has been found that when this grows compact, smooth, fine grain deposits of a high current efficiency can be obtained; the higher the current density, the more stirring should be done.

The primary role of stirring/agitation is to favour the homogenization of the ionic concentration in the cathode film and in the rest of the solution. It maintains the concentration of the solution constant, avoiding concentration polarization.

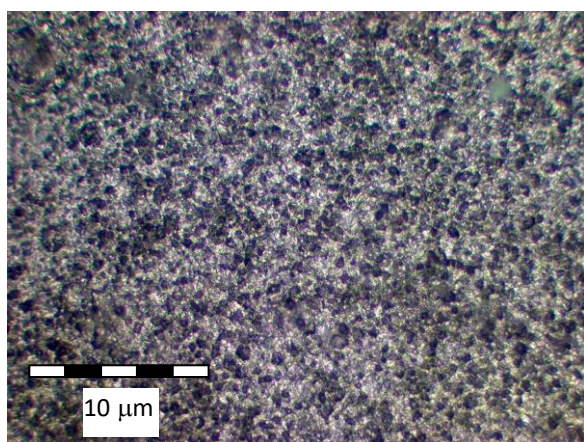
Fig. 2 shows the microstructural aspect of the electrochemical composite coatings in nickel matrix using kaolin particles as dispersed phase.

Analysing Fig. 2 it can be seen that the electrochemically obtained composite coatings in nickel matrix using kaolin particles as dispersed phase exhibit good homogeneity and compactness. Increasing the current density increases the degree of inclusion of the dispersed phase.

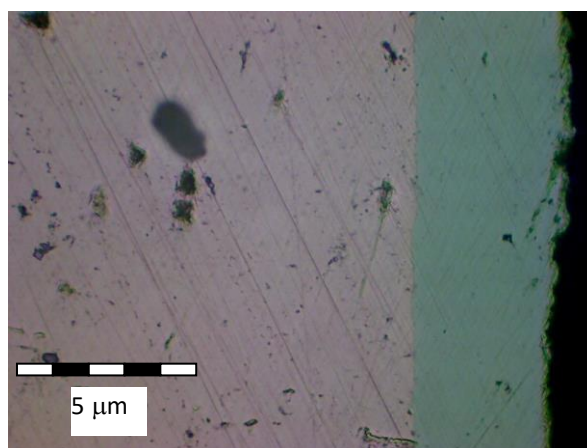
The kaolin particles led to the decrease of the crystallites' dimensions (compared to the pure nickel deposits) which further led to the decrease in the roughness of the deposits and the increase of the hardness (concomitantly blocking the displacement of the dislocations in the nickel matrix) (Fig. 7).

For the current density of 6 A/dm² it was considered that the optimal deposition regime was that of sample P3 (D_{crit} = 6 A/dm², v = 900 rpm, t = 60 minutes). At low stirring rates and low current densities (P1, P2), the growth rate of the crystalline germs exceeds the germination rate, which results in larger, less homogeneous and less compacted macrocrystalline deposits.

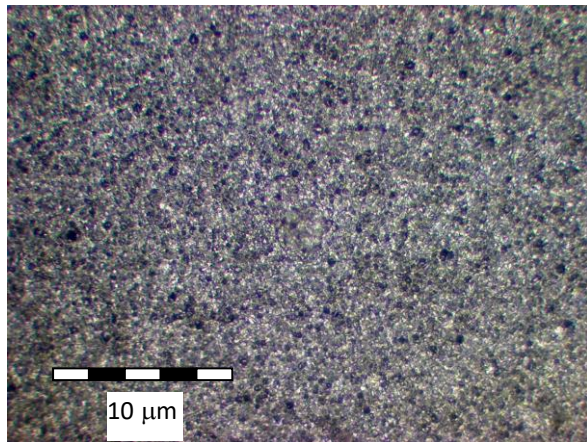
For the current density of 9 A/dm² it was considered that the optimal deposition regime was that of the P6 sample (D_{crit} = 9 A/dm², v = 900 rpm, t = 60 minutes). This has led to a compact, homogeneous, adherent deposit. As the current density increases, the germination speed increases and leads to more and more microcrystalline, fine-grained deposits.



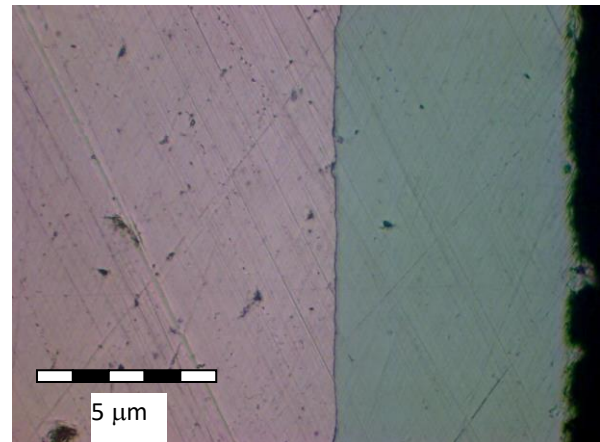
P01 – 6 A/dm², v = 500 rpm, 60 minutes



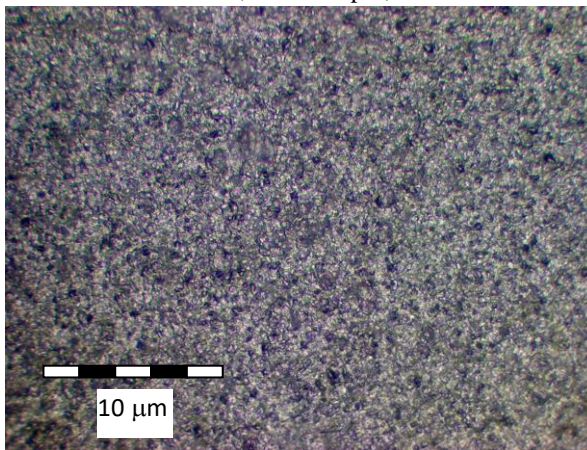
P01 – 6 A/dm², v = 500 rpm, 60 minutes



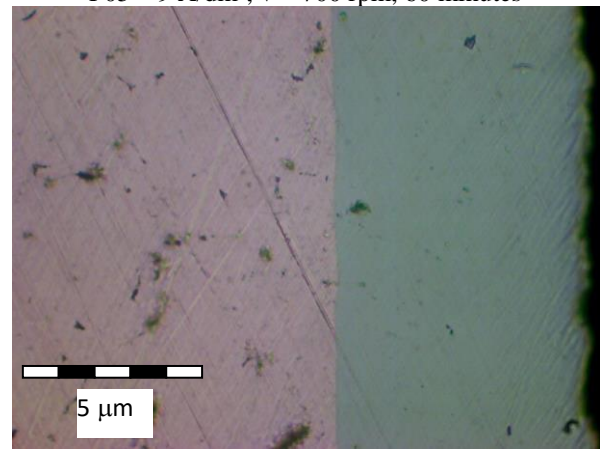
P05 – 9 A/dm², v = 700 rpm, 60 minutes



P05 – 9 A/dm², v = 700 rpm, 60 minutes

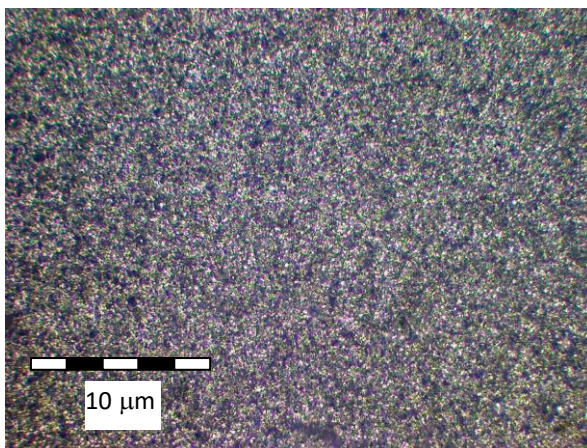


P09 – 12 A/dm², v = 900 rpm, 60 minutes

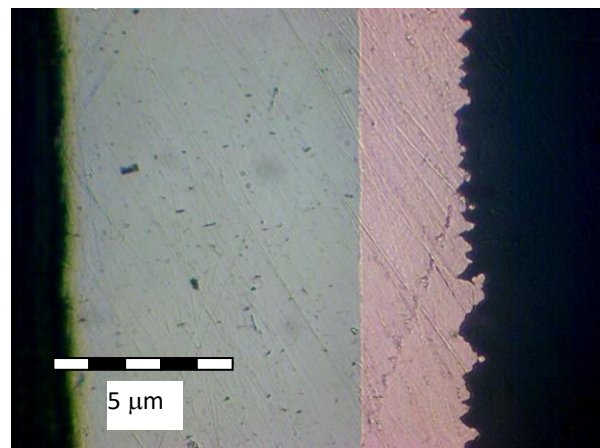


P09 – 12 A/dm², v = 900 rpm, 60 minutes

Fig. 1. Microstructural appearance of pure nickel coatings



P3 – 6 A/dm², v = 900 rpm, 60 minutes



P3 – 6 A/dm², v = 900 rpm, 60 minutes

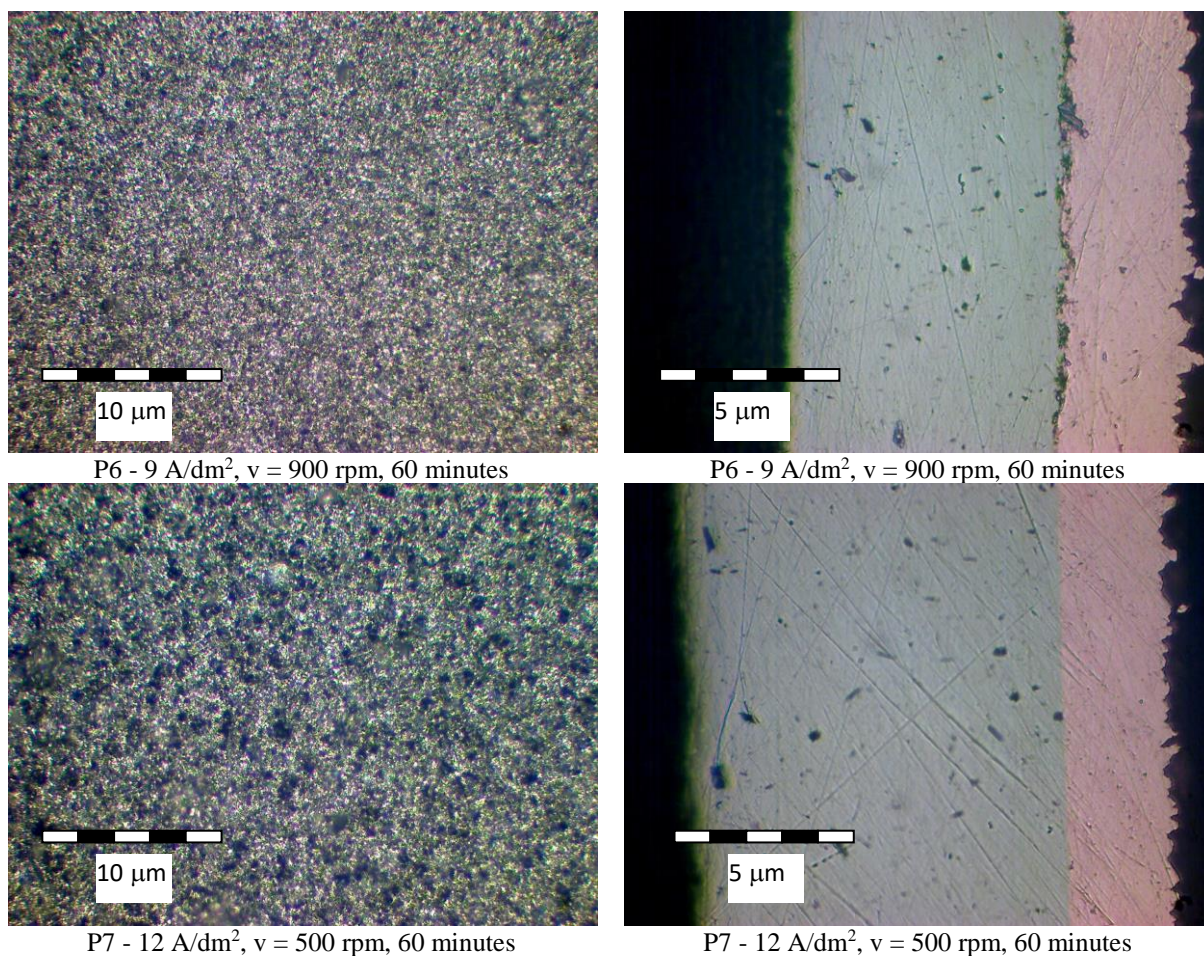


Fig. 2. The microstructural aspect of the electrochemical composite coatings in the nickel matrix using kaolin particles as dispersed phases

By adding kaolin particles at a concentration of 20 g/L, it has been found that layer thickness increases relative to pure nickel deposits which confirms the inclusion of dispersed phase particles into the metal matrix. As regards the morphology of the layer, there is a binary symmetry, both pyramidal and pseudo-pentagonal (Fig. 3).

Following the EDS analysis performed on the P6 sample both on surface and punctually, it was found that the distribution of the dispersed phase in the deposited layer is relatively uniform (Fig. 4 and 5).

For the current density of 12 A/dm², it was considered that the optimal deposition regime was that of the P7 sample (D_{crt} = 12 A/dm², v = 500 rpm, t = 60 minutes), the other regimes leading to less adherent and compact deposits.

With higher current densities, the concentration of metal ions in the immediate vicinity of the crystals decreases a lot and the crystals tend to grow towards the edges of the sample where the concentration of these ions is higher. Dendritic or spongy structures are thus obtained. Fig. 6 shows the influence of current density and stirring velocity on the layer thickness of pure nickel coatings and on electrochemical composite coatings in the nickel matrix using dispersed kaolin particles. It can be seen that increasing the current density and the stirring speed, the thickness of the obtained layer increases, while the temperature and the deposition time remain constant. The resulting composite coatings feature higher thicknesses compared to pure nickel deposits.

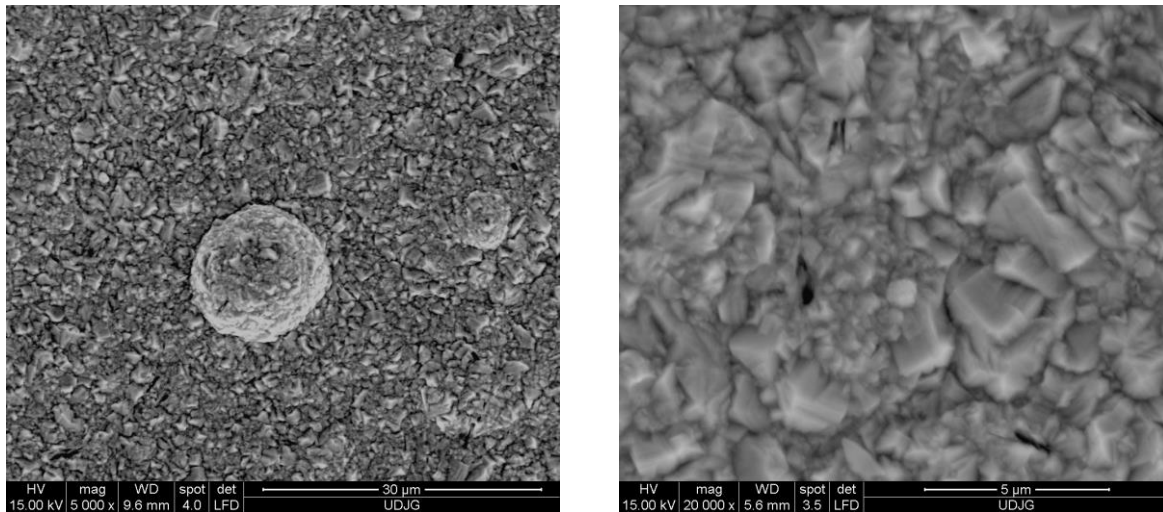


Fig. 3. SEM image of the deposited layer for sample P6

Fig. 7 shows the influence of the current density and stirring velocity on the microdurability of pure nickel coatings and on electrochemical composite coatings in nickel matrix using dispersed kaolin particles.

It can be seen that when increasing the density of the current and the rate of stirring, the microhardness of the obtained layer increases, the temperature and the deposition time being kept constant. This increase is due, on the one hand, to the increase in the stresses in the layer with the current density, and on the other hand to the better inclusion of the dispersed phase particles into the deposited layer.

Following the accelerated corrosion test performed in saline mist, it has been found that composite coatings exhibit a better corrosion behaviour compared to the pure nickel coating, as shown in Fig. 8. The presence of kaolin particles in the nickel matrix, correlated with the deposition parameters (current density, stirring rate), led to increased corrosion resistance in saline mist, the best behaviour being with samples P2, P5, P6, P7 where a higher passivation of the deposited layers was found.

4. Conclusions

The following conclusions can be drawn from the experimental researches:

- ❖ the nickel coatings obtained from variations in current density and stirring rate are homogeneous, crackles and have good adhesion to copper supports; the increase in the current density also increases the thickness of the obtained layer;

- ❖ the electrochemical composite coatings in nickel matrix using dispersed kaolin particles are homogeneous and crackles; the increase in the current density leads to the formation of finer structures as a result of the multiplication of crystallization germs on the cathode;

- ❖ when increasing both the current density and the stirring speed, the thickness of the layer thus obtained increases from 0.05 mm for pure nickel coatings obtained at a current density of 6 A/dm² and a stirring speed of 500 rpm to 0.12 mm for pure nickel coatings obtained at a current density of 12 A/dm² and 900 rpm, from 0.059 mm for ACE Ni - kaolin obtained at a current density of 6 A/dm² and a stirring speed of 500 rpm to 0.135 mm for ACE Ni - kaolin obtained at a current density of 12 A/dm² and 900 rpm, the temperature and deposition time being constant;

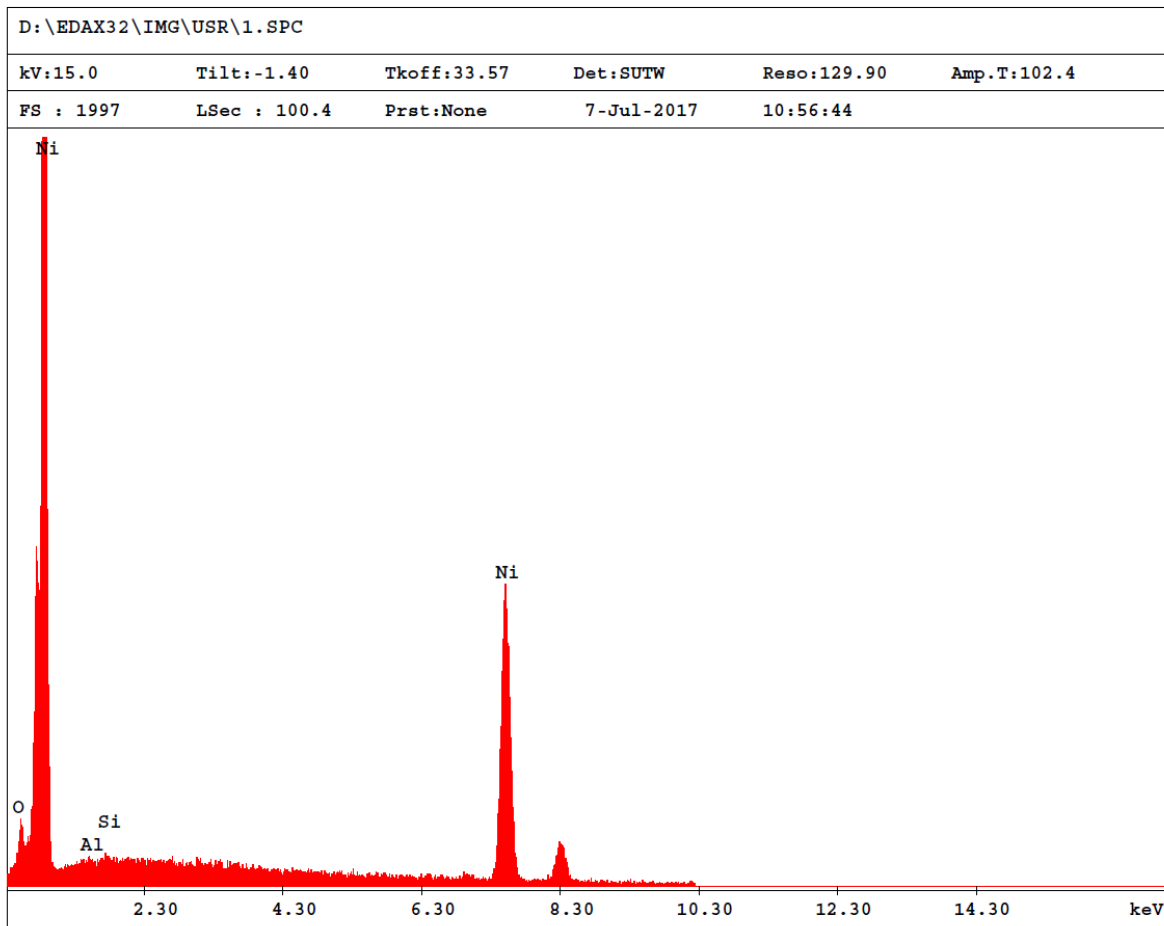
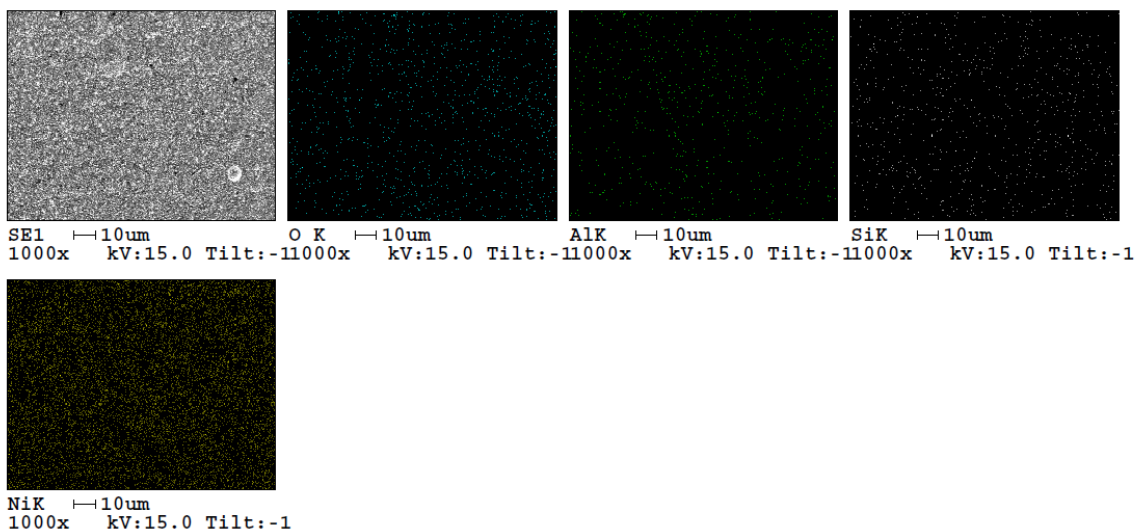


Fig. 4. Surface EDS analysis for sample P6

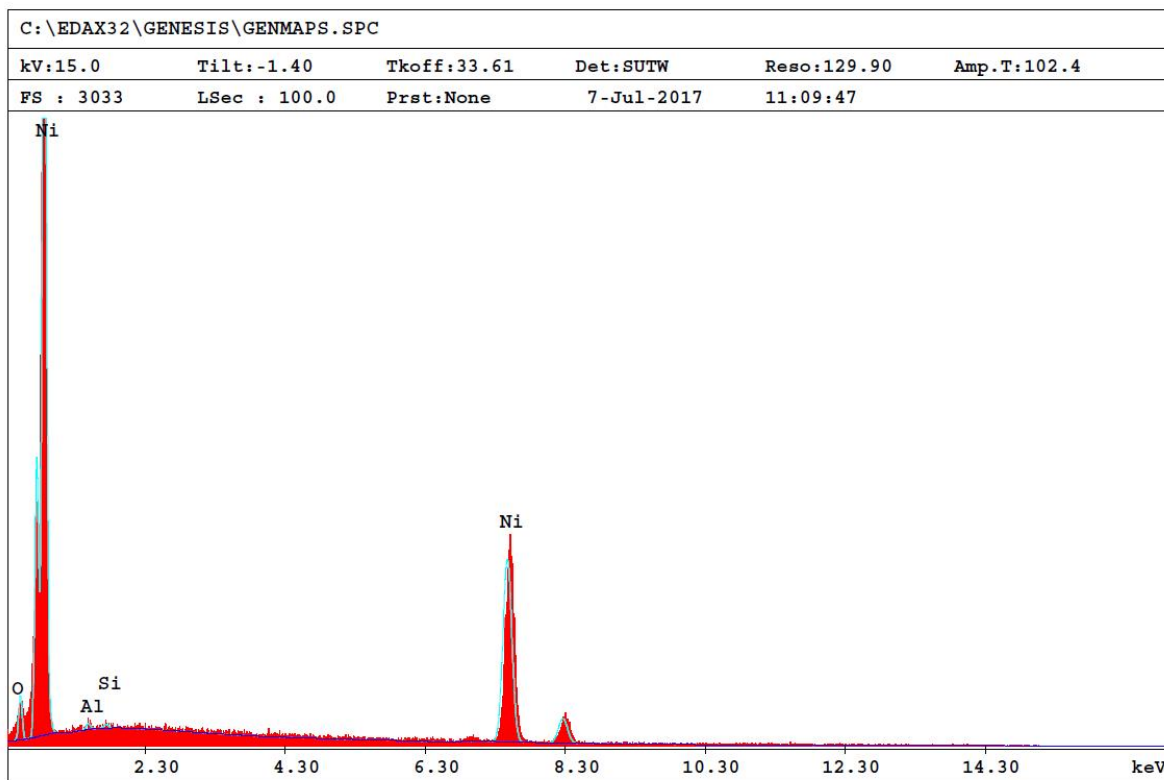
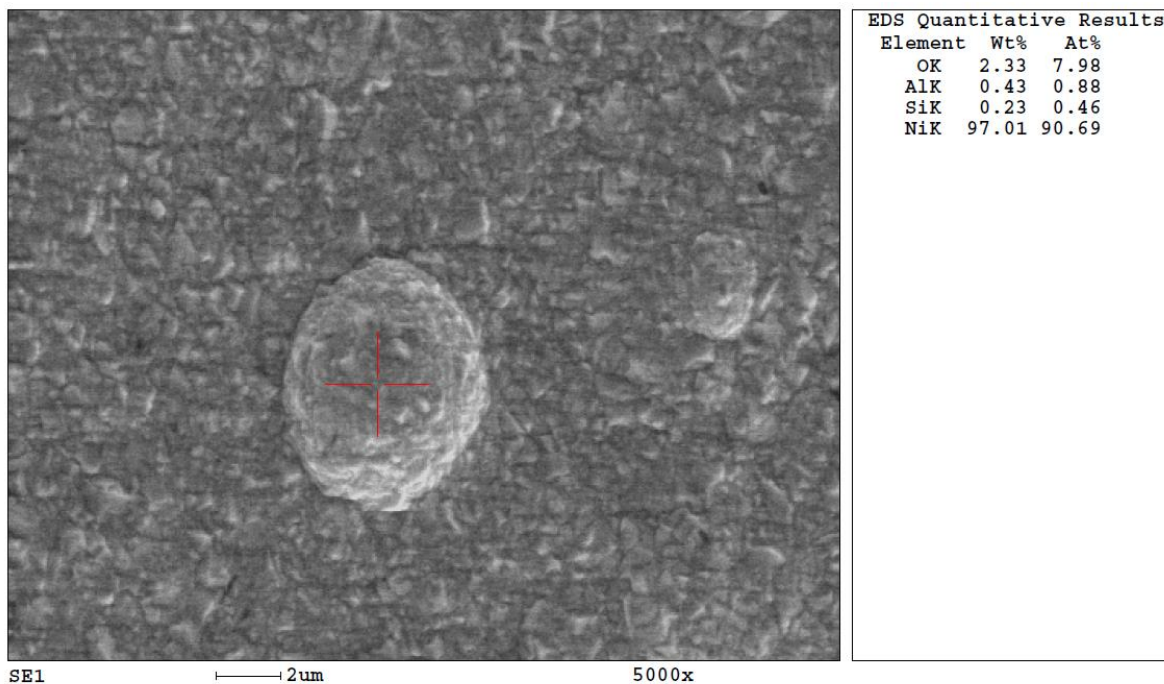


Fig. 5. Punctual EDS analysis on the dispersed phase particle

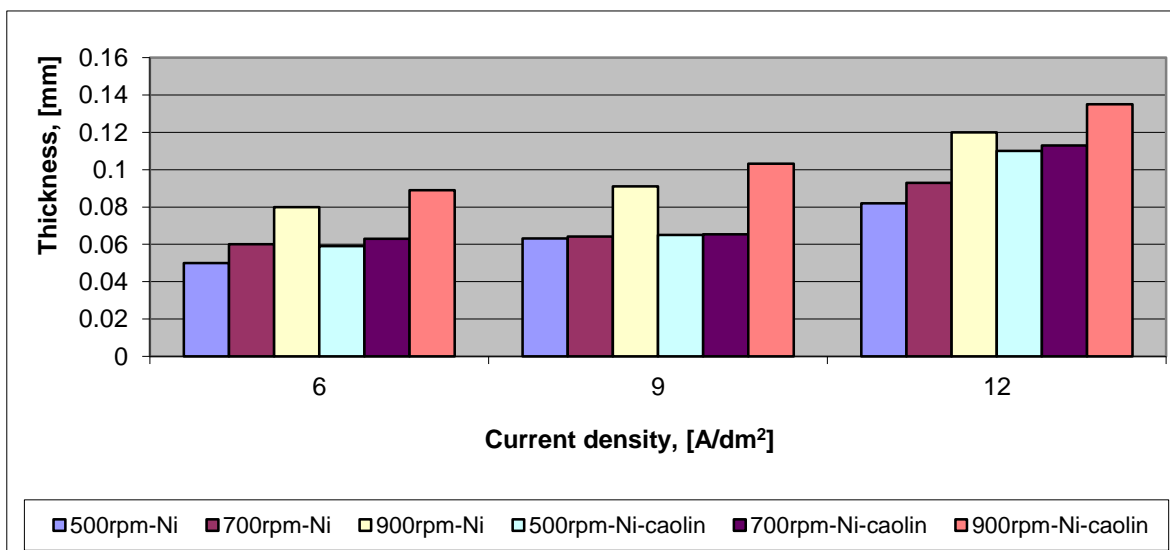


Fig. 6. The influence of current density and stirring velocity on the layer thickness of pure nickel coatings and on electrochemical composite coatings in nickel matrix using kaolin particles as dispersed phase

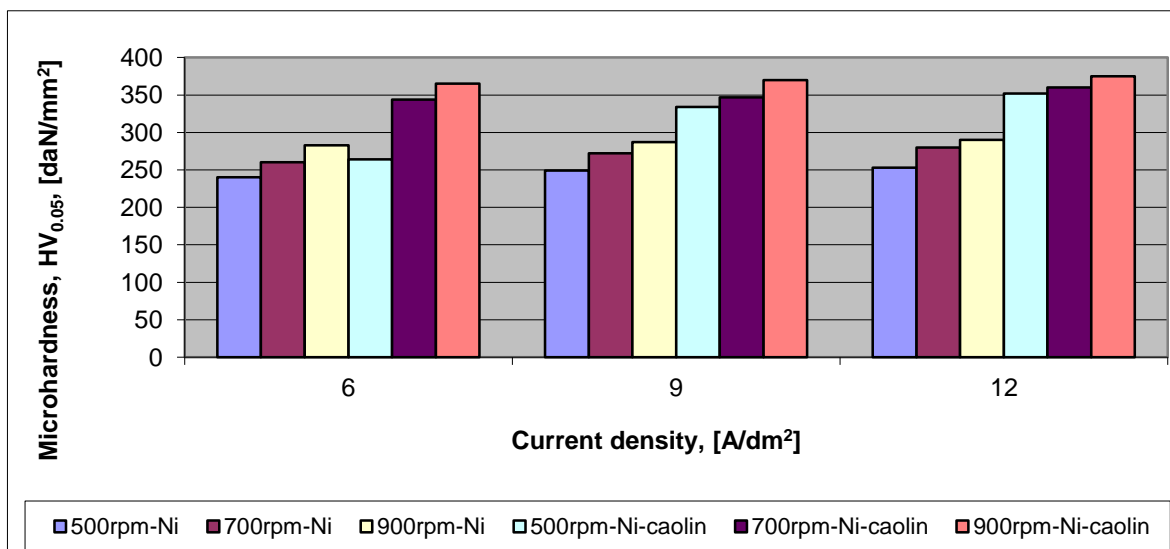


Fig. 7. The influence of current density and stirring velocity on the microdurity of pure nickel coatings and on electrochemical composite coatings in nickel matrix using kaolin particles as dispersed phase

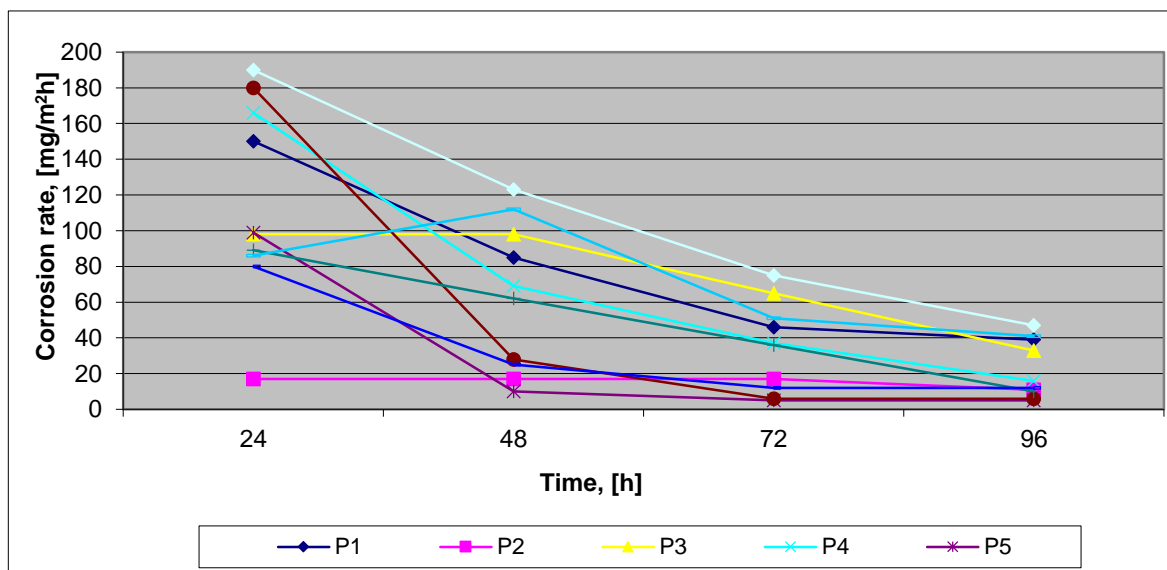


Fig. 8. Corrosion behaviour of electrochemical composite coatings in nickel matrix using kaolin particles as dispersed phase

❖ the electrochemical composite coatings in nickel matrix using dispersed kaolin particles exhibit higher microhardness compared to pure nickel coatings; thus the microdurty increases from 104.4 daN/mm² for copper support at 240 - 290 daN/mm² for pure nickel coatings, to 264 - 375 daN/mm² for ACE Ni - kaolin coatings obtained at different current densities and stirring velocities, temperature and deposition time being maintained constant; this increase is due, on the one hand, to the increase in the stresses in the layer with the current density, and on the other hand to the good incorporation of the disperse phase particles in the deposited layer and its hardening;

❖ salt mist corrosion behaviour of electrochemical ACE Ni - kaolin was superior to pure nickel layers, due to the passivation during the test.

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