

EXPERIMENTAL INVESTIGATION OF THE CORROSION RESISTANCE OF Ni-Al₂O₃ COMPOSITE COATINGS OBTAINED BY ELECTRODEPOSITION

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This article aims to prepare Ni-Al₂O₃ composite coatings from a conventional electroplating process. The coatings development parameters taken into account for this study of the corrosion resistance of these coatings are: Al₂O₃ concentration, bath temperature and current. The experimental tests are carried out by two lost mass and polarization techniques. The objective of the work is to determine the influence of elaboration parameters on the corrosion resistance of Ni-Al₂O₃ composite coatings. The study carried out in this article has shown that the corrosion rate decreases with the increase of the production parameters.

Keywords: Composite coatings, Ni-Al₂O₃, processing parameters.

1. Introduction

Metal matrix composite coatings are a very attractive and rapidly developing coating group that is of great interest in both research and industrial applications [1]. Over the past 20 years, interest in metal matrix composite coatings has been revived due to two main factors: (a) the need for new hard and wear resistant coatings to replace hard chrome coatings and (b) the development of new nano-technological methods for the production of carbide or oxide nanoparticles, the incorporation of which into metal matrices could bring completely different properties to composite coatings [2]. Nickel is usually used as a matrix to obtain electrochemical composite coatings. A nickel matrix is characterized by high corrosion resistance in weakly acidic and alkaline environments, including air, as well as considerable micro-hardness and good tribological properties [2]. The increase of the corrosion resistance of a nickel coating can be obtained by the incorporation of particles such as Cr₂O₃, SiC, Al₂O₃, CeO₂ and ZrO₂.

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Among the most studied composite coatings, there are composite coatings Ni-Al₂O₃. In general, nickel matrix coatings have been widely studied because of the high wear and corrosion resistance of nickel, which can be further enhanced by the introduction of hard particles [2-7].

The electroplating leads to a code position of particles in the nickel matrix. This technique has been widely used to produce composite coatings because of their simplicity and low cost. The properties of composite coatings are strictly related to electroplating parameters that directly affect the incorporation of particles into the metal matrix, which generally results in significant grain refinement and thus increased corrosion resistance.

It is proposed in this paper to use an experimental approach to study the effect of processing parameters on the corrosion resistance of Ni-Al₂O₃ coatings.

2. Experimental procedures

The bath used for electro-deposition of nickel-alumina composite coatings was a chlorinated nickel bath with the addition of alumina powder. The composition of the solution is given in Table 1. Different concentrations of alumina were used in the experiments to study its effect on the corrosion resistance of the coatings. The substrates used in this study have undergone various prior treatments to remove dirt and contaminants. Each bath was stirred using a magnetic stirrer for 2 hours before electroplating and also during electroplating with a rotational speed of 200 rpm. The preparation of the surfaces of E335 steel specimens was carried out through two stages:

Polishing: The specimens fixed in the mandrel of a parallel lathe are polished with abrasive paper of different particle sizes: 180, 400, 600 and 1000.

Degreasing: The test pieces were degreased ultrasonically in an acetone solution for 5 min, then rinsed in distilled water and then dried with hot air.

The rotational speed of the magnetic stirrer was constant (200rpm). Electro-deposition was performed in a 300 ml electrolytic cell with parallel electrodes. A DC power supply was used in the experiments for coatings deposition by DC currents.

Table 1

Composition of chlorinated nickel bath [8]

| components | NiCl ₂ +6H ₂ O | NH ₄ Cl | NaCl | H ₃ BO ₃ |
|-----------------|--------------------------------------|--------------------|-------|--------------------------------|
| Content [g / l] | 11.885 | 12.303 | 4.091 | 6.183 |

Different parameters were used in the tests to study their influence on the properties of composite coatings. A piece of steel E335 (surface 6.88 cm²) and two pieces of pure nickel (with a surface of 10 cm² for each piece) were used respectively as cathode and anode.

All electrodeposition tests were performed under the following conditions:

- Moderate agitation
- Bath pH equal 5.

The electroplating has been applied to 120 pieces, of which 60 are for the lost mass technique and 60 are for the polarization technique. The electroplating parameters (for a deposition time equal to 60 min) are given in Table 2.

Table 2

| Electroplating parameters of Ni / Al ₂ O ₃ coatings | | | | | | | |
|---|------------------|----|----|------------------------|----|----|----|
| Al ₂ O ₃ concentration (g/l) | Temperature (°C) | | | Current intensity (mA) | | | |
| 0 | 30 | 40 | 50 | 30 | 40 | 50 | 60 |
| 5 | 30 | 40 | 50 | 30 | 40 | 50 | 60 |
| 10 | 30 | 40 | 50 | 30 | 40 | 50 | 60 |
| 15 | 30 | 40 | 50 | 30 | 40 | 50 | 60 |
| 20 | 30 | 40 | 50 | 30 | 40 | 50 | 60 |

The lost mass technique (Fig. 1) was used to study the corrosion resistance of Ni-Al₂O₃ composite coatings as a function of the various electro-deposition parameters.

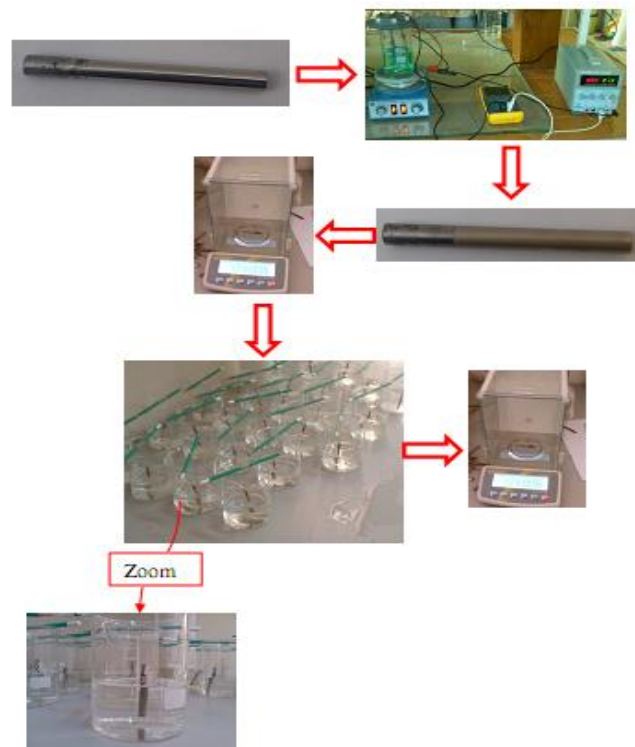


Fig. 1. Characterization of Ni / Al₂O₃ coatings by the lost mass method

This characterization technique consists of dipping each sample into a beaker, containing a solution of 3.5% sodium chloride, for a period of 15 days at room temperature. The specimens were weighed before immersion, the surface

not affected by the Immersion test is protected by a coating varnish that acts as an insulator. The test pieces were left exposed for two days in the open air so that the varnish dried properly. After 15 days of immersion, the specimens were removed from the beakers, cleaned with a nylon brush, to remove the corrosion products, then immersed in a beaker containing acetone and the whole is cleaned. Ultrasonically to remove the insulation varnish. Finally, the samples were rinsed with distilled water, dried and then weighed.

For the polarization technique (Fig. 2): the face of the samples, to be polarized, is left bare, while the rest has been covered with a layer of varnish. The test solution is 3.5% NaCl.

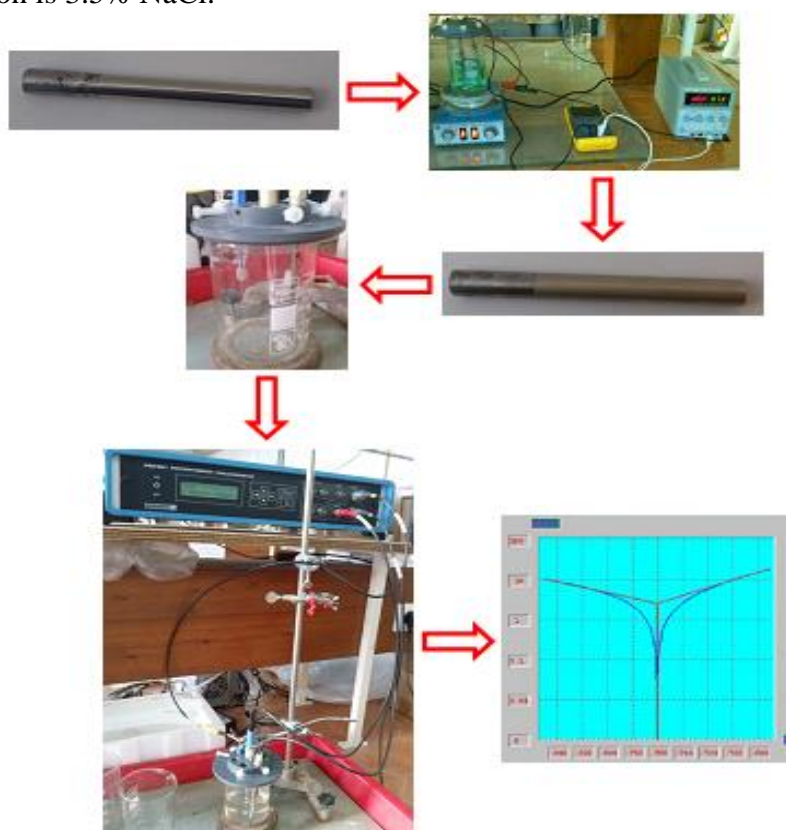


Fig. 2. Characterization of Ni / Al₂O₃ coatings by polarization method

For the determination of the polarization curve, using a potentiostat, **type PGP201 (manufactured by radiometer analytical SA France)**, different potentials are applied between the working electrode (ET) (sample to be studied) and the reference electrode (ER) (saturated calomel electrode).

Then, the stationary current which is established after a certain time in the electrical circuit between the working electrode and an auxiliary electrode (EA) (platinum electrode) is measured.

The potentiostat is connected to a computer, and using software (Votalab 21), the curves $I = f(E)$ (current versus potential) are plotted.

3. Results and discussion

Influence of Al₂O₃ concentration on corrosion rate of Ni-Al₂O₃ coatings

The influence of the Al₂O₃ concentration on the corrosion rate of the Ni-Al₂O₃ composite coatings is illustrated in Figs. (3-5).

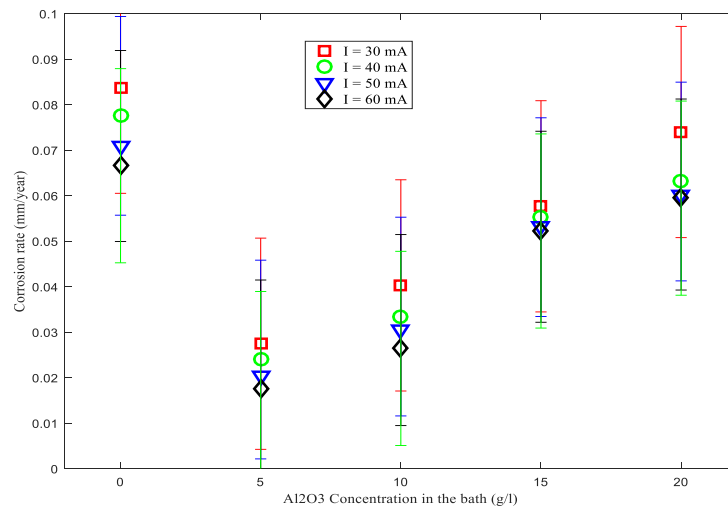


Fig. 3. Variation of corrosion rate as a function of Al₂O₃ concentration for T = 30 °C

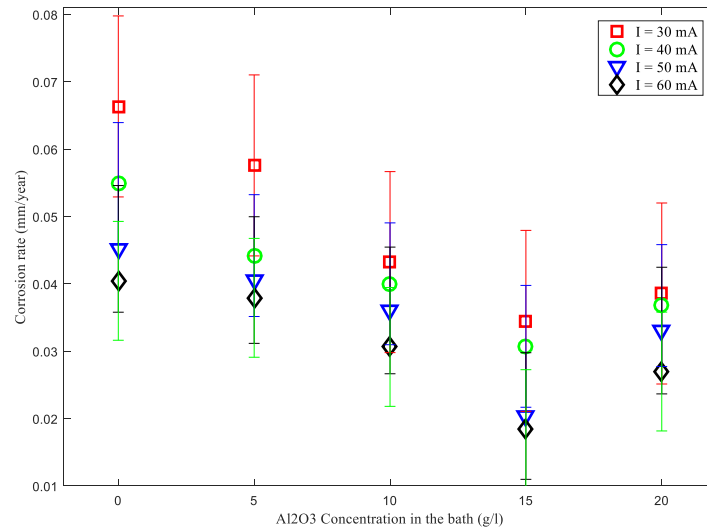


Fig. 4 Variation of corrosion rate as a function of Al₂O₃ concentration for T = 40 °C

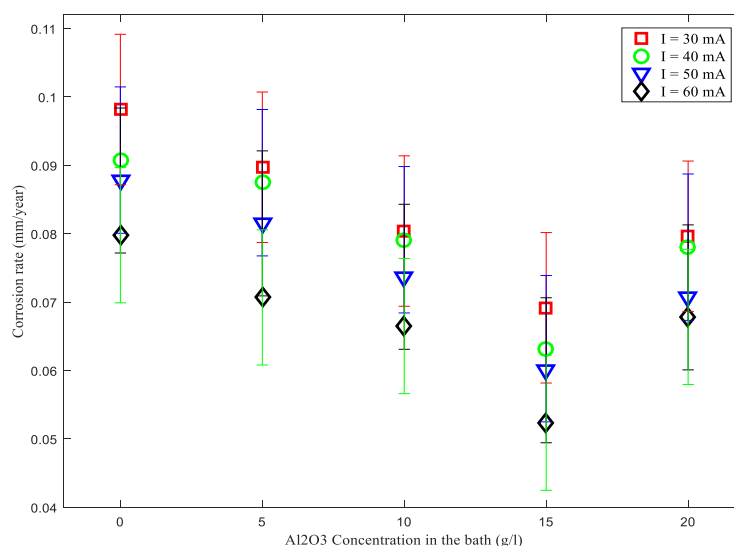


Fig. 5 Variation of corrosion rate as a function of Al_2O_3 concentration for $T = 50^\circ\text{C}$

The analysis of these corrosion rates allowed us to conclude that the increase of the concentration of Al_2O_3 in the bath causes a decrease in the corrosion rate of the composite coating up to a certain limit (5 g / l for a temperature of bath equals 30°C and 15 g / l for the temperatures of 40 and 50°C), which results in the increase of the incorporation rate of the Al_2O_3 particles in the Ni- Al_2O_3 composite deposit (adsorption of Al_2O_3 on the surface of the cathode, as suggested by Guglielmi's two step adsorption model) which causes a change in the metal / particle ratio in the coating. Garcia et al. [9] and Gül et al. [10] also showed similar results. However, the increase in Al_2O_3 concentration in the bath is not quantitatively comparable to the decrease in corrosion rate. For example, by increasing the concentration of Al_2O_3 in the bath from 5 to 15 g / l three times, the corrosion rate of the coating was halved.

The polarization tests were carried out on Ni coatings and Ni- Al_2O_3 composite coatings in a 3.5% NaCl solution. The polarization curves of Tafel are shown in Fig. 6 and the corresponding electrochemical parameters, extracted from the Tafel diagrams, are summarized in Table 3.

The results indicate that with the increase in the Al_2O_3 particle concentration, the corrosion potential values for the coatings are shifted towards the positive direction, showing a tendency towards a decrease in the corrosion current densities for the larger ones. Al_2O_3 concentrations ($C = 15$ g / l and $C = 20$ g / l). On the other hand, the corrosion current density decreased for the small Al_2O_3 concentrations ($C = 5$ g / l and $C = 10$ g / l).

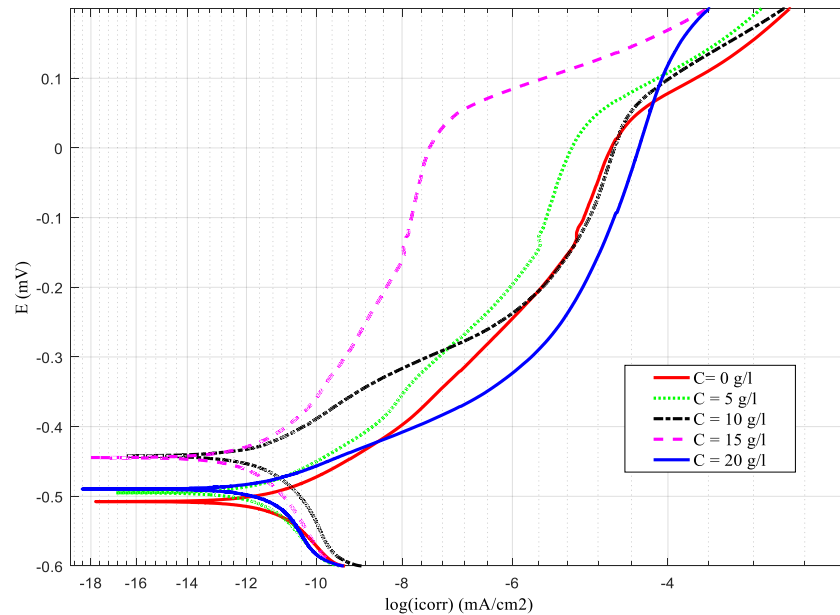


Fig. 6. Polarization curves of Ni-Al₂O₃ composite coatings deposited at different concentrations of Al₂O₃ in a solution of NaCl at 3.5% (bath temperature $T = 40\text{ }^{\circ}\text{C}$ and a current $I = 60\text{ mA}$)

However, an insufficient Al₂O₃ concentration in the electrolytic bath shows an increase in the corrosion current density and a decrease in corrosion resistance. This can be attributed to the change in the structure of the coatings as well as the porous structure of the coatings deposited at low concentrations of Al₂O₃ ($C = 5\text{ g/l}$ and $C = 10\text{ g/l}$). This means that the corrosion behavior of the Ni-Al₂O₃ composite coatings depends not only on the chemical composition, but also on the composition of the phases and the microstructure of the coating, as has been indicated in work of S. Ghaziof [11].

Thus, it is clear that increasing the Al₂O₃ content from 0 g/l to 10 g/l coatings leads to a displacement of the corrosion potential towards the positive direction.

Table 3

Electrochemical parameters obtained from Tafel curves for different concentrations

| Al ₂ O ₃ Concentration (g/l) | i_{corr} (mA/cm ²) | E_{corr} (mV)/ECS | Ba (mV) | Bc (mV) |
|--|---|----------------------------|---------|---------|
| 0 | 2.6475 | -507.8 | 81.8 | -133.2 |
| 5 | 1.7464 | -495.1 | 77.8 | -143.0 |
| 10 | 1.5625 | -422.1 | 85.5 | -150.4 |
| 15 | 1.0595 | -444.6 | 102.1 | -147.0 |
| 20 | 1.6619 | -489.8 | 54.8 | -183.9 |

Influence of current on corrosion rate of Ni-Al₂O₃ coatings

The influence of the current on the corrosion rate and the thickness of the Ni- Al₂O₃ composite coatings is illustrated in Figs. (7 to 11).

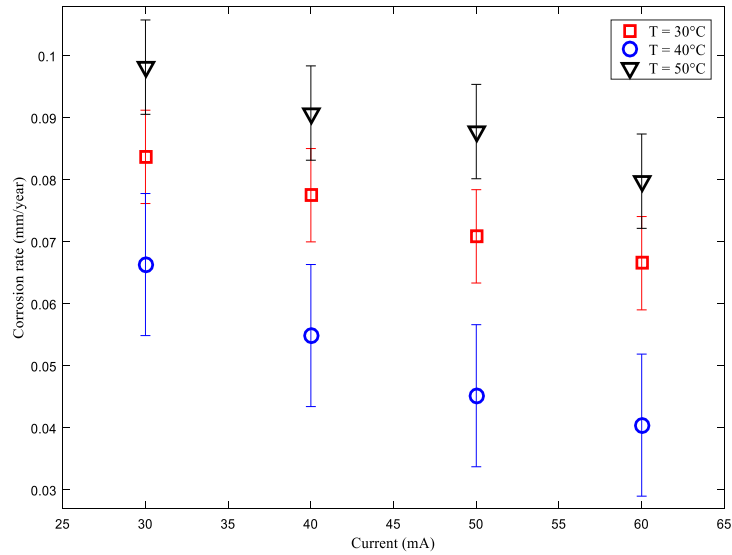


Fig. 7. Variation of corrosion rate as a function of current for $C = 0$ g / l of Al₂O₃

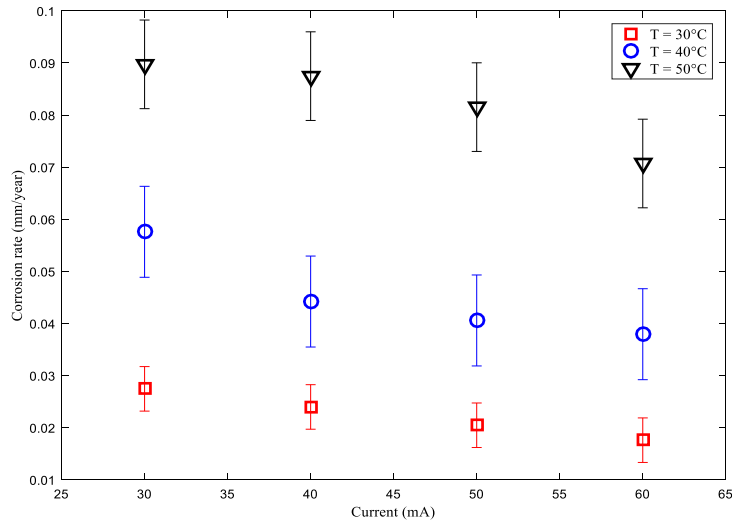
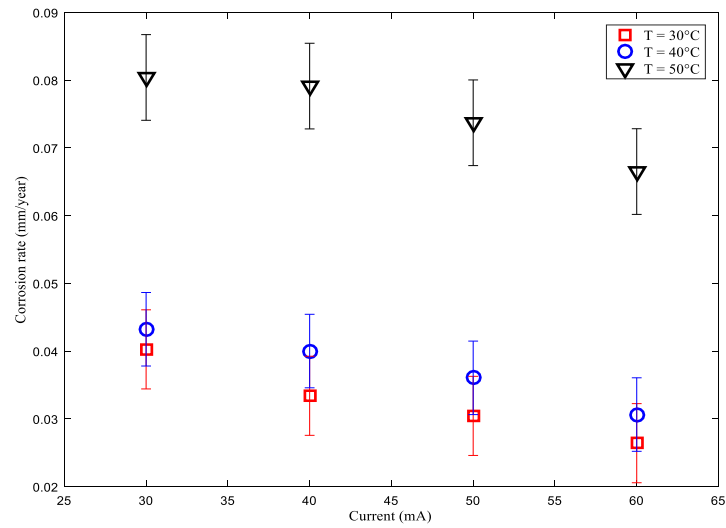
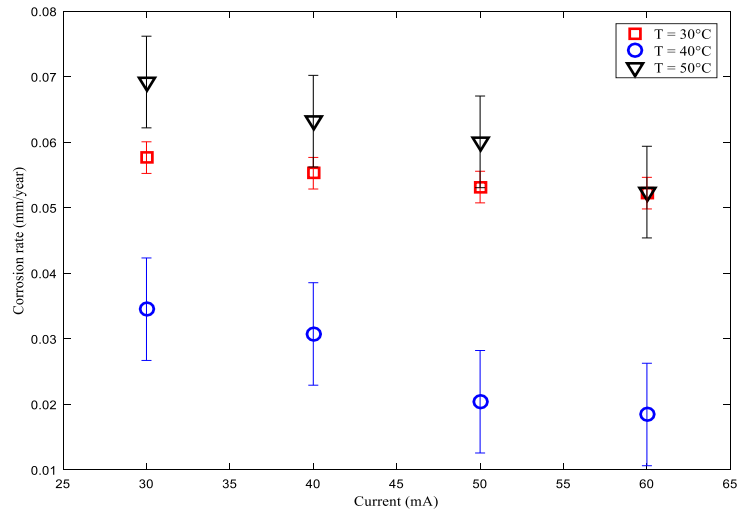


Fig. 8. Variation of corrosion rate as a function of current for $C = 5$ g / l of Al₂O₃


 Fig. 9. Variation of corrosion rate as a function of current for C = 10 g / l of Al₂O₃

 Fig. 10. Variation of corrosion rate as a function of current for C = 15 g / l of Al₂O₃

In order to determine the influence of the current on the corrosion rate of the resulting coatings, the Al₂O₃ concentration was maintained at 0 m / l, 5 m / l, 10 m / l, 15 m / l and 20 m / l. The analysis of the variation of corrosion rates allowed us to notice that the rate of corrosion is decreased by increasing the current, which results in the increase of the quantity of Al₂O₃ particles, incorporated in the nickel metal matrix. This increase is explained by the Al₂O₃ particle transfer rate which is faster than the nickel growth rate

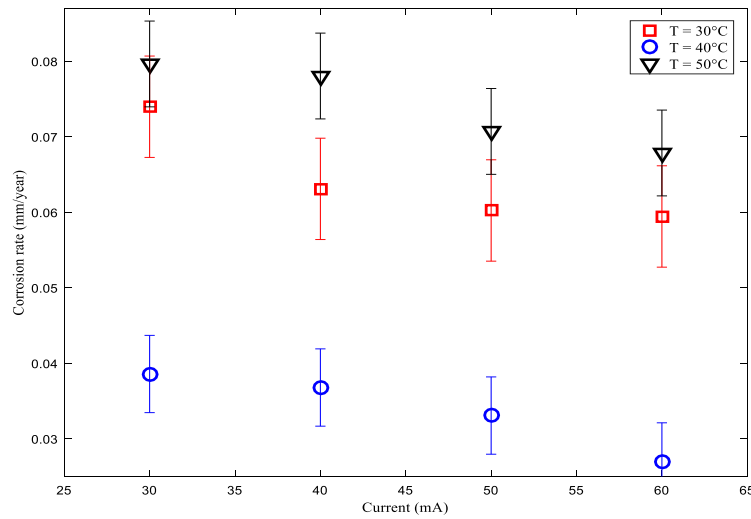


Fig. 11. Variation of corrosion rate as a function of current for $C = 20 \text{ g / l}$ of Al_2O_3

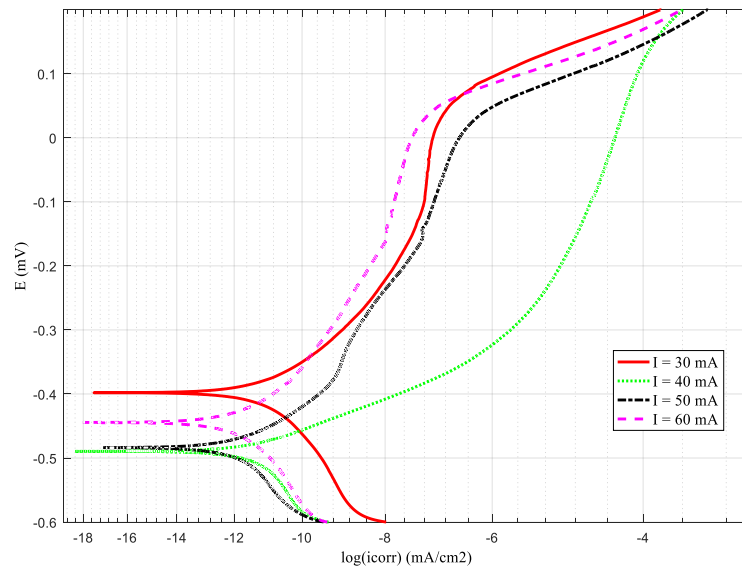


Fig. 12. Polarization curves of Ni- Al_2O_3 composite coatings deposited at different currents in a 3.5% NaCl solution (bath temperature $T = 40^\circ\text{C}$ and Al_2O_3 concentration, $C = 15 \text{ g / l}$)

The polarization curves of the composite coatings of Ni- Al_2O_3 on a steel substrate E335 are shown in Fig. 12. Table 4 shows the data deduced from the plot of linear Tafel curves. These polarization curves concern the Ni- Al_2O_3 composite coatings produced at different currents. It can be seen that all coatings, including composite coatings, exhibit similar cathodic behavior.

In accordance with the bias curves of Fig. 12, with the increase of the current from 30 mA to 40 mA, the values of the corrosion potential for the

coatings are shifted to the negative direction. On the other hand, the high increase of the current of 40 mA causes a displacement of the corrosion potential, for the coatings, towards the positive direction. As the anode potential increases, the current densities of the Ni-Al₂O₃ composite coatings developed at currents of 30 mA, 40 mA and 50 mA become slightly higher than those of the 60-mA matte coating, and such difference increases with increasing anodic potential. It is important to note that the degradation potential becomes higher for the developed coating at 60 mA than for other composite coatings.

Table 4

Electrochemical parameters deduced from Tafel curve plotting for different currents

| Current (mA) | i_{corr} (mA/cm ²) | E_{corr} (mV)/ECS | Ba (mV) | Bc (mV) |
|--------------|---|----------------------------|---------|---------|
| 30 | 2.3169 | -398.2 | 104.5 | -145.8 |
| 40 | 1.6619 | -489.9 | 54.8 | -183.9 |
| 50 | 1.2844 | -483.9 | 91.1 | -149.9 |
| 60 | 1.0595 | -444.6 | 102.1 | -147.0 |

Influence of bath temperature on corrosion rate of Ni- Al₂O₃ coatings

The influence of bath temperature on the corrosion rate of Ni- Al₂O₃ composite coatings is illustrated in Figs. (13 to 16).

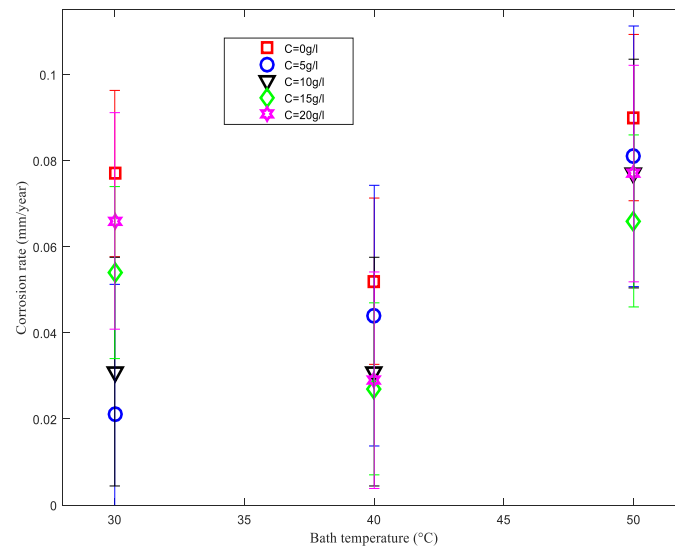


Fig. 13 Variation of corrosion rate as a function of temperature for I = 30 mA

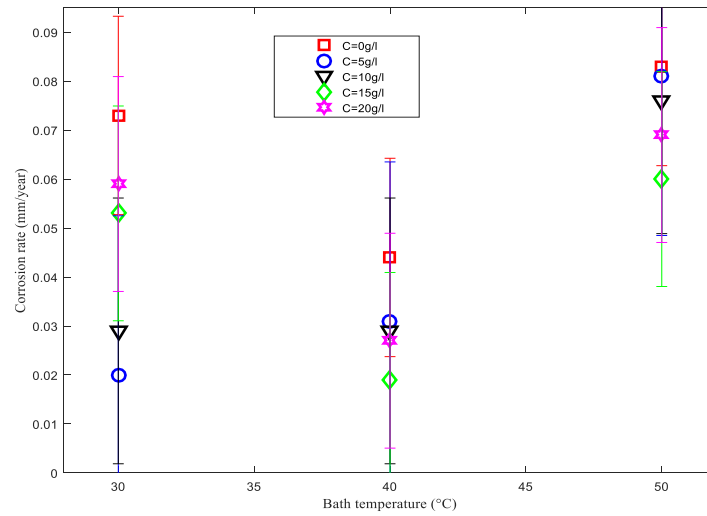


Fig. 14 Variation of corrosion rate as a function of temperature for $I = 40$ mA

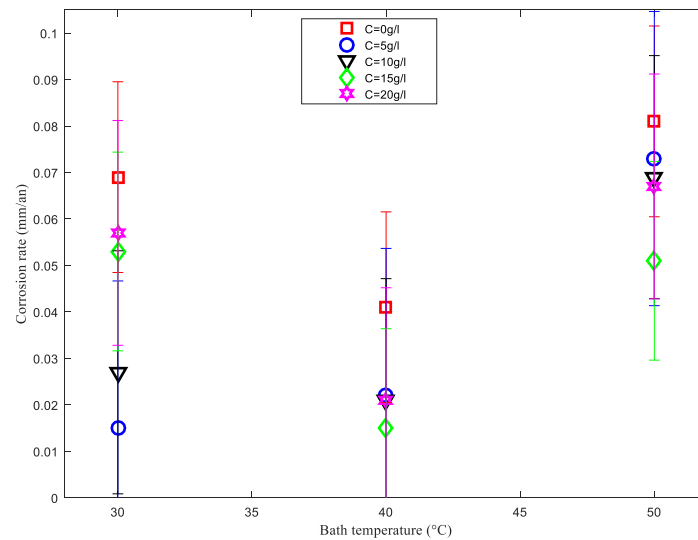


Fig. 15 Variation of corrosion rate as a function of temperature for $I = 50$ mA

The above Figs. showed that the corrosion rate decreases with the increase of the temperature of the electrodeposition bath up to 40°C . This behavior has been attributed to the increase of the activity of the particles with the temperature, which increases the percentage of co-deposited Al_2O_3 particles. However, at temperatures above 50°C , the overvoltage of the cathode decreases and therefore the adsorption of Al_2O_3 particles decreased the percentage of their incorporation into the nickel matrix.

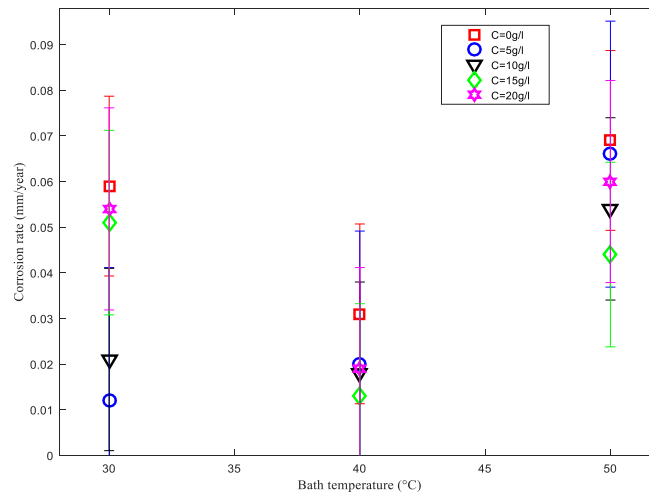


Fig. 16 Variation of corrosion rate as a function of temperature for $I = 60$ mA

The work of Vaezi et al. [4] and Ramesh Babu et al. [12] show an identical effect of the temperature on the properties of the Ni-SiC and TiCN composite coatings, respectively.

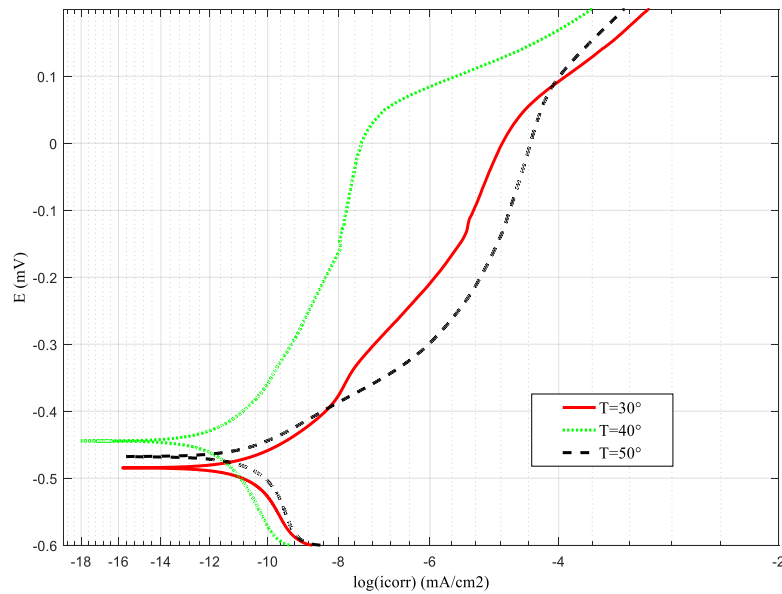


Fig. 17. Polarization Curves of Ni-Al₂O₃ Composite Coatings Dispensed at Different Temperatures in a 3.5% NaCl Solution ($i_{\text{current}} = 60$ mA and Al₂O₃ concentration, $C = 15$ g / l)

Fig. 17 shows polarization curves of Ni-Al₂O₃ composite coatings made at different bath temperatures (30 °C, 40 °C and 50 °C) and Table 5 shows the results obtained from the plotting of the Tafel curves.

The surface is protected by the sacrificial properties of the coating formed on it. The results show that the corrosion potential of coatings developed at high bath temperatures (40 °C and 50 °C) moves towards more positive potentials compared to the coating developed at 30 °C. These curves show a tendency to decrease the corrosion current densities as a function of the bath temperature increase from 30 °C to 40 °C.

In addition, by increasing the bath temperature up to 40 °C the corrosion current density has decreased. However, an increase in temperature above 40 °C caused an increase in the corrosion current density and consequently a decrease in the corrosion resistance of the composite coatings. Thus, an increase in temperature up to 40 °C results in a decrease in the corrosion current and therefore an improvement in the corrosion resistance of the composite coatings.

Table 5

Electrochemical parameters deduced from Tafel curve plotting for different temperatures

| Bath temperature (°C) | i_{corr} (mA/cm ²) | E_{corr} (mV)/ECS | Ba (mV) | Bc (mV) |
|-----------------------|---|----------------------------|---------|---------|
| 30 | 4.4213 | -484.4 | 92.9 | -190.4 |
| 40 | 1.0595 | -444.6 | 102.1 | -147.0 |
| 50 | 3.7797 | -468.1 | 73.1 | -209.2 |

4. Micrographic analysis

In the work of I. García-Lecina [9] et al., It was observed that the Ni surface exhibited a pyramidal structure formed by a relatively random distribution of dissimilar grains (Fig. 18 (a)).

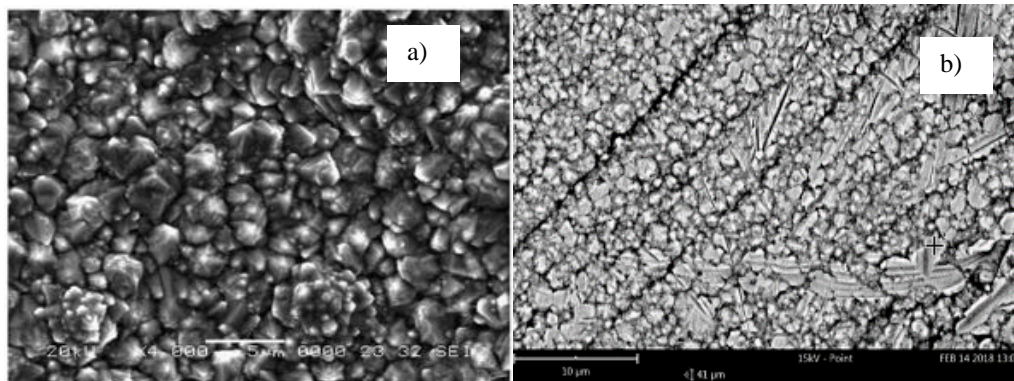


Fig. 18. Micrograph (by SEM) of the surface morphology of a: a) pure nickel coating; b) Ni-Al₂O₃ composite coating

When the Al₂O₃ particles were added to the electrolyte, the facet structure of the nickel grains was maintained, but a significant reduction in the size of the surface grains was observed (Fig. 18 (b)), which produces a greater refinement of the surface of the coating.

An analysis of the surface composition, associated with the micrograph, showed a presence of aluminum and oxygen (Fig. 19), demonstrating that the Al₂O₃ particles are incorporated into the nickel matrix.

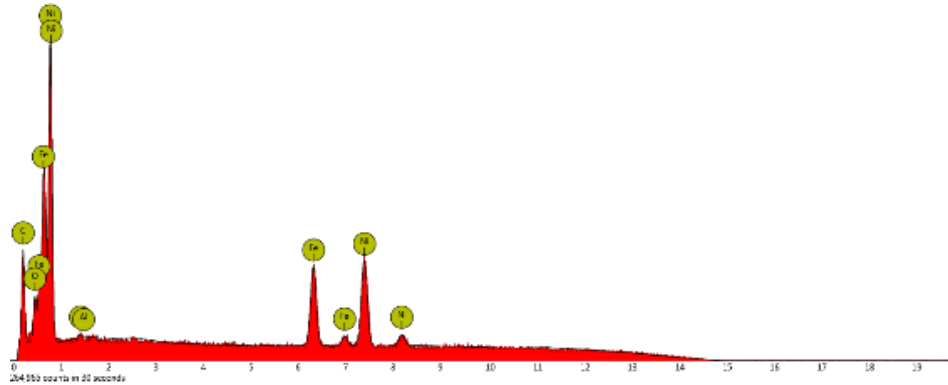


Fig. 19. Composition obtained during an analysis of a Ni-Al₂O₃ composite coating

Fig. 20 illustrates the micrograph obtained by SEM of a cross-section of a Ni-Al₂O₃ composite coating. The resulting coating had an approximate thickness of 10 μ m is almost free of pores, and there is no evidence of separation in the interface of the coating layer.

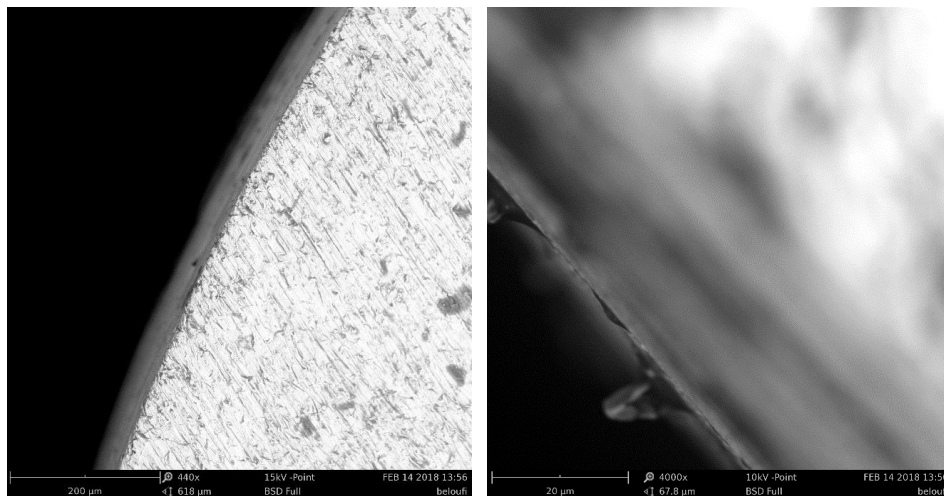


Fig. 20. SEM cross-sectional image of a Ni-Al₂O₃ composite coating

5. Conclusions

This study concluded that: aluminum oxide (Al₂O₃), a stable, hard and adherent compound, is a protective oxide which, added to chlorinated nickel-plating baths, tends to reduce the corrosion of the resulting deposits.

The Al₂O₃ content, the temperature of the electrolytic bath and the current constitute the main parameters which condition the qualities of the Ni-Al₂O₃

deposit. They are inseparable each from other. The effect of the electrical nature of the particles and bath composition on the anticorrosive characteristics of composite coatings should be studied. The Al_2O_3 content plays a critical role in the corrosion resistance, so that the corrosion rate of the coating decreases with increasing Al_2O_3 content. The increase in the concentration of Al_2O_3 in the bath is not quantitatively comparable to the decrease in the rate of corrosion. Increasing the current above 50 mA decreases the influence of the current on the corrosion rate and the degradation potential becomes higher for the coating developed at a current of 60 mA than for the other composite coatings. Increasing the bath temperature up to 40 °C the corrosion current density has decreased. However, an increase in temperature above 40 °C caused an increase in the corrosion current density and consequently a decrease in the corrosion resistance of the composite coatings.

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