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CHARACTERIZATION AND RESISTANCE TO CORROSION OF COATED PARTS MADE OF STEEL

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ABSTRACT

A characterization and resistance to corrosion study of parts made of steel, which are protected by nickel-alumina composite coatings, has been carried out. The influence of various experimental parameters has been considered. Various techniques of characterization have been used to study the coatings, namely the scanning electron microscopy, the atomic force microscopy and the X ray diffraction. Subsequently, the coatings have been submitted to a solution of NaCl in order to study their resistance to corrosion. For that purpose, the corrosion rates have been obtained using polarization tests. Thanks to this work, some interesting results have been obtained, such as the determination of the coatings morphology. The most appropriate electrical current densities to obtain more resistant coatings have also been determined. Concerning the influence of the electrolytic bath, it has been found that the chloride bath allows obtaining coatings with better resistance to corrosion, compared to those electrodeposited in the sulfate bath. The influence of the bath temperature has also been considered and it has been found that the deposit corrosion rates do depend on the bath temperature and its optimum value has been obtained. The coating hardnesses have also been obtained.

Keywords: composite, coating, electrodeposition, characterization, and corrosion.

INTRODUCTION

Anti-corrosion coatings are used to protect metallic parts and their structures from failure in a corrosive environment. Details on such coatings may be found in the review report that covers research work carried out till 2009 [1]. Among anti-corrosion coatings, electrodeposited composite coatings are used for surfaces that need to be protected against corrosion and wear. It is worth mentioning, however, that most of the research activities carried out on composite coatings have dealt with nickel deposits containing silicon carbide particles or carbon fibers, despite the fact that Ni-Al_2O_3 coatings are more resistant to wear, abrasion, and corrosion [2]. Indeed, Ni-Al_2O_3 composite coatings can be used to protect parts which are submitted to harsh thermo-mechanical solicitations. Therefore, they may be a good alternative to classical chrome based coatings [3].

Research works carried out recently on nano-materials, in particular on nano-composite coatings lead to more investigations on co-deposition conditions and to look for means to improve the properties of nickel based coatings by adding alumina particles having sizes less than 100 nm [4]. Nano-composite nickel-alumina coatings are mainly used to increase the abrasion resistance of micro-component metallic surfaces.

Nevertheless and despite the achieved results of researches carried out on such coatings, some issues concerning the uniformity of the alumina particles distribution in the nickel matrix still need to be resolved [5]. Indeed, it has been proven that the disturbance of the metallic matrix due to an inappropriate incorporation of these particles may induce internal constraints, cracks and pores which may increase the probability of corrosion peak appearance [6].

To address and try to resolve the above mentioned problems, some studies have been carried out. For example, in [7], nickel-alumina composite coatings have been electrodeposited in a Watts bath. To study their resistance to corrosion, the coatings have been submitted to a Na_2SO_4 solution. It has been found that the resistance of the composite coatings is higher than that for nickel coatings without adding alumina. Indeed, the corrosion kinetics of the later is three times faster than that of the composite coatings.

In [8], an experimental study has been carried out, in which, resistance to corrosion, to abrasion and to wear of electrodeposited composite coatings have been considered. They compared the behavior of nickel coatings to composite ones with added silicon carbide nano-particles having a 20 nm mean diameter. Electronic microscopy, micro-hardness and electro-chemical impedance spectroscopy have been used for that purpose. The most important result is that composite coatings have a better resistance to corrosion, abrasion and wear.

The influence of some electrodeposition parameters on the rate of deposition and hardness of nickel coatings have been considered by Kang *et al*. [9]. They studied the effect of the electrolytic bath temperature and the electric current density. They used X rays and electronic microscopy to characterize the deposits. As examples of results, it has been found that the maximum deposition rate is obtained for a temperature bath of 60 °C and this rate decreases beyond this value. As for the electric current density, the deposition rate increases with density. Concerning the hardness, it decreases with bath temperature and increases as a function of the electric current density.

In [10], nickel coatings electrodeposited on steel have been studied. In order to improve the coatings,

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saccharin has been added in the electrolytic bath. The saccharin has been added and its concentration varied in

Using X rays and electronic microscopy, a change of the preferred crystallographic orientations of the structure and grain sizes from 22 nm to 585 nm have been observed in [10]. Hardness tests and electrochemical measurements in a NaCl solution have showed that structures with a grain size distribution have better resistance to corrosion. Better adhesion to substrates and hardnesses, compared to coatings with a uniform grain size, have also been observed for coatings with grain size distribution.

In [11], in order to obtain the optimum electroplating conditions of nickel coatings, the authors considered the influence of parameters such as the bath temperature, the current density and saccharin concentration on the microstructures.

Hence, considering the studies reported early, one can conclude that detailed studies dealing with the optimization of the electrodeposition parameters of Ni-Al_2O_3 composite coatings, particularly without adding any surfactant, are lacking as well as the cause of changes in protecting properties of such coatings. Therefore, we believe that it is interesting to study the influence of various electrodeposition parameters (bath type, applied electric current density and bath temperature) on the coating properties. In addition, various complementary characterization techniques such as X ray diffraction (XRD) scanning electronic microscopy (SEM) and atomic force microscopy have been employed.

Experimental set up and procedure

In this section, the experimental set-up and procedure for the coating electrodeposition are briefly described. The coated parts are cylinders made of steel with 6 mm diameters and 60 mm lengths. The coatings were prepared by electrodeposition using Watt baths.

The experimental set-up is a classical electroplating apparatus which is composed of three parts, namely a direct current generator, an electrolytic cell of 300 ml volume which contains three electrodes, two of them are anodes made of nickel and the third one is the cathode, which is the cylinder made of steel, to be coated (Figure-1).

The operating conditions are imposed and monitored using a Ph meter, a thermometer, a heating magnetic stirrer, a multimeter and a chronometer. In this study commercially alumina particles (Sigma-Aldrich, Germany) having minimum purity of 99.5 % with a mean diameter ≤ 10 μm were added to the solution in order to obtain nickel-alumina composite coatings.

Some of the operating conditions have been taken as follows: pH = 4, the deposit time = 60 mn and a moderate agitation. It has been proven by other authors [11] that pH = 4 is the most appropriate value that allowed obtaining coatings without voids and cracks. As for the speed of the magnetic stirrer, it has been taken moderate (= 250 rpm) because such agitation has been found to be the optimum one in [12] who studied the influence of the order to obtain a structure with a grain size distribution instead of a structure with a uniform grain size.
stirrer rotation speed on the coating hardness. Concerning the deposit time, some tests have been undertaken by us and it has been found that 1 hour is the optimum time for electrodeposition. Each electrodeposition bath has been stirred for 1 hour prior the plating and during it. The alumina concentrations have been chosen as in [13] who studied the influence of the alumina concentration and obtained the optimal values (i.e. 15 g/l concentration of alumina in the chloride bath and 25 g/l content in the sulfate one) that allow getting coatings with the lowest corrosion rates.

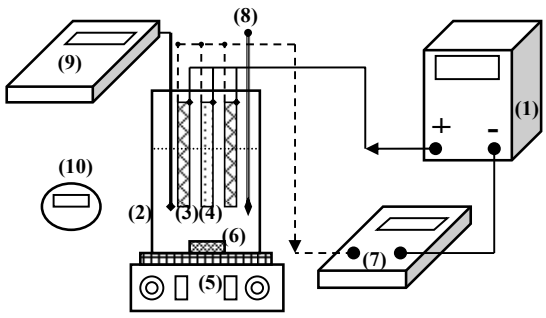

Figure-1. Schema of the electrodeposition experimental set-up. (1) direct current generator, (2) electrolytic cell, (3) anodes made of nickel, (4) cathode made of steel, (5) heating magnetic stirrer, (6) magnetic rod, (7) multimeter, (8) thermometer, (9) pH meter, (10) chronometer.

In order to obtain the most appropriate electrolytic bath temperature and electric current densities corresponding to coatings with the lowest corrosion rates, temperature of the bath has been varied from 313 to 343 K and the electric current density from 0.25 to 3.6 A/dm^2.

Characterization techniques

The various characterization techniques used to study the coatings are briefly described below.

XRD (X ray diffraction) tests

Characterization using X rays allows determining the structure of the coatings. The X ray apparatus used is a "Philips X'Pert MPD". Operating conditions are as follows: scanning region from 30.025 ° to 69.975 ° with a 0.05 ° step and a 5s/step counting. The split resolution has been taken equal to 1 mm. Using this technique, diffractograms displaying peaks are obtained from which the structure of the coating can be deduced.

Microscopy by SEM and AFM

The SEM technique is used to visualize and observe the quality of the coatings. Properties such as the compactness, the homogeneity, refinement and the distribution of alumina particles in the composite coatings are looked for. A JEOL JSM-6390 microscope has been

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used in this work. Two magnification rates have been considered (respectively 1000 and 2000) for that purpose.

Coating characterization has also been carried out by AFM with a "Veeco autoprobe Cp, Park scientific instruments" microscope.

Polarization tests

During these tests, the coated parts are submerged in a corrosive media in order to obtain their corrosion kinetics and rates. In this work a NaCl solution has been used with a 35 g/l concentration. A "Voltalab" polarization set-up has been used to obtain potentiastic polarization curves as well as corrosion rates using the "Voltamaster" software (Figure-2).

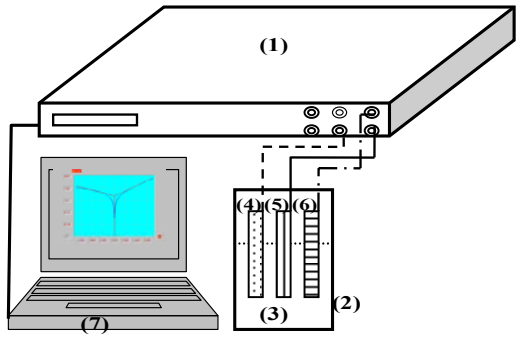

Figure-2. Polarization test experimental set-up. (1) potentiostat, (2) experimental cell, (3) NaCl solution, (4) coated part, (5) reference electrode (calomel), (6) auxiliary electrode (made of platine), (7) computer with "Voltamaster" software.

Micro-hardness tests

The coatings have also been characterized by measuring their hardnesses. Penetration tests have been used for that purpose. Conducted under very weak loads, micro-hardness tests allow much localized measurements (on about 100 μm^2). The hardnesses of the composite coatings have been measured using a "Shimadzu HMV-M" microhardness tester with Vickers indenter. A load of 50 g during 10 seconds has been used for the coatings thicker than 25 µm and a 25 g load for the coatings with thicknesses less than 25 µm. Four hardness measurements have been carried out for each deposit and an average value calculated. The averaged values are plotted versus the various experimental parameters.

RESULTS AND DISCUSSION

In this section the results obtained experimentally will be displayed and discussed. Various electrodeposition operating conditions have been varied such as the electric current density, the electrolytic bath (sulphate or chloride), bath temperature, and alumina particle addition. The goal is to obtain the optimum electrodeposition parameters that allow obtaining coatings with the best properties from the point of view of corrosion resistance.

Xray diffraction

X rays tests have been conducted. A typical XRD profile is displayed in Figure-3. It could be seen that the difractogram clearly shows three diffraction peaks at at about 44, 52 and 65 degrees, respectively.

Coating visualization using SEM and AFM

In the following, non intrusive characterization of coatings obtained in two baths (chloride and sulfate) with alumina is carried out. SEM technique is used for that purpose.

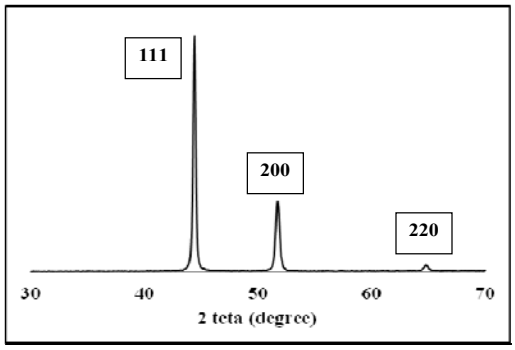

Figure-3. X rays diffractogram. Part coated in a chloride bath with alumina.

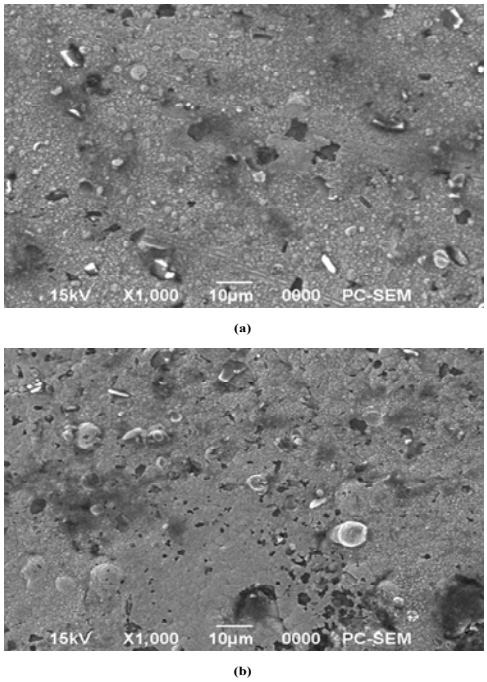

Figure-4. Coatings visualized by scanning electron microscopy. (a) chloride bath. (b) sulfate bath.

In Figure-4(a) the coating, corresponding to the chloride bath, visualized by SEM is displayed. It has been observed, as in [8], that the composite coating is compact and consequently better mechanical and anticorrosive

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properties can be obtained. Indeed, it can be noticed the fair homogeneity, compactness and alumina distribution which allows obtaining better coatings from the point of view of corrosion resistance. On the other hand, in Figure-4(b), a SEM image of a coating electroplated in a sulfate bath is displayed for comparison. It is obvious that the distribution of alumina particles is non uniform inducing an inhomogeneity of the coating. It has also been observed in Figure-4(b) that some of the alumina particles tend to form conglomerates, which are not covered by a layer of nickel because of their dielectric properties. Thus forming surface hollows which increases the roughness of the composite coating.

In order to characterize more deeply such composite coating and recognize its structure and morphology, the AFM technique has been used. For that purpose, various regions of the coating have been observed and it has been found that the surface aspect is homogeneous with a coating showing a morphology looking like "cabbage" (Figure-5). The coating roughness has also been measured. The mean roughness is of 403 nm and the standard deviation of 500 nm for a 50.50 μm^2 area.

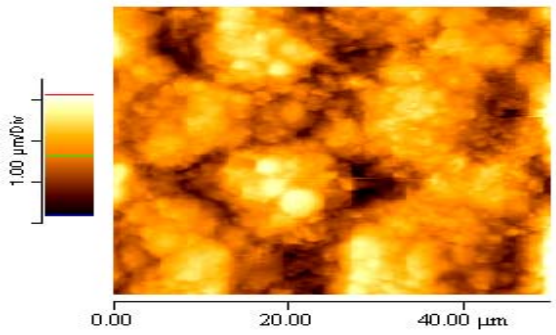

Figure-5. Coating visualized by atomic force microscopy (AFM).

Corrosion rates

In this section, results obtained by polarization tests are displayed. An example of a polarization curve, from which corrosion current and rate are deduced, is shown in Figure-6. As for the influence of the bath temperature on corrosion currents and rates, in Figure-7, it can be noticed that for T > 323 K, the corrosion currents do not depend on the bath type (sulfate or chloride) and temperature and reach the same value (around 90 $\mu A/cm^2$).

In Figure-8, corrosion rates obtained by polarization for the optimum bath temperature (T = 323 K), are plotted as functions of the electric current density for various experimental conditions (bath type, addition of alumina).

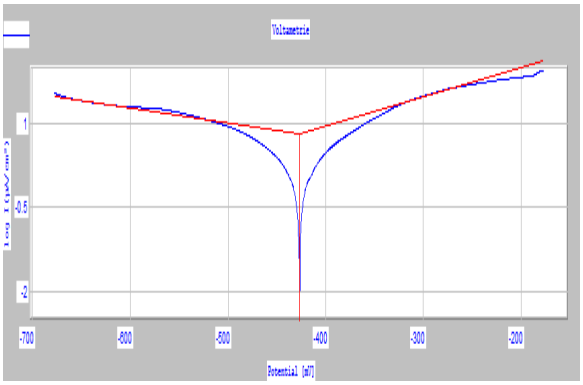

Figure-6. Example of a polarization curve.

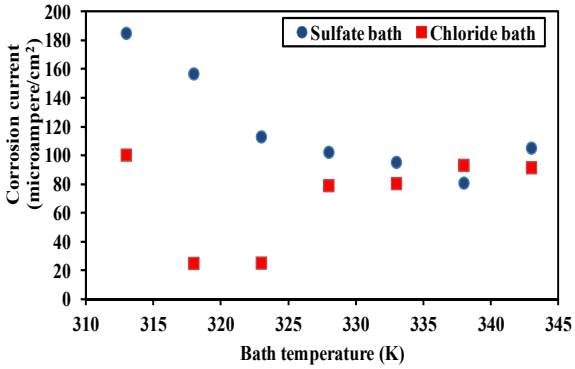

Figure-7. Coating corrosion current as a function of the bath temperature for two baths (sulfate or chloride) with alumina.

In Figure-8, it can be noticed that for the chloride bath without alumina, the corrosion rate generally increases with its minimum value obtained for the current density equal to 1.15 A/dm^2.

In Figure-8, the minimum corrosion rate in the chloride bath with alumina is obtained for an electric current density equal to = 0.25 A/dm^2 whereas the highest value of the corrosion rate is observed for 0.6 A/dm^2. The most appropriate current densities depend on the bath type (with or without alumina), such results have also been noticed in [14].

The addition of alumina particles contributes to the acceleration of the passivation of the nickel matrix. Subsequently, the corrosion resistance of the composite coatings is higher as also noticed in [15] who gave three physical mechanisms that describe how alumina particles allow improving the coating corrosion resistance.

In Figure-8, it can also be noticed that for the sulfate bath with alumina, all current densities allow obtaining low corrosion rates (from 0.001 to 0.021 mm/year). The best and worst current densities from the point of view of corrosion resistance are 1.8 A/dm^2 and 2.7 A/dm^2 respectively.

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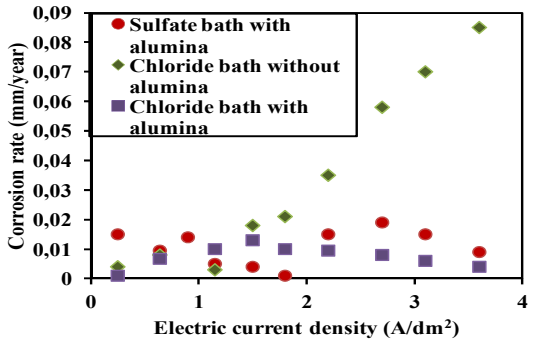

Figure-8. Coating corrosion rates (obtained by polarization) as functions of the electric current density. Two baths (sulfate or chloride) with or without alumina. Bath temperature T = 323 K.

By comparing the obtained results with those of other authors [13, 14], coatings more resistant to corrosion have been obtained in this work. Indeed, low corrosion rates have been reached by us (0.002-0.001 mm/year) while minimum corrosion rates in [13] (0.005 to 0.006 mm/year) and the corrosion rates obtained in [14] are relatively higher (0.645-0.705 mm/year).

Micro-hardness tests

Micro-hardness tests have been conducted using the apparatus and procedure described above. The obtained results for various experimental conditions are shown in Figure-9. The bath temperature is the optimum one obtained previously (T = 323K). It can be noticed, as observed in [9] for nanocrystalline nickel coatings, that for all experimental conditions, the coating hardness increases with the electric current density. The increase rates are larger for the chloride bath compared to the sulfate one. It is also worth noting that hardnesses of the coatings obtained in the sulfate bath with alumina seem to reach an asymptotic value around 300 Kg/mm^2 for current electric densities larger than 0.9 A/dm^2. Finally, it has been observed that the coatings obtained in the chloride bath have larger hardnesses than those in the sulfate one.

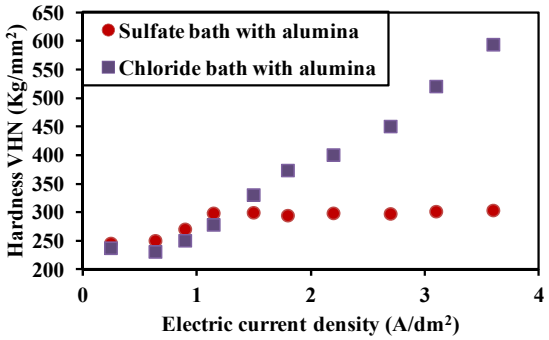

Figure-9. Coating hardnesses versus the electric current density. Two baths (sulfate or chloride). Bath temperature T = 323 K.

GENERAL CONCLUSION

In this paper an experimental study of nickel-alumina composite coatings has been carried out. For that purpose, the influence of various operating conditions has been considered.

With this study, some interesting results have been obtained such as:

- The determination of the structure and the morphology of the coating.
- The chloride bath with alumina allows obtaining better coatings from the point of view of corrosion resistance and hardness.
- The optimum values of the bath temperature and electric current densities have also been found for both baths (sulfate and chloride).

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