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COMPARATIVE STUDY OF THE MORPHOLOGICAL DEGRADATION IN NICKEL THIN FILMS EXPOSED TO H_2S MEDIA AND DEPOSITED BY MAGNETRON SPUTTERING AND ELECTROLYTIC PROCESS

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1. Introduction

Corrosion process in H_2S environment has been widely studied [1–3] due to the interest that petrochemical industry have shown to understand the mechanisms involved in corrosion processes The presence of sulphides compounds in pipelines and tanks that are used to store and transport oil and gas has resulted in economical losses to petrochemical industry because corrosion produces failures in pipelines and equipments due to wet cracking. Many works have been focused on the inhibition corrosion mechanisms in the presence of sulphide species, as well as on the development of protective coatings that guarantee the isolation of this aggressive media to the materials used as storage. Petrochemical industry has been used widespread the carbon steel on pressure vessels, pipelines and other equipments; nevertheless, this material and its welded joints are easily attacked by the sulphur atoms during corrosion events.

Metallic coatings can be used as a protective film in sulfurous media because their properties promote the resistance to oxidation [4, 5]. In the present work we study the properties of a passive nickel film deposited on a steel sheet by two different techniques. This nickel film can be used as a protective film for the metallic substrate because the interaction of the electrolytes will occur with the nickel oxide instead of the nickel metal or the steel. The deposition techniques used in this work were the magnetron sputtering and the electrolytic deposit. Magnetron sputtering [6, 7] has been reported in literature as a promising technique in the deposit of metallic thin films, even in large areas, acting as an anticorrosive barrier [8–10].

2. Experimental

Mild carbon steel AISI 1018 (UNS G 10180) sheets (2×2×0.1cm) were used during the study. Samples were exhaustively cleaned, degreased and washed with a commercial detergent. Afterwards they were ultrasonically cleaned using acetone during 10 minutes. In order to finish the cleaning process, these samples were dried.

Once the steel samples were cleaned, they were coated with nickel using two different techniques in order to obtain different deposit characteristics. The first technique was the electrolytic film deposit, where a typical Watt's bath [11] was employed. The electrolytic solution used during the film deposit was 1.07M $NiSO_4$, 0.15M $NiCl_2$ and 2.38M H_3BO_3; the process was galvanostatically carried out with a current density of 0.08 A/cm^2 and a pH = 4. The steel samples were immersed in the bath at 60°C for 90 s. The second technique carried out during the study was the magnetron sputtering technique using a 99.99% nickel circular target with a 500 mm diameter and a 6 mm thickness. 99.99% purity argon was used as the gas during the plasma process. The sputtering pressure, the potential and the time during the deposit were 34.6 Pa, 1000 V and 15 minutes, respectively. These values were kept constant during all the deposits.

Structural, morphological and topological studies of the samples surfaces were carried out using a scanning electron microscope Jeol 5600-LV. The SEM micrographs were obtained with backscattering electrons at 20 kV. Samples were observed without any special (metallic) recovering in order to study the surface characteristics of the as-deposited films, as well as the ones that were electrochemically attacked during the corrosion processes. Cross fractured sectional samples were also prepared to determine the films thickness from SEM observations.

For this study, the nickel oxide film NiO_2 [12, 13, 14, 15] was electrochemically obtained. The synthesis of nickel oxide thin films procedure was controlled by an ACM Gill AC potentiostat version 4.2.9 used in the polarization mode. An over potential around 1500 mV and a 15 min exposure in a solution of 28% wt NaOH at pH 12 (current density = 6.5 mV/min) was used. The Electrochemical Impedance Spectroscopy (EIS) technique was employed for the evaluation and characterization of the nickel thin films in order to identify imperfections in the films and to evaluate the protective properties when the metal is put in contact with the acid medium. The typical configuration of three electrodes was the following: platinum wires were used as reference together with auxiliary electrodes, while a coated sample was used as the working electrode. The electrochemical measurements were carried out in an aggressive acid media (saturated, pH=3): H_2O+H_2S. The impedance conditions used during this test were the following: maximum and minimum frequencies 10.000 Hz and 0.01 Hz, respectively; amplitude of 10 mV and the number of integration of 10 cycles.

3. Results and Discussion

3.1 SEM results

From SEM observations, it was found that film thickness was 1300 nm in average. The SEM micrographs show an irregular texture in the surface of the mild steel in all the samples. After applying the different nickel deposits and evaluating them by SEM, difference in texture and morphology has been detected. It was observed that samples made by the electrolytic deposition technique (figures 1,*b* and 1,*d*) show an increase in their surface roughness compared to those made by the sputtering technique (Fig. 1,*a* and 1,*c*). This behavior can be due to the way the samples were made. In the case of the sputtering deposition, the film is deposited in a regular way forming a homogenous film, contrary to the way it is formed when the electrolytic technique is used. The heterogeneity of the sample's surface made by electrolytic deposit is shown as roughness, porosity, unfilled zones and fractures. This heterogeneity was observed on the samples even before their exposure to the corrosive environment, what make us think that the nickel deposit made by the Watt's bath technique is a deficient deposit technique. Actually, nickel deposit coming from the acid bath produces internal stresses in the coating as is explain in references [16–18]. Samples with the nickel oxide layer also show non regular deposits (see figure 1,*d*) and imperfections in the surface that could result in localized corrosion.

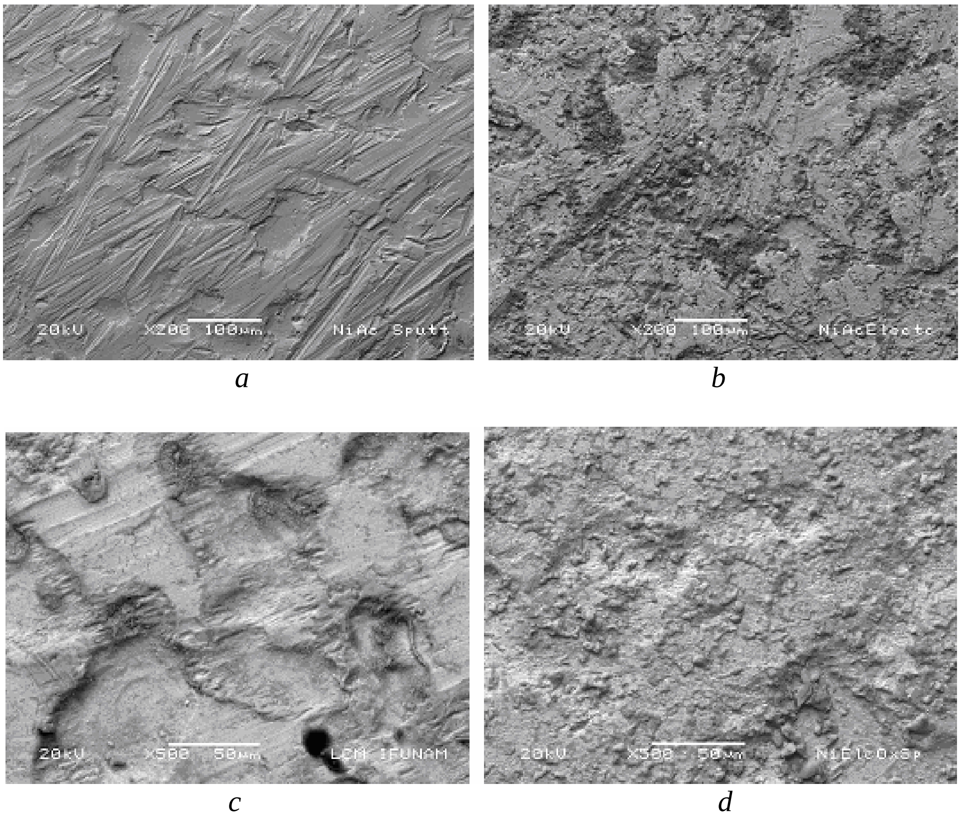


Fig. 1. SEM micrographs of: a) Steel-Nickel made by sputtering process, b) Steel-Nickel made by electrolytic process, c) Steel-Nickel made by sputtering with a nickel oxide film, d) Steel-Nickel made by electrolytic process with a nickel oxide film

On the other hand, the surface of Steel-Nickel coating made by sputtering is shown in figure 1,*a*. A more regular texture in almost all specimens made by this technique was obtained. The morphology of the coating shows that nickel has grown in the same way as the steel substrate without any pores or pollution.

After oxidation of these non homogenous films a localized damage can be observed. This oxidation is promoted by the defects produced during the electrolytic deposit as can be seen if figure 1,*d*, and not due to the NaOH electrolyte. This is a clear example that a poor application of a protective coating at a small depth in a material results in localized corrosion and damage, instead of getting a protective layer on the substrate.

Figure 1,*c* does not show the presence of localized corrosion for the sputtering deposit of nickel followed by the film oxidation. We think that the sputtering process is able to cover the "valleys and peaks" present in the steel surface. Even if this surface seems to be more heterogeneous than the electrolytic nickel one, no defects were observed in the coating.

3.2 Electrochemical Impedance Spectroscopy (EIS)

Nyquist and Bode diagrams present the spectra of corrosion process evaluating the different coatings. A noisy signal as well as some disperse points complicated the explanation of the behavior of Nyquist diagrams. In the same way, Bode diagrams show different time mechanism for all the deposits and techniques, which didn't allow making any kind of analysis for the results, even using a Faraday's cell. We continue working on Bode diagram in order to get a better understanding of our results. To explain three different steps during the electrochemical process, Bode values that correspond to three zones with different frequencies (10^0, 10^1, 10^2 Hz) were chosen Figure 2 shows the impedance spectroscopy results in presence of H_2O+H_2S (sat) that correspond to the mild steel, the sputtering and the electrolytic techniques, as well as their respective oxides. The aim of this test was to compare both deposit techniques.

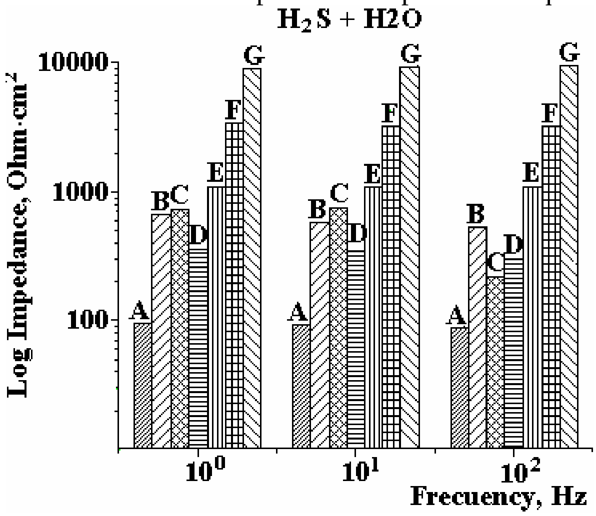


Fig. 2. Behavior of different materials exposed to H2O+H2S electrolyte for frequencies of 10^0, 10^1 and 10^2 Hz with the Bode values, for the following coatings materials: (A) mild steel, (B) Ni bulk, (C) Ni bulk oxide, (D) steel Ni electrolytic, (E) steel Ni electrolytic oxide, (F) steel Ni sputtering, (G) steel Ni sputtering oxide

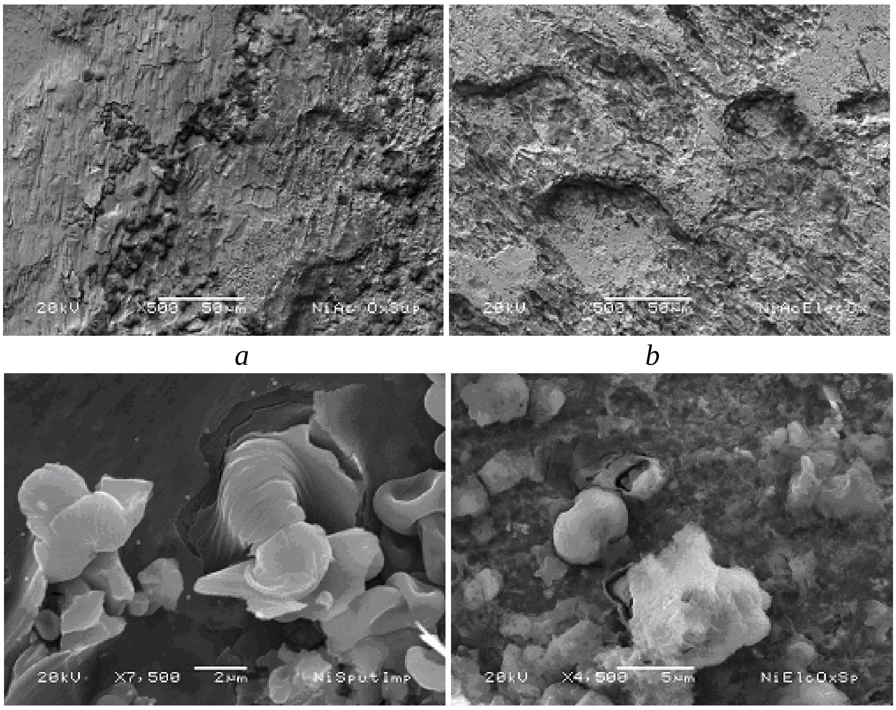
As can be seen in figure 2 the impedance's value of mild steel exposed to this media is the lower value obtained for all the frequencies used in this work. It means that mild steel behaves as the most corrosive material even though it is compared with the films made by the electrolyte deposit. The corrosion rate can be measured by an indirect way using the impedance values and the Stern and Geary equation. The impedance values indicate an inverse relation with Rp.

The results show that nickel bulk and his oxide layer present a better behavior than mild steel for any frequency. This fact demonstrates that nickel is a good option to be used as an inhibitor barrier for this media. The nickel thin film coating in any configuration presents better impedance values than the one obtained by the naked steel. It was also seen that nickel and nickel oxide deposited by the electrolytic technique show better properties than the mild steel and even than the nickel bulk for all the frequencies studied in this work. The electrolytic depositions showed total protection for this medium.

Nickel and the nickel oxide deposited by sputtering show the higher impedance value compared with other deposits. From another point of view, the corrosion rate is lower in the presence of the steel nickel sputtering oxide when compared to mild steel. These values are those who have the higher anticorrosive properties for this media.

When performing the impedance characterization to the Nickel/Nickel oxide (NiO_2) it shows that its anticorrosive protection is much better than the protective coating formed on other samples. In the presence of saturated water with sulfhidric acid, the nickel oxide can act as a protective film that presents the properties of being highly adherent and stable.

Differences between the nickel film textures made by the sputtering process and the electrolytic deposit are shown in figures 3,*a* and 3,*b*, respectively. The coating which presents the worst deterioration in the surface is the electrolytic nickel oxide. However, this was observed before the pre-oxidation process and also after the coating was exposed to the sulphur media.



a *b*

c *d*

Fig. 3. SEM micrographs of nickel corrosion products in the thin film deposits after Impedance technique with H_2O+H_2S (Sat) electrolyte. a, c) Steel- Nickel Sputtering Oxide, b, d) Steel- Nickel electrolytic Oxide

The coatings, after the electrochemical test, present surface corrosion attack. The coating in both cases has been deteriorated, but in the case of the electrochemical coating the destruction of the film was more aggressive than the one presented when it was done by the sputtering coating.

The behavior observed during the impedance test can be related with the SEM micrographs. The best impedance values got from the nickel coatings were obtained by the sputtering technique. In figure 3,*c*, the film brake down in located corrosion type. This micrograph shows that the film is not destroyed completely, but the corrosion product grew from inside the metal to its surface. A devastation of the surface sample in the case of the electrolytic process in shown in figure 3,*d*, where steel nude zones are exhibited and no presence of the nickel film is observed. The best anti-corrosive properties are presented in the case of the steel-nickel sputtering oxide thin film. The presence of the oxide in the film created a dramatic modification of the surface film, which promoted a passive barrier. This effect inhibited the interaction of electrons between the metallic interphase and the electrolyte reducing the corrosion rate.

The corrosion behavior of the coated steel is strongly influenced by the deposit technique. It not only depends on the electrochemical properties of the coating, but also on the surface defects (such as roughness, deposited droplets, porosity, cracks and scratches) present in the coating. This result can be observed in the micrographs showed in this work.

4. Conclusions

The nickel coatings made by sputtering present homogeneity in the entire surface, contrary to the results obtained by the electrolytic deposit, which can be corroborated by the impedance results. Electrochemical characterization shows that work must be done in the electrolytic deposit process in order to form a thicker coating that can be able to protect the steel from the corrosive acid media. We obtained that nickel oxide sputtering thin film supports the corrosive media much better than the other coating techniques do. The EIS technique seems to be suitable to evaluate the optimal thickness in the metallic thin film.

Acknowledgements

The authors wish to thanks to J. Genescá, C. Ojeda, G. Rayo, J. Morales, H. Manjarrez, J. Martínez, N. González, C. Ramirez, C. Rodriguez, M. Aguilar and I. Puente, as well as the Laboratorio Central de Microscopía IFUNAM for the performance in this work.

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Received 07.12.09

Summary

Nickel thin films with regular configuration and similar thickness were deposited on steel AISI 1018 (UNSG 10180) by two different techniques: magnetron sputtering and electrolytic process. The main aim of this work is to compare the surfaces deposited films made by the two techniques using the scanning electronic microscopy and to identify their morphological differences and imperfections. We evaluate the protective coatings properties when the films are in contact with an acid medium. We also study the thin films coatings by the spectroscopy impedance technique. We obtain that the sputtering deposits present a homogeneous thin film coating that is better than the one obtained by the electrolytic technique. It is expected that the thin film coatings made in this work can protect the steel against corrosion when it is in contact with an acid environment.