



Democratic and Popular Republic of Algeria

Ministry of higher Education and Research

University Mohamed Boudiaf of M'Sila



Faculty of Sciences

Department of chemistry

Master Memory

Specialty: Chemical of Materials

Students:

Souad Talhi and Soumeya Souyeh

THEME

**Corrosion behavior of Steel coated with sprayed
ZnO, ZnS, CZTS and SnO₂ in NaCl solution**

2020-2021

Members of the Jury:

President: Dr. Mahmoud Lebid

University of M'sila

Supervisor: Pr. Yazid Bouznit

University of M'sila

Examiner: Pr . Nadjia Latelli

University of M'sila



Acknowledgements

First of all, we would like to express our deepest sense of gratitude to our memory advisor, Pr. Yazid Bouznit, for his strong scientific supervision and guidance on our work during all these three months, for his precise and valuable comments on the manuscript.

We would like to express our sincere regards to the jury members, Dr. Lebid Mahmoud and Pr. Nadjia Latelli for devoting their precious time to the review of our manuscript and for their scientific evaluation.

We must acknowledge Ahmed Saoudi for his collaboration in this work, his initial instructions for the preparation of the coating, and her instructions on spray deposition technique.

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General introduction



General introduction

General introduction

The economy of both developed and developing countries is badly affected by the damages caused by corrosion, which leads to the loss of around 3.4% of the world GDP [1]. The majority of this cost is allocated to the examination of corroded parts of the structures, the repair of the structures using various methods including protective coatings (paints, surface treatments, etc.) [2].

There are different techniques for preventing the corrosion of iron metal, especially in presence of aggressive ions like chloride, and various corrosion protection methods have been explored, including coating techniques (provide a barrier between the metal surface and the corrosive environment) such as Chemical Vapor Deposition (CVD) [3], plasma deposition [4], electrodeposition [5], use of inhibitors [6], self-assembled monolayers [7] and spray pyrolysis [8].

The choice of deposition method has a significant impact on the physical and chemical properties of the synthesized coatings. Among these techniques, spray pyrolysis is recognised as an important and facile technology for the production of powdered materials and thin films owing to its simplicity, cost effectiveness, and potential for large-scale industrial production.

In the present work, different coatings were deposited on steel disks at 350°C by spray technique. Corrosion protection was investigated in NaCl (2wt%) aqueous solution by combining Linear Polarization and Electrochemical Impedance Spectroscopy (EIS).

After providing a brief basics on the corrosion and its protection strategy in chapter one, and presenting the applied experimental techniques and conditions in second chapter, the study of the corrosion protection efficiency of the coating is covered in third chapter.

Chapter 1



Chapter 1 « Generalities »

1. Corrosion basics

1.1. Background

Corrosion is a process through which metals in manufactured states return to their natural oxidation states (see figure below). This process is a reduction-oxidation reaction in which the metal is being oxidized by its surroundings, often the oxygen in air. This reaction is both spontaneous and electrochemically favored [9]. The importance of corrosion studies is threefold includes economic losses, improved safety and conservation. Corrosion control of metals is of technical, economical, environmental and aesthetical importance [10].



Fig. 1 Corroded old iron piece

1.2. Forms of corrosion

Corrosion damage can occur in many ways, for example, in failure by cracking, loss of strength, etc. Forms of corrosion are uniform attack, galvanic corrosion, selective leaching, erosion corrosion, stress corrosion, crevice corrosion, pitting and inter-granular corrosion like summarized in the figure below [11].

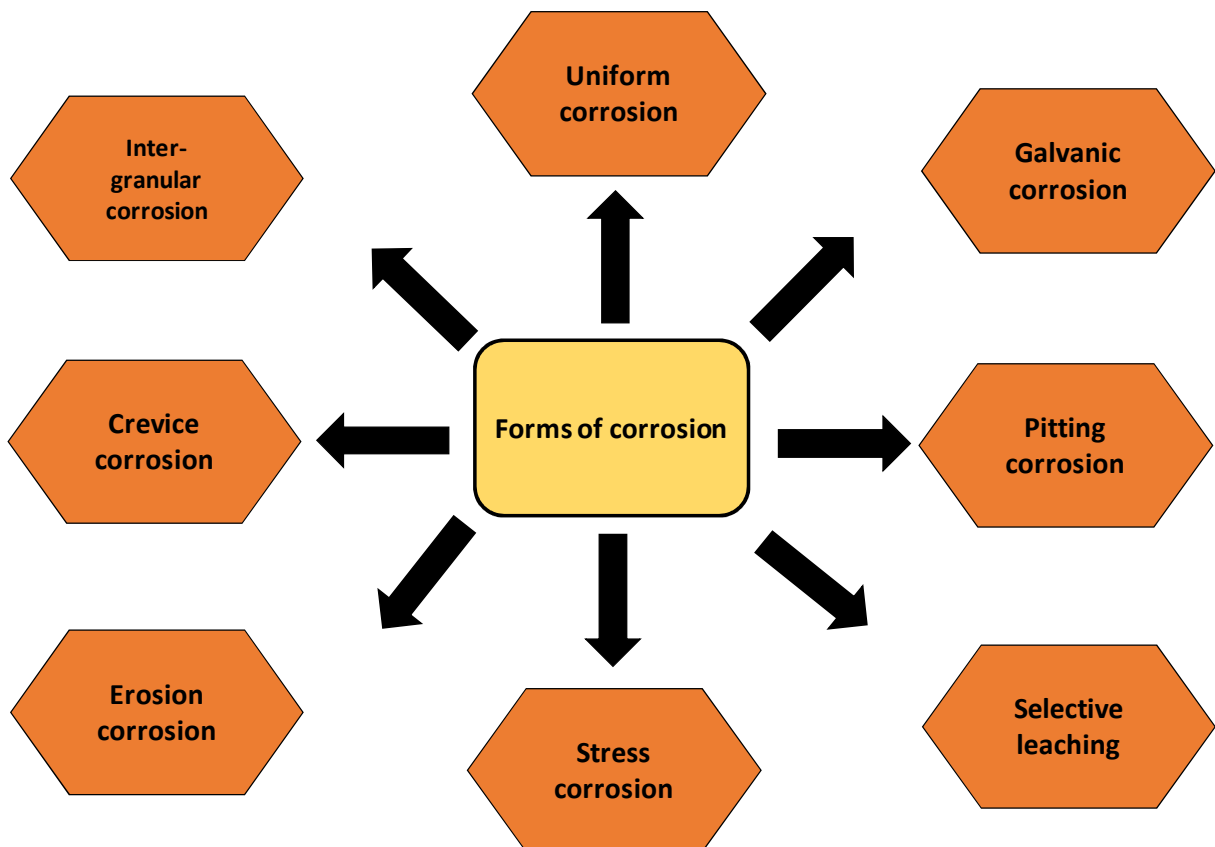


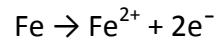
Fig. 2 Forms of corrosion

1.3. Iron and Steel

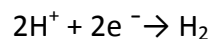
Steel is an alloy that consists mostly of iron and has a carbon content between 0.2% and 2.1% by weight, depending on the grade. Carbon is the most common alloying material for iron, but various other alloying elements are used, such as manganese, chromium, vanadium, and tungsten. Varying the amount of alloying elements and the form of their presence in the steel (solute elements, precipitated phase) controls qualities such as the hardness, ductility, and tensile strength of the resulting steel. Steel with increased carbon content can be made harder and stronger than iron, but such steel is also less ductile than iron.

The electrochemical theory of corrosion was described as the short circuited galvanic cells on the metal surface (see the mechanism in figure below). Metal ions go into solution at

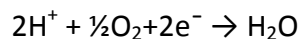
anodic areas in an amount chemically equivalent to the reaction at cathodic areas. At anodic areas, the following reaction takes place:



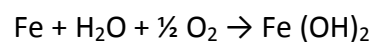
This reaction is rapid in most media. When iron corrodes, the rate is usually controlled by the cathodic reaction, which is much slower (cathodic control). In deaerated solutions, the cathodic reaction is:



This reaction proceeds rapidly in acids, but only slows in alkaline or neutral aqueous media. The cathodic reaction can be accelerated by dissolved oxygen in accord with the following reaction, a process called depolarization



Dissolved oxygen reacts with hydrogen atoms adsorbed at random on the iron surface, independent of the presence or absence of impurities in the metal. The oxidation reaction proceeds as rapid as oxygen reaches the metal surface. And the reaction:



Ferrous oxide $[\text{Fe}(\text{OH})_2]$ will then react with oxygen to give iron oxides: Fe_2O_3 (red) and Fe_3O_4 (black). Iron and steel corrosion rates can vary with different environments and factors like aqueous environment, metallurgical factors and atmosphere.

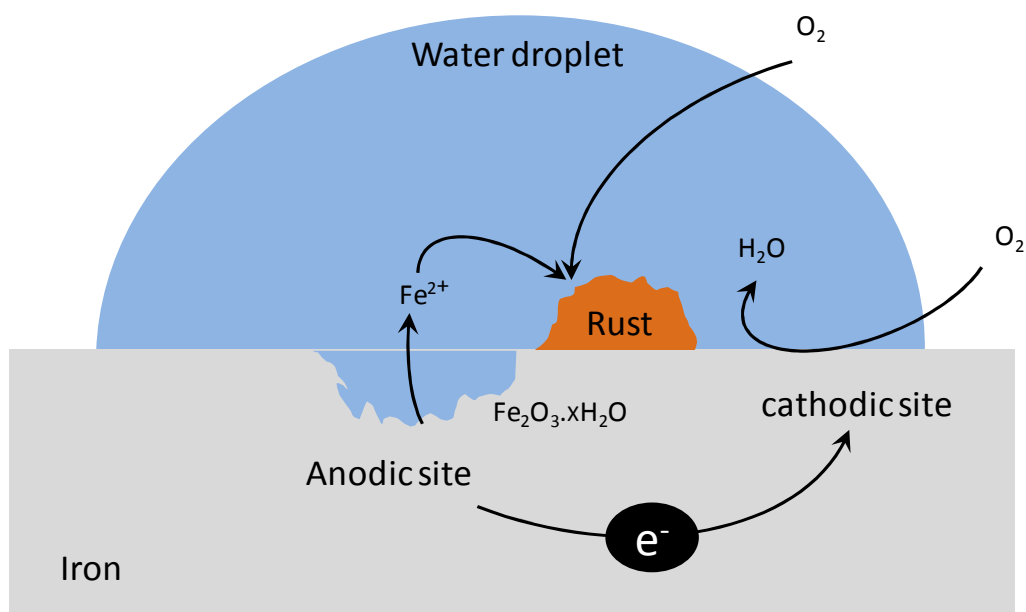


Fig. 3 Mechanism of corrosion [12].

1.4. Pourbaix diagram of iron

Pourbaix diagram is one of the most classical tools to investigate electrochemical stability of metals. It allows a quick determination of possible stable phases for a given potential as a function of pH or a ligand chemical potential like presented in figure 4. It gives a representation of a system's thermodynamic equilibrium redox properties and it is classically used in all fields of electrochemistry ranging from the energy conversion to corrosion. Although they were initially built from experimental data [13] However, this remains particularly challenging in solution as it requires computing ionic species with different oxidation numbers, solvent coordination, electrostatic interactions and entropic contributions. Nevertheless, Pourbaix diagrams are built for the bulk of a solution and it is not clear whether they give a proper description of the stability of species close to an electrode surface, in particular, for the electrochemical double layer [14].

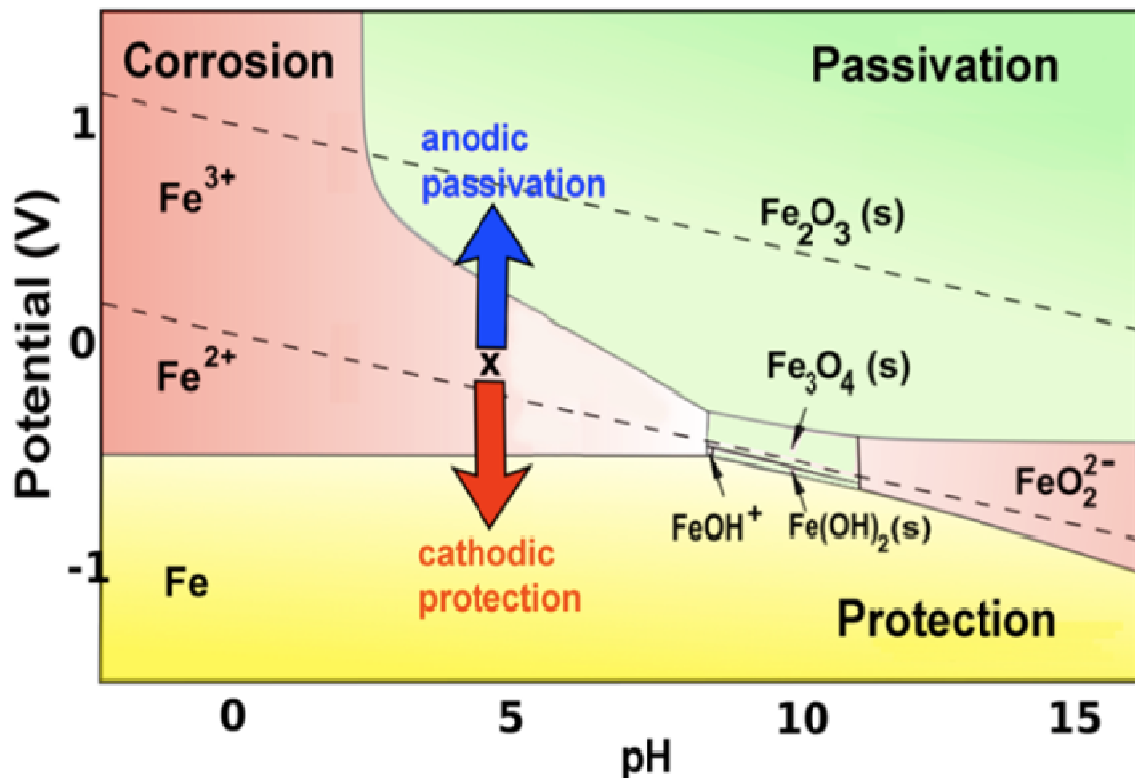


Fig. 4 Schematic Pourbaix diagram of iron

1.5. Corrosion protection

In order to control some of the corrosion problems, several preventive measures are taken.

1.5.1. Cathodic protection

This is an effective method to control corrosion on structures either buried or immersed in an electrolyte; according to the operation mode, anodes are classified as impressed current and sacrificial.

1.5.2. Corrosion Inhibitors

These are substances that added in small concentrations (parts per million, ppm) to a corrosive environment decrease the corrosion rate effectively. This method has its main application in the interiors of pipelines, vessels and equipments.

1.5.3. Anticorrosive coating

A coating is a covering that is applied to the surface of an object, usually referred to as the substrate. The purpose of applying the coating may be decorative, functional, or both. The coating itself may be an all-over coating, completely covering the substrate, or it may only cover parts of the substrate. An example of all of these types of coating is a product label on many drinks bottles—one side has an all-over functional coating and the other side has one or more decorative coatings in an appropriate pattern (the printing) to form the words and image. Paints and lacquers are coatings that mostly have dual uses of protecting the substrate and being decorative, although some artists paints are only for decoration, and the paint on large industrial pipes is presumably only for the function of preventing corrosion. Functional coatings may be applied to change the surface properties of the substrate, such as adhesion, wettability, corrosion resistance, or wear resistance. In other cases, e.g. semiconductor device fabrication (where the substrate is a wafer), the coating adds a completely new property, such as a magnetic response or electrical conductivity, and forms an essential part of the finished product. A major consideration for most coating processes is that the coating is to be applied at a controlled thickness, and a number of different processes are in use to achieve this control, ranging from a simple brush for painting a wall, to some very expensive machinery applying coatings in the electronics industry. A further consideration for non-all-over coatings is that control is needed as to where the coating is to be applied. A number of these non-all-over coating processes are printing processes [15].

1.6. Types of coating

The main type of the protection coating of the corrosion are listed in the figure below.

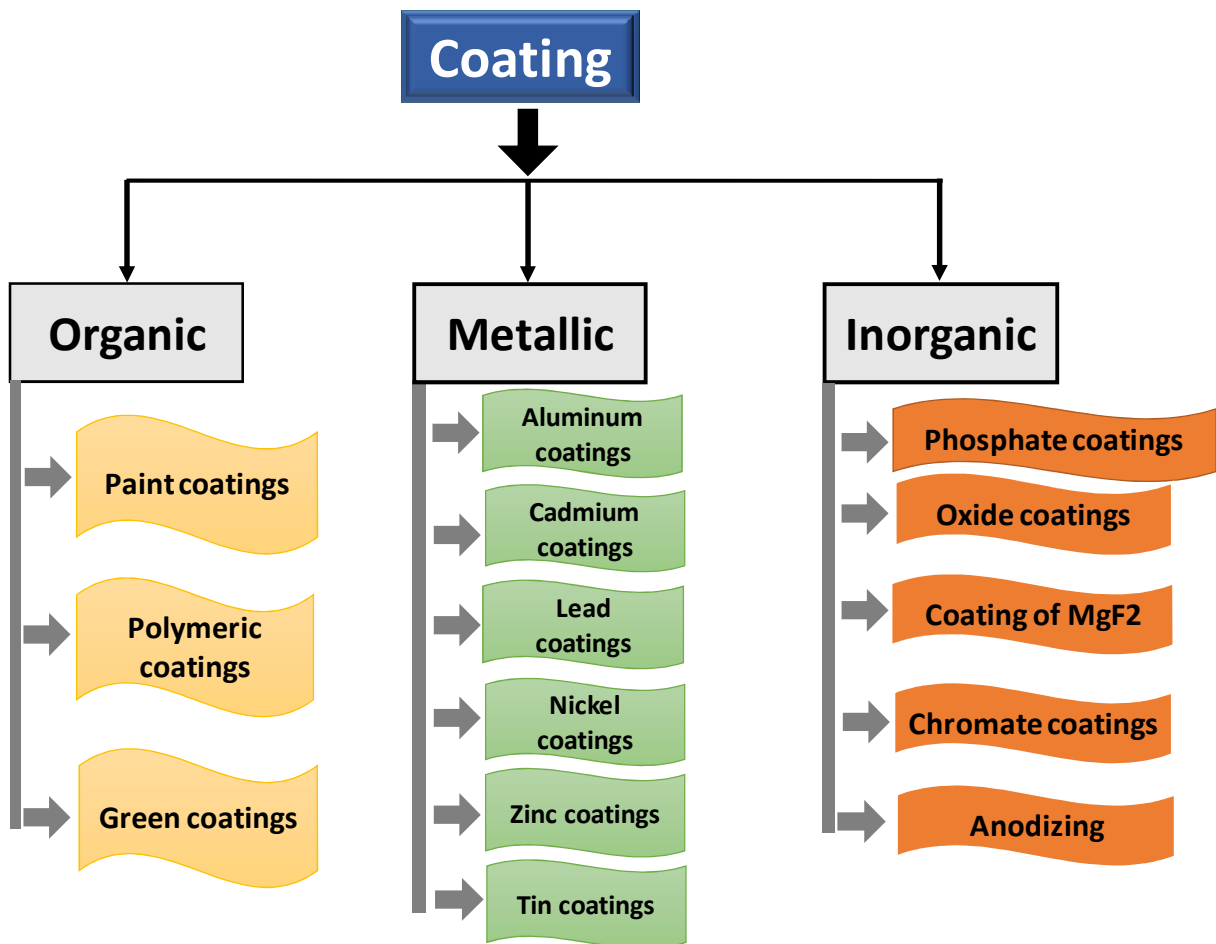


Fig. 5 Types of coating for corrosion protection of metals

1.6.1. Organic coatings

Organic coatings provide protection either by a barrier action from the layer or from active corrosion inhibition provided by pigments in the coating. In actual practice, the barrier properties are limited because all organic coatings are permeable to water and oxygen to some extent. The average transmission rate of water through a coating is about 10 to 100 times larger than the water consumption rate of a freely flowing surface; and in normal outdoor conditions, an organic coating is saturated with water at least half of its service life. For the remainder of the time, it contains a quantity of water comparable in behavior to an atmosphere of high humidity [16].

1.6.2. Metallic coatings

Metallic coatings are applied to metal substrates for several purposes. Typical purposes include improved corrosion resistance, wear resistance, and appearance. Primary concern is corrosion resistance by providing a barrier between the substrate and the environment, or by cathodically protecting the substrate. Coatings of chromium, copper, and nickel provide increased wear resistance and good corrosion resistance. However, these noble metals make the combination of the substrate (mostly steel or an aluminum alloy) with the protective layer sensitive to galvanically induced local corrosion[17]. Non noble metallic layers such as zinc or cadmium provide good cathodic protection but show poor wear resistance. From a corrosion point of view, metal coatings can be divided into two classes: noble and sacrificial. Silver, copper, nickel, chromium, tin, and lead coatings on steel constitute the former group, whereas the coatings of zinc, aluminum, and cadmium belong to the latter group. A coating of a corrosion-resistant metal on a corrosion-prone substrate can be formed by various methods. The choice of coating material and the selection of an application method are determined by the end of the use [18].

1.6.3. Inorganic coatings

The class of coatings designated as inorganic is comprised of native metal oxides, augmented oxides, or a layer of material that is made up of elements other than the principal organic constituents, i.e., carbon, hydrogen, and oxygen. Inorganic coatings may be formed by a variety of chemical, electrochemical, and thermal methods, and may be used as either a standalone coating for corrosion protection, or as a surface pretreatment for a subsequent organic finish.

1.7. Coating deposition methods

Coating processes provide protection to a specific part or area of a structure exposed to harsh and corrosive environments in different fields ranging from aerospace and the automotive industry to tiny biomedical devices and implants inside the human body [19].

1.7.1. Physical Vapor Deposition (PVD) Coating

PVD process is famous for offering corrosion and wear resistance and thin protective films on the surface of the materials that are exposed to corrosive media, and its applications range from decorative objects to industrial parts [20]. The advantage of this method is that the mechanical, corrosion, and aesthetic properties of the coating layers could be adjusted on demand. In general, PVD is a process that takes place in a high vacuum and the solid/liquid materials transfer to a vapor phase followed by a metal vapor condensation, which creates a solid and dense film. The most known types of PVD are sputtering and evaporation. Since the coating layers created by PVD are thin in nature, there is always a need for multilayered coatings while the materials selection should be considered carefully.

1.7.2. Chemical Vapor Deposition (CVD) Coating

Another type of vapor deposition is called CVD. This process undergoes a high vacuum and is widely used in the semiconductors industry providing a solid, high quality, and a high resistance coating layer on any substrate [21]. CVD can be used for mechanical parts in constant contact, which need protection against corrosion and wear. In this process, the substrate, known as a wafer, would be exposed to a set of volatile material precursors where a chemical reaction creates a deposition layer on the surface of the material. However, some byproducts of these chemical reactions, which are removed by constant airflow of the vacuum pump, can remain in the chamber. The vaporized CVD materials are pumped from

the right side and the heaters keep the temperature high enough to facilitate the chemical reaction between the substrate and vaporized materials.

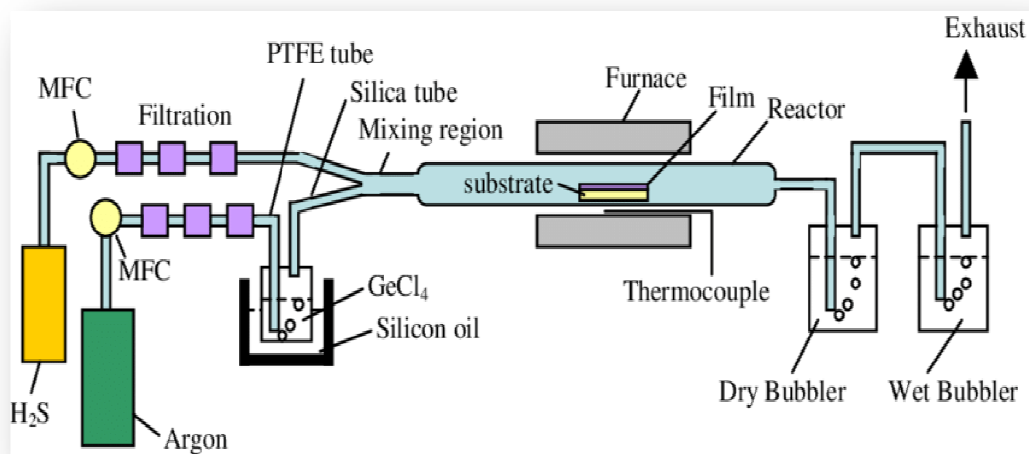


Fig. 6 Schematic chemical vapor deposition (CVD) setup [22].

CVD technique provides a wide selection of materials in different compositions and forms such as carbides, nitrides, oxynitrides, a composition of Si with O and Ge, carbon in forms of fluorocarbons, diamond, polymers, graphene, fibers/nanofibers/nanotubes, Ti, and W. In addition, these materials could be provided in different microstructures such as monocrystalline, polycrystalline, and amorphous [23]. Moreover, CVD of polymers has been shown to be a reliable process in applications such as biomedical device implants, circuit boards, and durable lubricious coatings [24].

1.7.3. Electrodeposition coating

In this process, a difference in potential between anode and cathode poles causes an ion transfer in the unit cell and a coating layer forms on the submerged sample by receiving ions from the other electrode. The common group of metals that have been intensively studied includes, but is not limited to, Ni-P, Ni-P/Sn, Ni-P-W, Ag/Pd, Cu/Ag, Cu/Ni, Co/Ag, and Co/Pt [25]. According to these studies, the electrodeposited coatings significantly

enhance the corrosion properties of the substrate. Moreover, this technique has been shown to be promising in producing superhydrophobic polymeric coatings such as polythiophene [26].

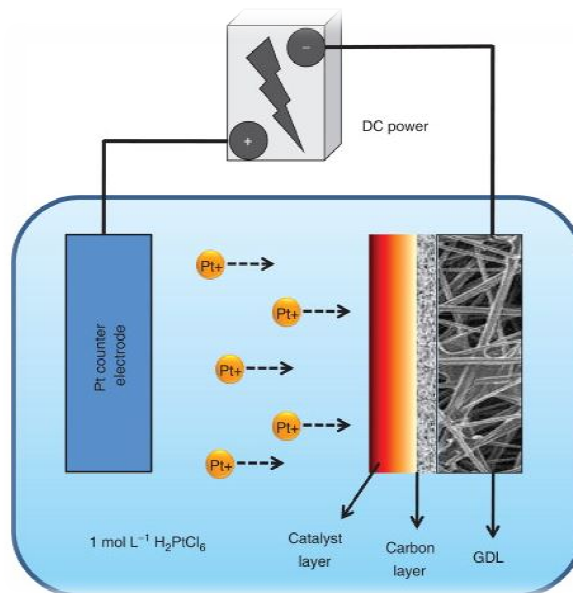


Fig. 7 Schematic electrodeposition coating [27].

1.7.4. Sol-gel Coating

Sol-gel coating is one of the most successful coating processes of enhancing previously existing coating layers from corrosion [28].

Due to its liquid-permeating nature, sol-gel can easily seal porous coating structures or damaged layers. This process may be repeated to achieve a multilayered coating or thicker coating of the same material. Advantages of the sol-gel process include high adhesion of the coating layer, ability to coat complex geometries, flexibility in the composition of the coating layer, and lower cost than other similar coating processes. Additionally, there is no need to have a conductive material as a substrate as there is no extreme heating or vacuum applied to the parts meaning that the substrate will be virtually untouched during the coating process. Sol-gel coating is done in different forms such as dip-coating, spraying, and spinning [29]. One disadvantage of this process could be that a constant speed of dipping and with

drawing is needed to maintain a uniform thickness of coating throughout the substrate surface. There is also always a possibility of coating failure during heat treatment on multilayered coating structures. Sol-gel coating for industrial applications is considered a slow process and is not cost effective in high production rates [30].

1.7.5. Spray coating

Spray is classified as a solution based chemistry deposition method. Solution based methods for films deposition are becoming more popular, providing high purity products at low cost, starting from easily available materials. SPT is useful for depositing varieties of thin film. Spray coating is a simple and effective method of coating a substrate because it is inexpensive, easily scalable, and applicable to a variety of surfaces. The versatility of this approach permits any number of treatments to be applied to a single type of roughened surface. Spray pyrolysis is a processing technique being considered in research to prepare thin and thick films, ceramic coatings, and powders. Unlike many other film deposition techniques, spray pyrolysis represents a very simple and relatively cost-effective processing method (especially with regard to equipment costs). It offers an extremely easy technique for preparing films of any composition. Spray pyrolysis does not require high-quality substrates or chemicals. The method has been employed for the deposition of dense films, porous films, and powder production [31].

Chapter 2



Chapter 2 « Experimental »

1. Samples preparation procedures

1.1. Mechanical polishing of working electrodes

The working electrodes are Steel disks (figure 8 (a)). The area of working electrode is 1cm^2 . The Steel disks were mechanically polished (like shown in figure 8 (b)) starting with P800 to P4000 abrasive SiC papers. At the end of the mechanical polishing, the samples are polished on sheets impregnated with diamond pastes for decreasing grain size. Diamond pastes of $6\mu\text{m}$, $3\mu\text{m}$, $1\mu\text{m}$, and $1/4\mu\text{m}$ are used, depending on the initial roughness. The result obtained is samples without roughness, very smooth and shiny (figure 8 (c)). Samples, to be coated were placed in dry boxes.

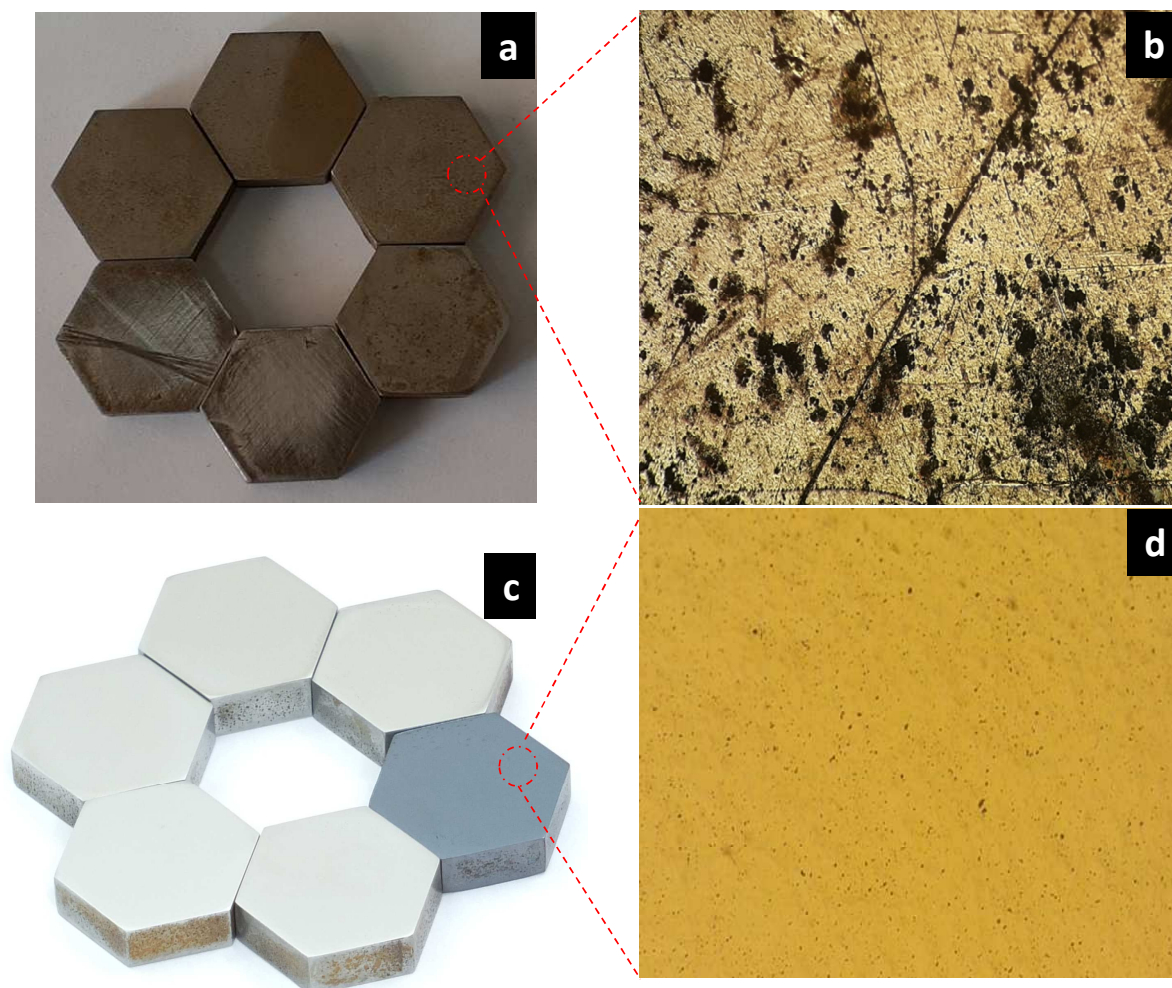


Fig. 8 Photographs and the corresponding optical microscope top view of the Steel disks before (a) and after mechanical polishing

1.2. Coating deposition by spray method

1.2.1. Precursor solutions

The solutions preparation steps are summarized in the table below.

Table 1. *Summarized solutions preparation steps*

Coating	[C] mol/L	Solvents	Precursors			
ZnO	0,1	Methanol			Zinc Acetate	
ZnS	0,2	Methanol + Ethanol			Thiourea	Zinc Acetate
CZTS	0,2	Ethanol	Copper(II) Nitrat	Zinc Acetate	Tin(II) Chlorid	Thiourea
SnO ₂	0,2	Ethanol	Copper(II) Nitrat	Tin(II) Chlorid		

1.2.2. Deposition of the coating

The resulting solution were sprayed at different temperature from 200°C to 400°C by a step that equals (50°C). Heating the substrate for a minute, then we turn on the air pressure device (1bar) and the spraying process takes place for four minutes, with little moving to obtain a homogeneous coating on the surface of the Steel disks (see figure below).



Fig. 9 The spray technique used to deposit the coating

1.3. Electrochemical cell

All electrochemical tests were performed in a homemade three-electrode cell. It consisted of a working electrode (WE), a counter (CE) or auxiliary electrode and a reference electrode (RE). The WE is the electrode being studied, where the electrochemical reactions take place. In corrosion experiments, the WE is the material that is corroded. The CE is the electrode with which the current path is completed. All the current needed to balance the current produced at the WE passes through the CE. The RE is used to measure the voltage between the WE and the electrolyte. It has a constant potential and serves as an experimental reference point. Therefore, no current should pass through the reference electrode. A typical Potentiostat/Galvanostat (Reference 300, EC-Lab) was used to carry out the experiments in 2wt% NaCl solution at ambient temperature. A three-electrode electrochemical cell comprising of working (bare and coated steel), Ag/AgCl as a reference electrode and platinum as a counter electrode, was used to conduct the electrochemical

tests like shown in figure 10. The work electrode is steel, having hexagonal shape with a surface area of 1 cm².

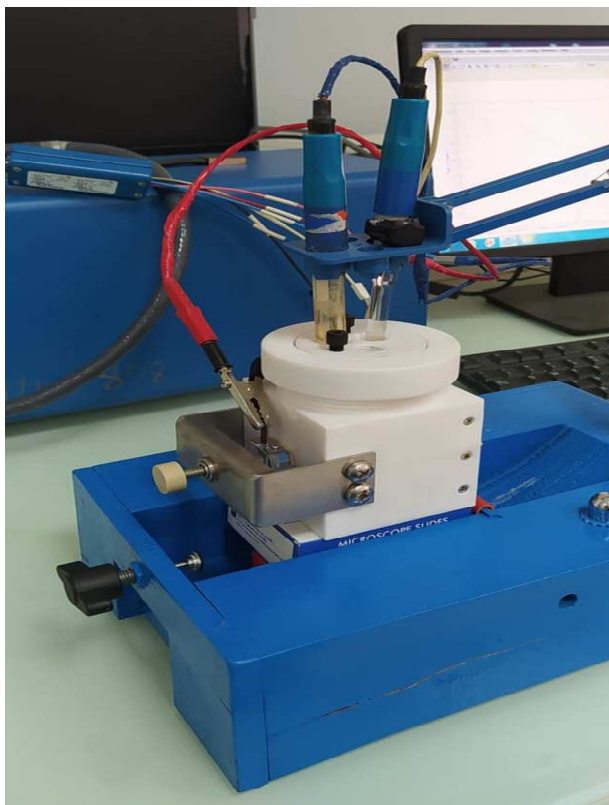


Fig. 10 Three-electrode set up and the electrochemical cell used in the present study

2. Electrochemical analyses techniques

2.1. Chronopotentiometry

Chronopotentiometry (CP) is a galvanostatic method in which the current at the working electrode is held at a constant level for a given period of time. The working electrode potential and current are recorded as a function of time. Researchers employ this method to study chemical reaction mechanisms and kinetics. It is also frequently used to study batteries and electrodeposition. CP is typically performed in an unstirred electrochemical cell, although, some researchers employ rotating electrodes in conjunction with CP[32].

Typically, current is held constant between working and counter electrodes while potential is measured at the working electrode, relative to the reference electrode. Redox-active species diffuse to the working electrode surface to balance the applied current, until the diffusion-limited concentration of redox species reaches zero at the electrode surface, at which time potential changes to the redox potential of the next species, if present, in solution (which could be solvent). CP is also commonly used during battery charge and discharge experiments [33].

2.2. Linear polarization

Tafel extrapolation is one of the polarization methods widely utilized to measure corrosion rates, a faster experimental technique compared with the classical weight-loss estimation [34]. It is known that the corrosion rates obtained using Tafel extrapolation of polarization curves are not usually the same as those measured by the weight loss.

$$I_{TOT} = I_a - I_c$$

$$I = nF \left(K_A C_A \exp \frac{(1-\alpha)nF\eta}{RT} - K_B C_B \exp \frac{-\alpha nF\eta}{RT} \right)$$

$$\eta = E - E_{eq}$$

For low overvoltages:

Two areas can be used:

- The field of cathodic overvoltages.
- The field of anodic overvoltages.

Cathodic overvoltage ($\eta < 0$)

$$\ln \frac{I}{I_0} = \frac{-\alpha_c nF}{RT} \eta_c$$

$$\eta_c = a + b_c \log I$$

$$a = \frac{2,3RT}{\alpha nF} \log I_0 \quad \text{and} \quad b_c = \frac{2,3RT}{\alpha nF}$$

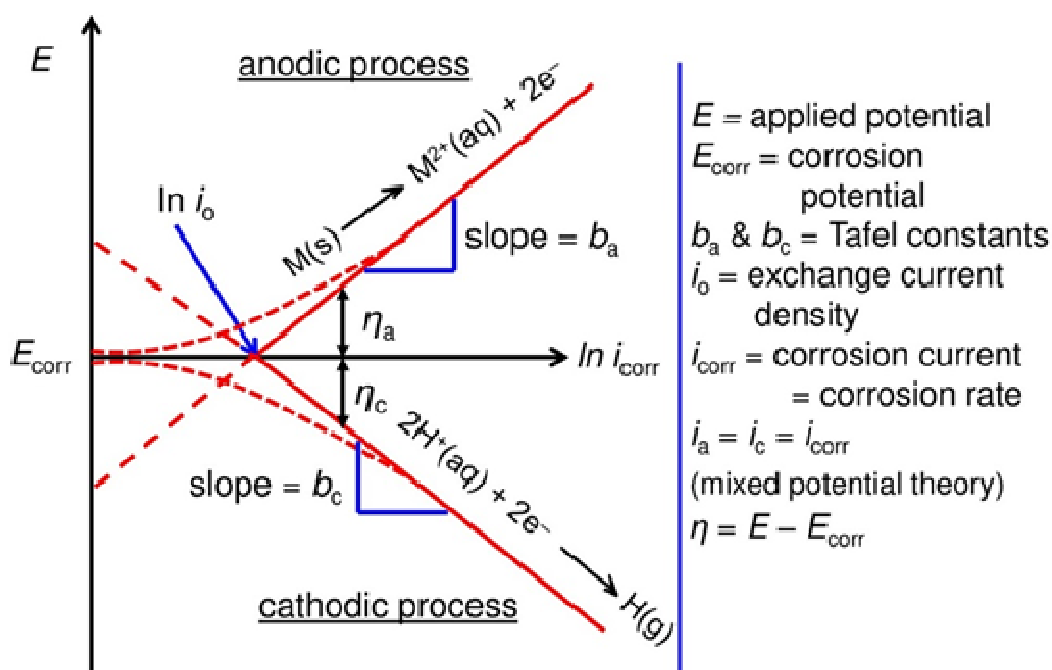
Anodic overvoltage ($\eta > 0$)

$$I = I_0 \left(\exp \frac{(1-\alpha)nF\eta}{RT} - \exp \frac{-\alpha nF\eta}{RT} \right)$$

$$\text{Ln} \frac{I}{I_0} = \frac{(1-\alpha_c)nF}{RT} \eta_a$$

$$\eta_a = a' + b_a \log I$$

$$a' = \frac{2,3RT}{(\alpha-1)nF} \log I_0 \quad \text{and} \quad b_a = \frac{2,3RT}{(1-\alpha)nF}$$



The linear polarization of all samples was carried out from -1.5 V to +1.5V potential window with respect to the open circuit potential (OCP) at the scan rate of 20 mV/second. Tafel fit software was used to calculate the polarization resistance (Rp) by calculating the

slope of the linear part of the curve in between ± 10 mV potential range with respect to the OCP.

The polarization resistance was calculated using the equation:

$$R_p = \frac{\beta_a \times \beta_c}{2.3 \times i_{corr} \times (\beta_a + \beta_c)}$$

The protection efficiency (PE) was calculated using the following formula:

$$PE (\%) = \frac{i_{corr}(\text{uncoated}) - i_{corr}(\text{coated})}{i_{corr}(\text{uncoated})} \times 100\%$$

2.3. Electrochemical impedance spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a non-stationary method that provides information on the elementary steps that make up the overall electrochemical process. It also makes it possible to follow the evolution of the electrochemical properties of a coated or uncoated conductive sample. EIS is a powerful technique for rapidly evaluating the performance of coated metals by measuring impedance values. It can quickly monitor changes in barrier properties of coatings compared to traditional methods. EIS also provides precise data that can be used to predict the effectiveness of a coating over time. System impedance is the ratio of the imposed sinusoidal voltage to the resulting current. It can be defined by a complex number

$$Z(\omega) = \frac{\Delta V}{\Delta I} \exp j\phi$$

$$Z(\omega) = Z \exp(j\phi) = \text{Re}Z + j\text{Im}Z$$

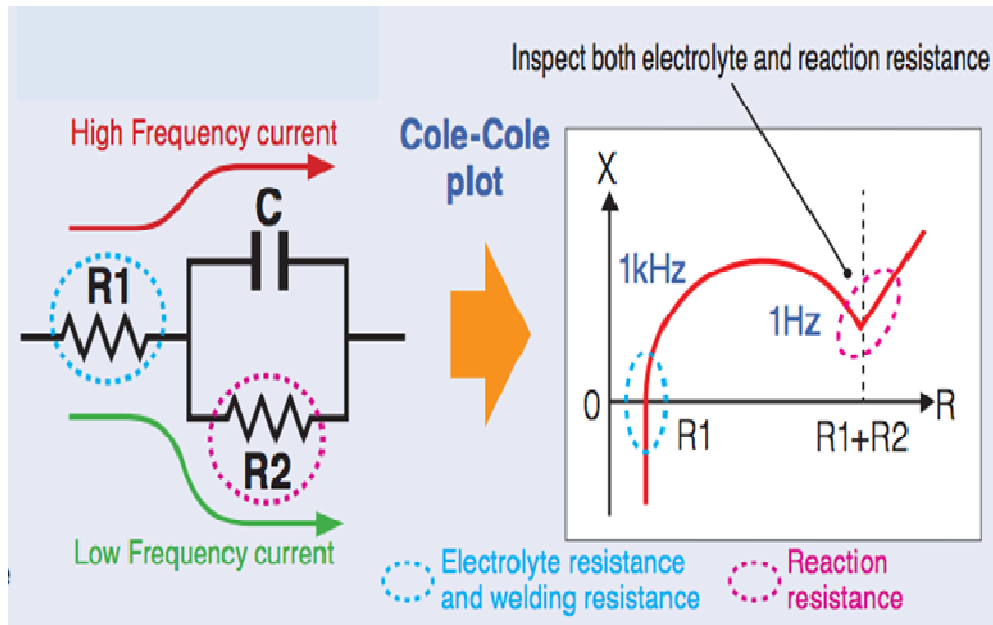


Fig. 12 Schematic representation of electrochemical impedance spectroscopy

Chapter 3



Chapter 3 « Results and discussion »

1. Effect of deposition temperature (optimization)

Deposition temperature is one of the most important parameters influencing the coating properties.

1.1. Linear polarization curves

1.1.1. Uncoated Steel

The potentiodynamic measurement results of uncoated steel just heated under different temperatures (200–400°C) in 2wt % NaCl solution are shown in figure 13. An increase in the value of the corrosion potential (E_{corr}) and a decrease in the value of the corrosion current (I_{corr}) with respect to the increase of the heating temperature can be seen. This indicates that steel heated at $T=200^{\circ}\text{C}$ has better corrosion resistance than steel heated at other temperatures. These results address the effect of temperature on corrosion. The corrosion parameters I_{corr} , E_{corr} , β_a , β_c and R_p are recorded in table 2. The table shows that the β_a decrease with increasing heating temperature and β_c did not change much with change the heating temperature.

Uncoated steel heated at $T=200^{\circ}\text{C}$ has a high polarization resistance, compared to uncoated steel heated at high temperatures ($T= 250, 300, 350$ and 400°C). The high polarization resistance gives the uncoated steel good corrosion protection.

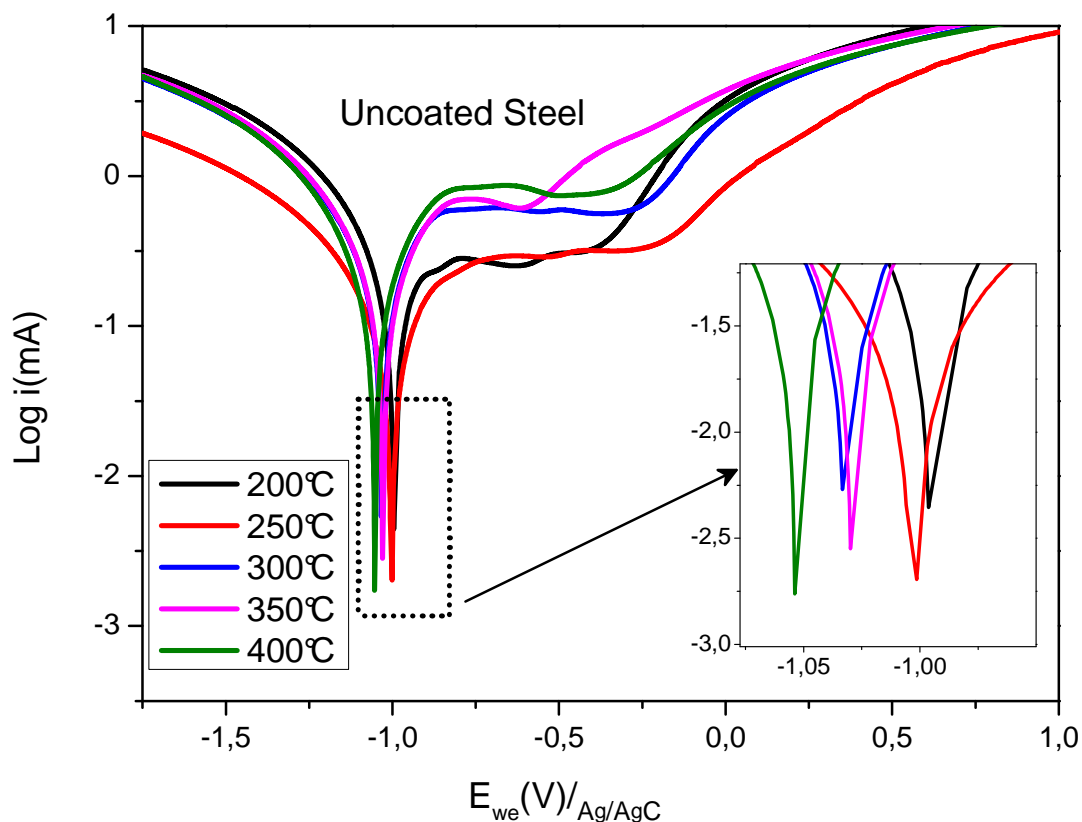


Fig. 13 Potentiodynamic polarization curves of uncoated steel disks as a function of heating temperature. The inset represent the corresponding enlarged view of the polarization curves.

Table 2. Polarization parameters for uncoated Steel in 2wt% NaCl solution

T (°C)	I_{corr} (μ A)	E_{corr} (mV)	β_a (mV)	β_c (mV)	R_p (Ω)
200°C	165	-995	827	260	521
250°C	69	-1004	316	265	908
300°C	163	-1030	297	273	379
350°C	157	-1029	285	261	377
400°C	151	-1054	265	253	372

The curves of figure 14 present the changes of corrosion potential (E_{corr}) and the corrosion current (I_{corr}) of uncoated steel as a function of deposition temperature. Heating the uncoated steel at different temperatures did not change the value of the corrosion

current as it was estimated at 163 μA . However, heating uncoated steel increases the rate of corrosion and decreases its protective ability.

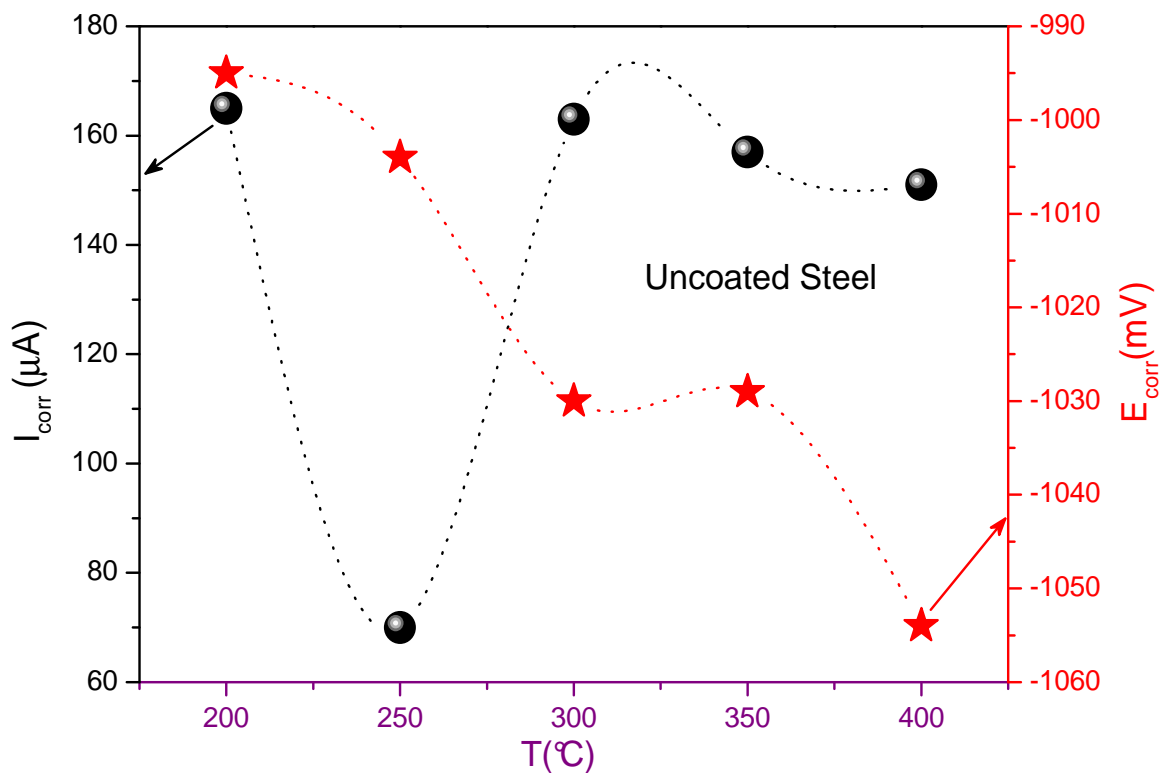


Fig. 14 Corrosion current and corrosion potential as a function of heating temperature for uncoated steel disk

1.1.2. ZnO coating

The potentiodynamic measurement results of coated steel with ZnO with different deposition temperatures (200–400 °C) in 2wt% NaCl solution are shown in figure 15. An increase in the value of the corrosion potential (E_{corr}) and a decrease in the value of the corrosion current (I_{corr}) with respect to the increase of the deposition temperature can be seen. This indicates that the ZnO coating at $T=400^{\circ}\text{C}$ has better corrosion resistance than steel coated at other temperatures.

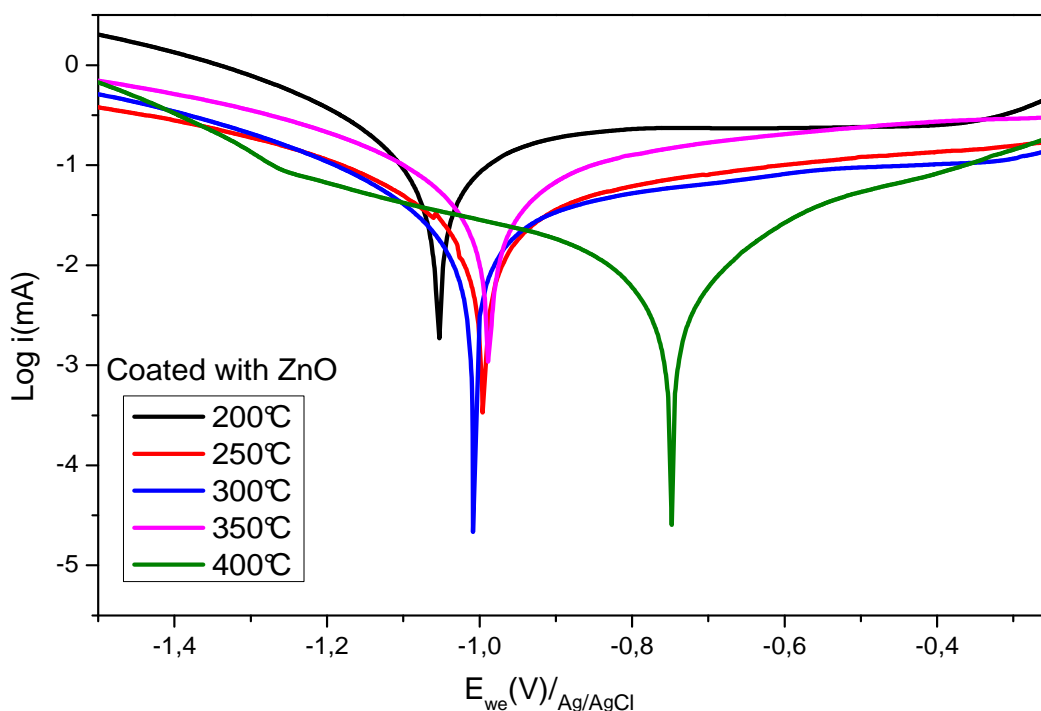


Fig. 15 Potentiodynamic polarization curves of the as sprayed ZnO coating as a function of the deposition temperature

The values of the polarization parameters, namely; corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic Tafel slope (β_c) and anodic Tafel slope (β_a) was calculated from the corresponding polarization curves at 200°C – 400 °C and are summarized in table 3 . It is seen that the corrosion current densities decrease and shifts the E_{corr} toward more positive values even at relatively high temperatures. It was observed that the most decrease corrosion current density was obtained for Steel coated with ZnO at $T=400^\circ\text{C}$. These results corroborate the idea that the steel coated at $T= 400^\circ\text{C}$ has much better than barrier efficiency against the attack of corrosive species like dissolved oxygen and chloride ions, than other coating temperature. The β_a decreases with increasing the deposition temperature as can be seen from Table 3, the β_c value increases with increasing coating temperature.

In general, the corrosion current is inversely proportional to the polarization resistance (R_p). For the ZnO coating formed at $T=400^\circ\text{C}$ the decrease in the value of the corrosion current leads to an increase in the value of the polarization resistance.

Table 3. Polarization parameters for disk steel coated with ZnO

Samples	I_{corr} (μA)	E_{corr} (mV)	β_a (mV)	β_c (mV)	R_p (Ω)
200°C	84	-1052	436	232	783
250°C	19	-996	367	256	3450
300°C	17	-1007	371	235	3679
350°C	34	-982	279	260	1721
400°C	6	-747	239	326	9992

Figure 16 represents the changes of corrosion potential (E_{corr}) and the corrosion current (I_{corr}) of ZnO coating as a function of the deposition temperature. According to the figure, the corrosion current has a maximum value of $I_{\text{corr}}=84 \mu\text{A}$ for ZnO coating formed at $T=200^\circ\text{C}$. After that, it decreases gradually with increasing the deposition temperature reaching $I_{\text{corr}}=6 \mu\text{A}$ at $T=400^\circ\text{C}$. On the other hand, the corrosion potential reaches its lowest value $E_{\text{corr}}=-1052\text{mV}$ at $T=200^\circ\text{C}$ and it increases gradually with increasing temperature, reaching its greatest value $E=-747\text{mV}$ at $T=400^\circ\text{C}$. The results indicate that the ZnO coating presents a relatively better corrosion resistance at $T=400^\circ\text{C}$.

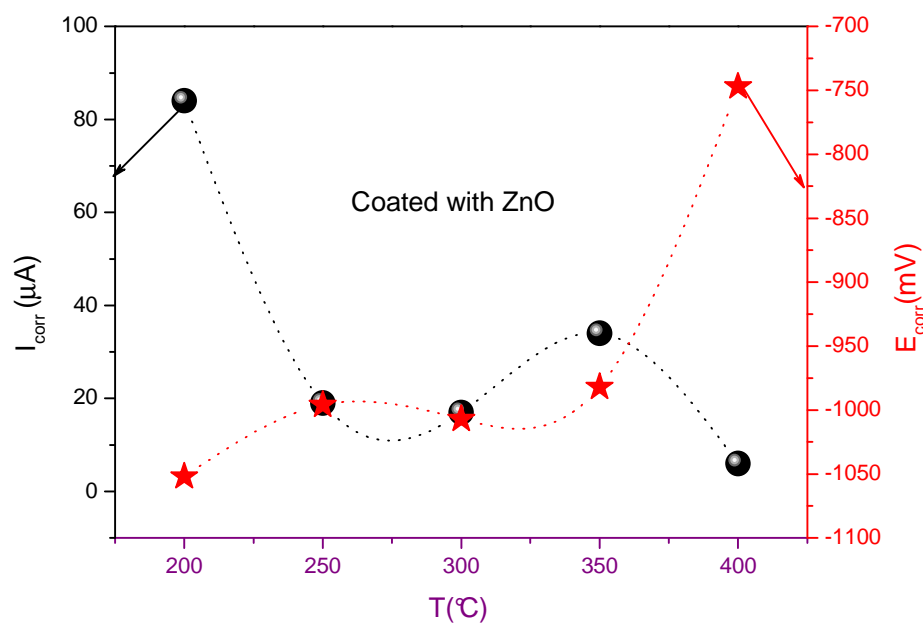


Fig. 16 Corrosion current and corrosion potential as a function of the deposition temperature for steel disk coated with ZnO.

1.1.3. ZnS coating

The potentiodynamic measurement results of film ZnS on steel under different temperatures (200–400 °C) in 2wt% NaCl solution were presented in figure 17. As can be seen after formed ZnS film on steel, a reduction in both cathodic and anodic currents was observed with decreasing temperature. The ZnS coating decreased both anodic metal dissolution and also retards cathodic hydrogen evolution reactions. The cathodic Tafel slopes diminished with ZnS coating.

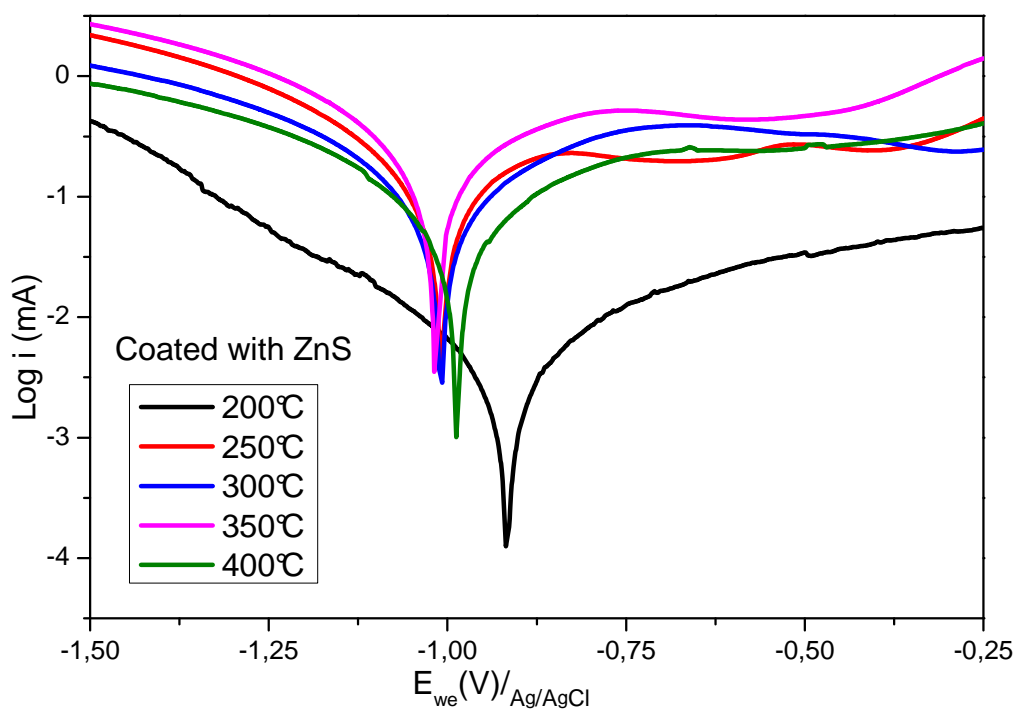


Fig. 17 Potentiodynamic polarization curves for steel disk coated with ZnS

The figure 18 represents the changes of corrosion potential (E_{corr}) and the corrosion current (I_{corr}) of ZnS coating with temperature changes. At $T=200^{\circ}\text{C}$, we record a low value of the corrosion current of $2\ \mu\text{A}$ and then raised to its highest value $I_{corr} = 117\ \mu\text{A}$ at $T=250^{\circ}\text{C}$. While the value of the corrosion potential is estimated at $E_{corr} = -918\text{mV}$ as the largest value at $T=200^{\circ}\text{C}$ and it decreases with increasing temperature. The result indicated that the ZnS coating has the ability to protect Steel against corrosion at $T=200^{\circ}\text{C}$.

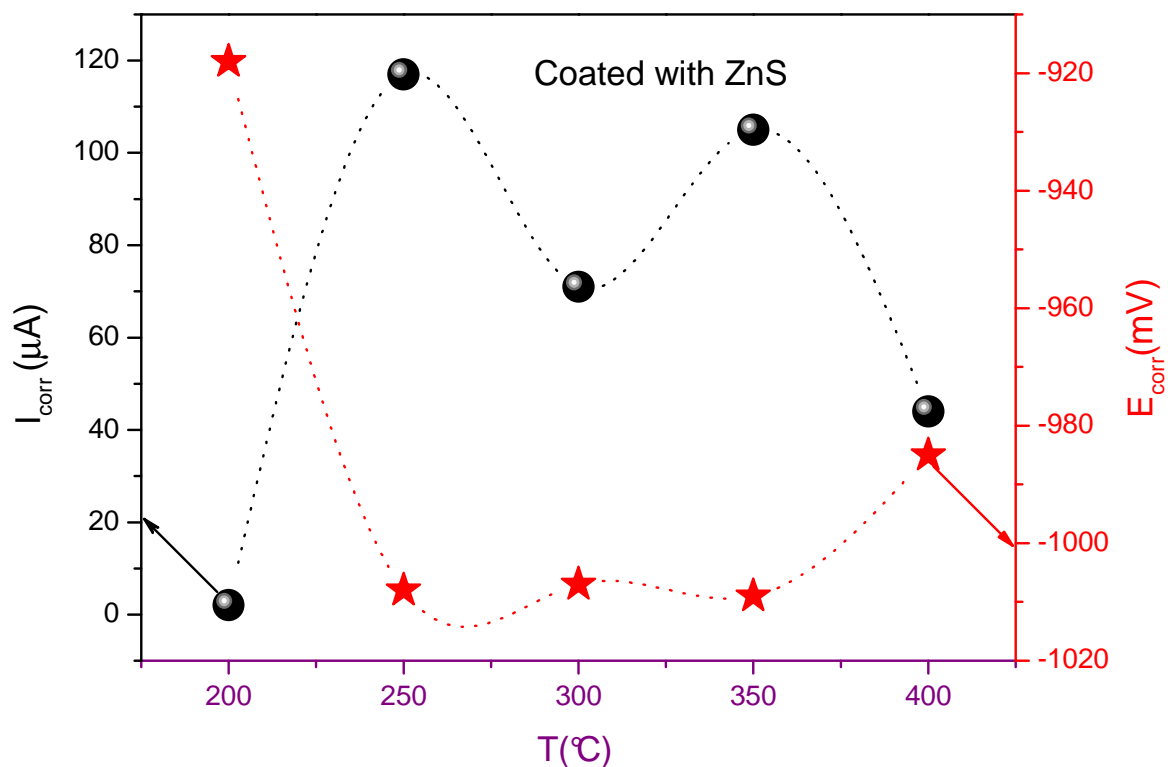


Fig. 18 Corrosion current and corrosion potential as a function of the deposition temperature for steel disk coated with ZnS

Table 4. Polarization parameters for coated ZnS in 2wt % NaCl solution

Samples	I_{corr} (μA)	E_{cor} (mV)	β_a (mV)	β_c (mV)	R_p (Ω)
200°C	2	-918	269	224	26570
250°C	117	-1008	590	277	700
300°C	71	-1007	319	258	873
350°C	105	-1009	399	252	639
400°C	44	-985	310	247	1358

1.1.4. Cu_2SnZnS_4 coating

Potentiodynamic polarization curves of CZTS coatings formed at different temperature (200-400°C) in 2wt% NaCl solution are presented in Figure 19 . Values of electrochemical parameters, including E_{corr} , I_{corr} , Tafel constants (β_a and β_c), and polarization resistance (R_p) are summarized in table 5. From this table, it can be concluded that the CZTS coatings formed at T=250 °C exhibited higher corrosion resistance compared to the coating

formed at other temperature. The greatest value of the corrosion current is obtained at $T=400^{\circ}\text{C}$, indicating a poor resistance to corrosion. These results confirm that the formation of the CZTS coating on steel at $T=250^{\circ}\text{C}$ is more effective in protecting the it from corrosion than the coating formed at other temperature. The CZTS coating formed at $T=250^{\circ}\text{C}$ has the highest value of polarization resistance, while the CZTS coating formed at $T=400^{\circ}\text{C}$ has the smallest polarization resistance. The table 5 shows that the β_a increases with increasing the temperature and β_c decreases with increasing the deposition temperature.

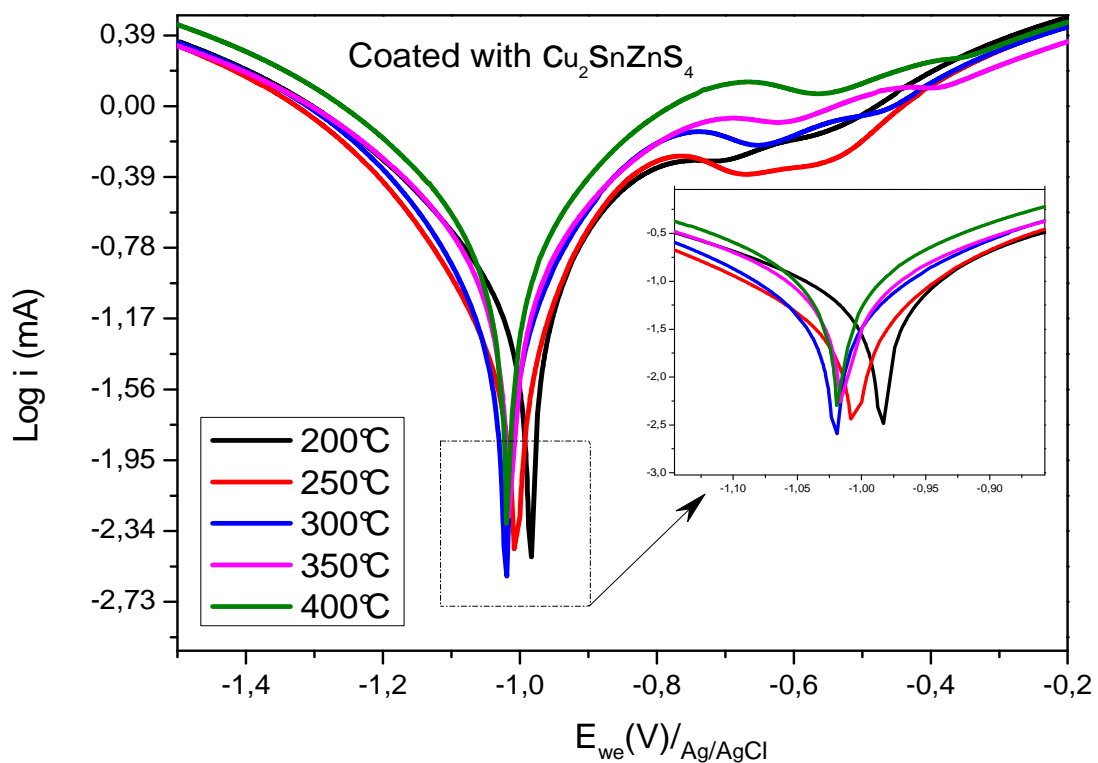


Fig. 19 Potentiodynamic polarization curves for steel disk coated with $\text{Cu}_2\text{SnZnS}_4$. The inset represent the corresponding enlarged view of the polarization curves.

Table 5. Polarization parameters for coated CZTS in 2wt % NaCl solution

Samples	$I_{\text{corr}}(\mu\text{A})$	$E_{\text{cor}}(\text{mV})$	$\beta_a(\text{mV})$	$\beta_c(\text{mV})$	$R_p(\Omega)$
200°C	75	-984	129	256	497
250°C	40	-1005	147	197	915
300°C	58	-1021	185	199	718
350°C	97	-1014	250	252	562
400°C	128	-1017	242	253	420

Figure 20 presents the changes of corrosion potential (E_{cor}) and the corrosion current (I_{cor}) of $\text{Cu}_2\text{SnZnS}_4$ coating with respect to the deposition temperature. The lowest corrosion current was obtained for the coating at 250-300 °C. But the higher corrosion potential was obtained for coating at 200°C.

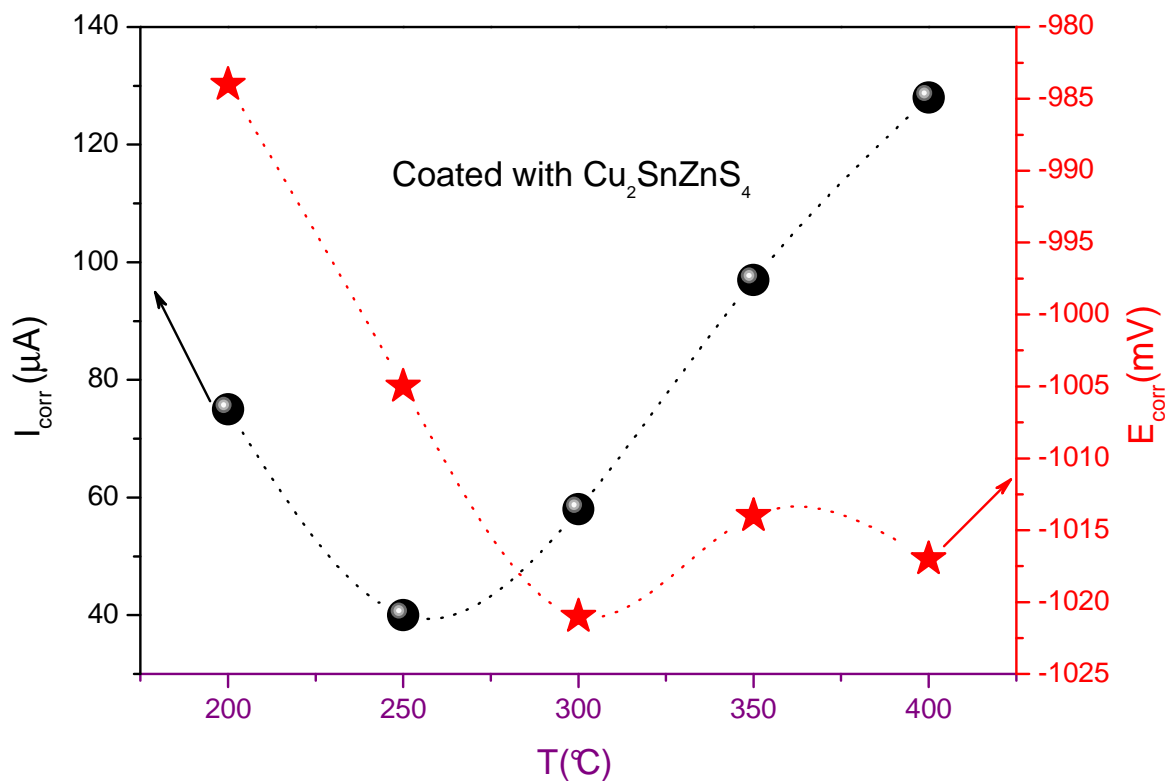


Fig. 20 Corrosion current and corrosion potential as a function of the deposition temperature for steel disk coated with $\text{Cu}_2\text{SnZnS}_4$

1.1.5. SnO₂ coating

Figure 21 shows the polarization curve of SnO₂ films formed at different temperature. The SnO₂ film formed at T=400 °C presented a short zone as the potential swept negatively, which formed a passivation zone to prevent the steel from corrosion compared to SnO₂ coatings formed at others temperatures. The corrosion potential E_{corr} of SnO₂ coating progressively shifted towards higher values, and corrosion current I_{cor} progressively shifted towards lower values with increasing the deposition temperature.

The data of polarization curves (figure 21) are listed in table 6. The corrosion current I_{corr} of SnO₂ coating formed at (T= 400°C) was the lowest among the SnO₂ coatings formed at (T= 200, 250, 300, 350 °C) indicating that the SnO₂ coating formed at (T= 400°C) exhibited the highest corrosion resistance. The value of the polarization resistance is greater for the coating formed at T=400°C, indicating a good protection against corrosion compared to the weak polarization resistance of the SnO₂ coating formed at other temperature.

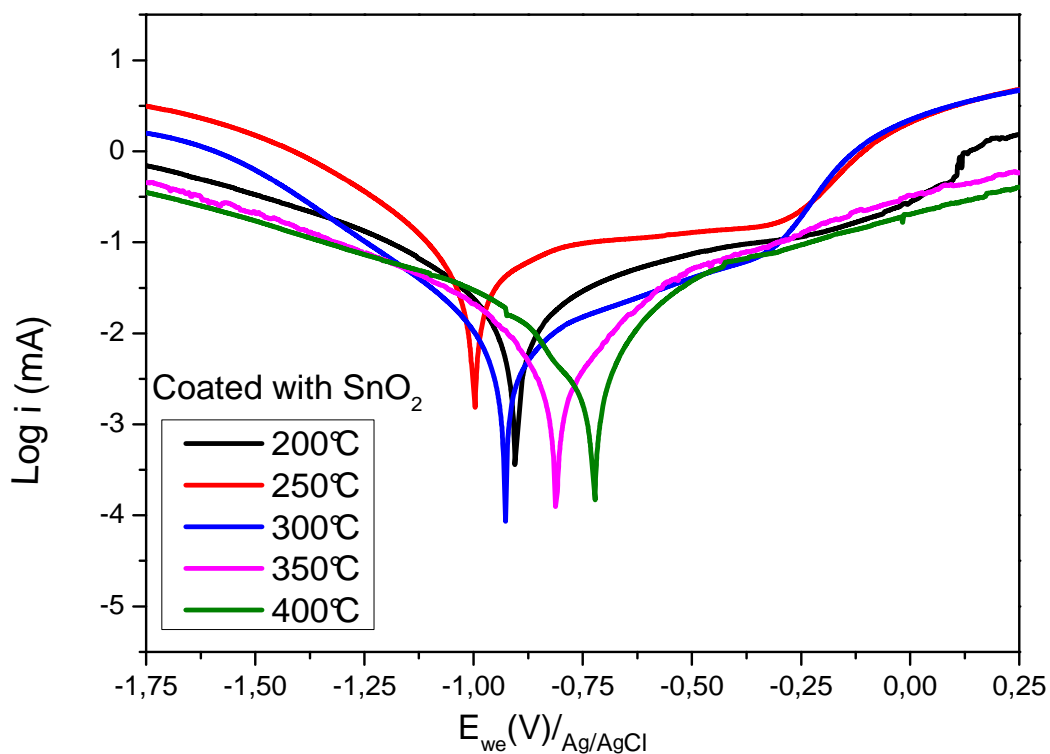


Fig. 21 Potentiodynamic polarization curves for steel disk coated with SnO₂.

Table 6. Polarization parameters for coated SnO₂ in 2wt % NaCl solution

T (°C)	I_{corr} (μA)	E_{cor} (mV)	β_a (mV)	β_c (mV)	R_p (Ω)
200°C	9	-904	341	243	6854
250°C	31	-997	432	218	2032
300°C	5	-927	414	226	12712
350°C	3	-801	233	224	16551
400°C	1	-723	119	195	32130

Figure 22 represents the change of the (E_{cor}) corrosion potential and the (I_{corr}) corrosion current of the SnO₂ coating in terms of the change in temperature. Initially at T= 200°C the I_{corr} is about 8 μA, and the E_{cor} is (-925mV). As soon as the temperature rises T= 250°C we record a decrease in the value of I_{corr} to reach its lowest value of 0 μA, followed by an increase in the corrosion potential to reach its greatest value E_{cor} =-725mV. At T=300°C the value of I_{corr} increase up to 6 μA and continues to increase with increasing temperature to reach 32,5 μA at T=400°C. At the same time , the value of E_{cor} decreases to become E_{cor} =- 930mV at T=- 300°C and continues to decrease with increasing temperature to reach E_{cor} =- 980mV at T=400°C. The values of the corrosion current are inversely proportional to the values of the corrosion potential.

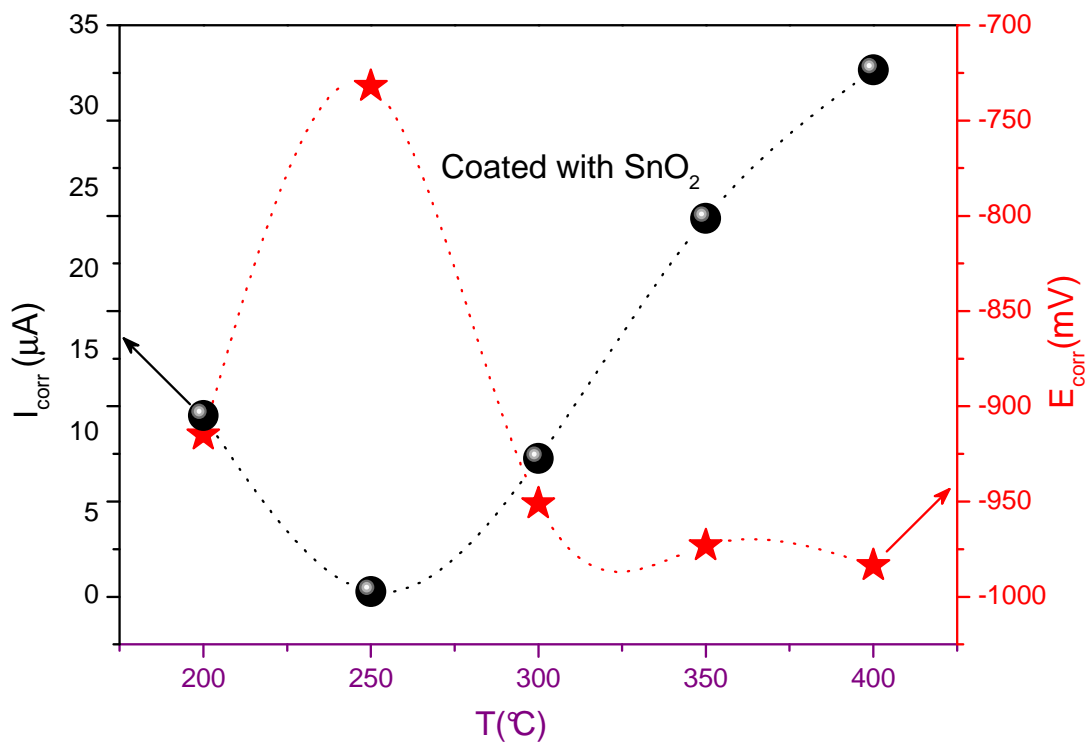


Fig. 22 Corrosion current and corrosion potential as a function of the deposition temperature for steel disk coated with SnO_2

2. Investigation of corrosion protection at 350°C

2.1. Linear polarization curves

Polarization curves of the uncoated and coated Steel disks with various coatings at $T=350^\circ\text{C}$ in 2wt % NaCl solution are shown in figure 23. The corrosion parameters: E_{corr} the corrosion potential, I_{corr} corrosion current, β_a , β_c and polarization resistance R_p were calculated from polarization curves and the results are summarized in table 7. It can be seen that the SnO_2 coating have a high corrosion potential (E_{corr}) and low corrosion current (I_{corr}) value compared to other coating and heated steel. SnO_2 coating prevents the diffusion of corrosive ions via pores/capillaries and enhances the corrosion protection ability of the Steel. The table 7 shows that the β_a and β_c did not change notably with changing the coating.

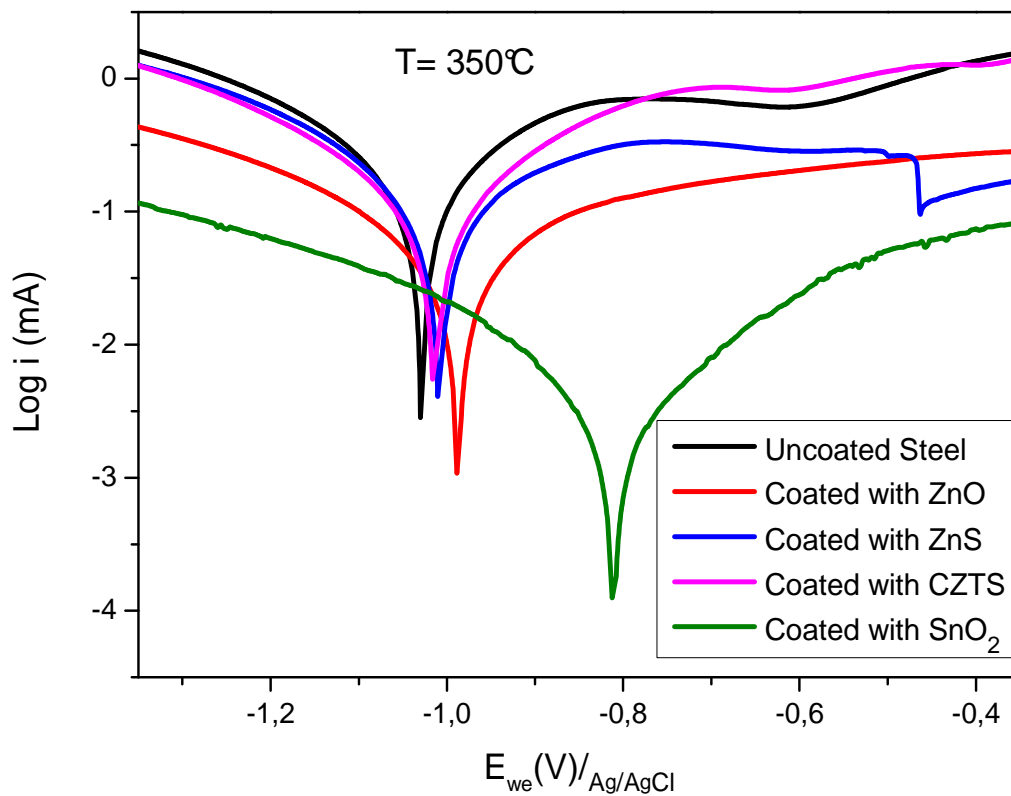


Fig. 23 Potentiodynamic polarization curves of the as sprayed coatings and uncoated steel disks.

Table 7. Polarization parameters for various coating at $T= 350^{\circ}\text{C}$

Samples	i_{corr} (μA)	E_{coor} (mV)	β_a (mV)	β_c (mV)	R_p (Ω)
Steel	157	-1029	285	261	377
ZnS/ Steel	105	-1009	399	252	639
CZTS/ Steel	97	-1014	250	252	562
ZnO/ Steel	34	-982	279	260	1721
SnO ₂ / Steel	3	-801	233	224	16551

2.2. Electrochemical impedance spectroscopy (EIS) study

Figure 24 shows the Nyquist diagrams of uncoated steel, and steel coated with SnO₂, ZnO, ZnS, CZTS. It can be seen from the figure that the capacitance arc radius of SnO₂ coating is larger than of the ZnO coating, uncoated steel and other coatings, which means that the SnO₂ has higher charge transfer resistance than ZnO, uncoated Steel and others coatings. In other words, SnO₂ is more corrosion resistant than ZnO, ZnS, CZTS. At the same time, the

capacitance arc radius of SnO_2 coating is larger than ZnO, ZnS and CZTS coatings, which indicates further that the SnO_2 coating has better corrosion resistance than others coatings. Obviously, the impedance analysis result is consistent with that of the polarization curves.

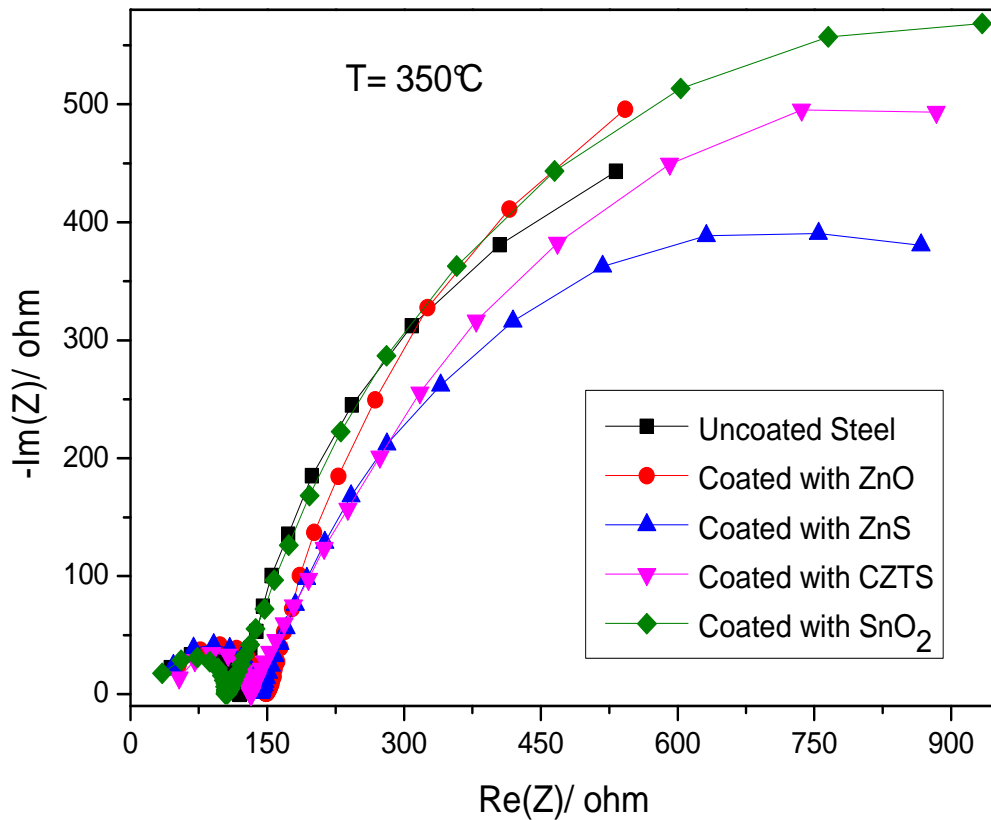


Fig. 24 Nyquist plots for the as sprayed coatings and uncoated steel disks. exposed to 2wt% NaCl solution.

In contrast

Figure 25 represents the variations of the corrosion current, corrosion potential and charge transfer resistance for uncoated steel and coated steel with SnO_2 , ZnO, ZnS, CZTS at $T = 350^\circ\text{C}$. For uncoated steel, we record a low value of corrosion potential of about -1045mV and a very high current value of up to $160\ \mu\text{A}$ with relatively high charge transfer resistance. For ZnS and CZTS coatings, we record the average value of the corrosion current between 100 and $110\ \mu\text{A}$ and weak corrosion potential of -1025mV . The ZnO coating has a low corrosion current of $30\ \mu\text{A}$ and a high charge transfer resistance in the range of $1600\ \Omega$

with a corrosion potential of -975 mV. The SnO₂ coating has a relatively low corrosion current of about 2 μA corresponding to low charge transfer resistance value of about 900 Ohm with a high corrosion potential value of -800mV. This indicates that the SnO₂ coating has good corrosion resistance. Through the results, we conclude that SnO₂ coating has better corrosion resistance than ZnO, ZnS and CZTS.

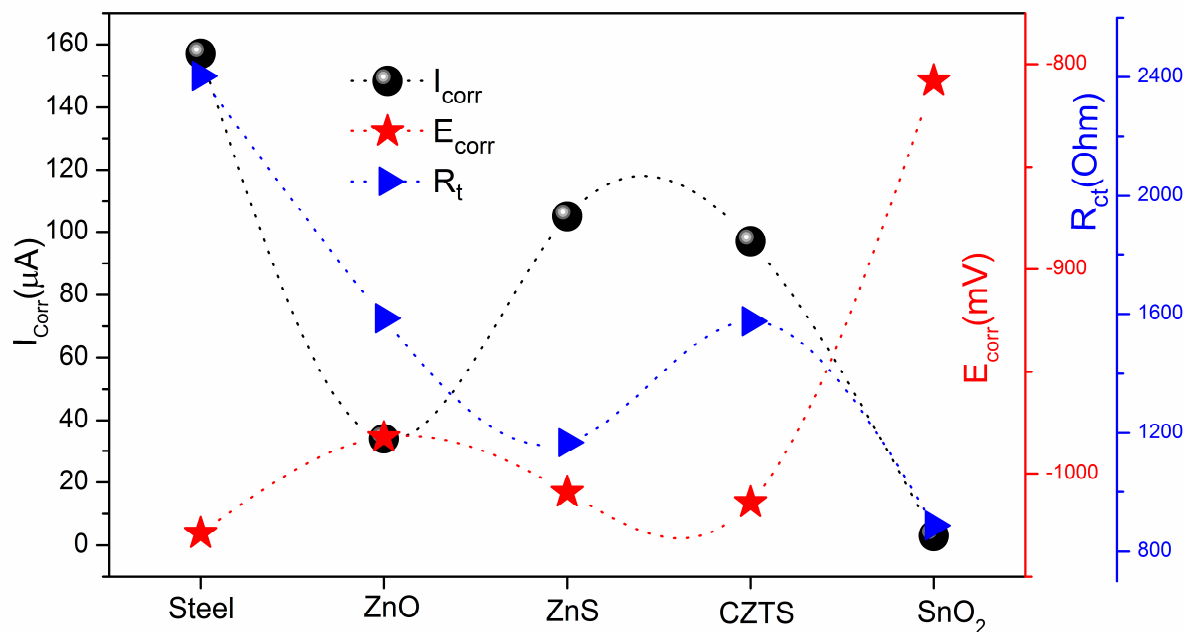


Fig. 25 Variations of corrosion current, corrosion potential and charge transfer resistance for various coating at T= 350°C.

2.3. Protection efficiency

The image below represents a bar graph expressing the percentage of corrosion protection of uncoated steel and coated with different materials. The coatings were formed at T=350°C and at the same time the steel was heated at the same temperature. The SnO₂ coating has the highest protection ratio of 98%, indicating that it has good resistance to corrosion followed by the ZnO coating with 82%, as for ZnS coating and CZTS coating. The uncoated steel protection efficiency was weak and this is due to the of effective resistance against corrosion.

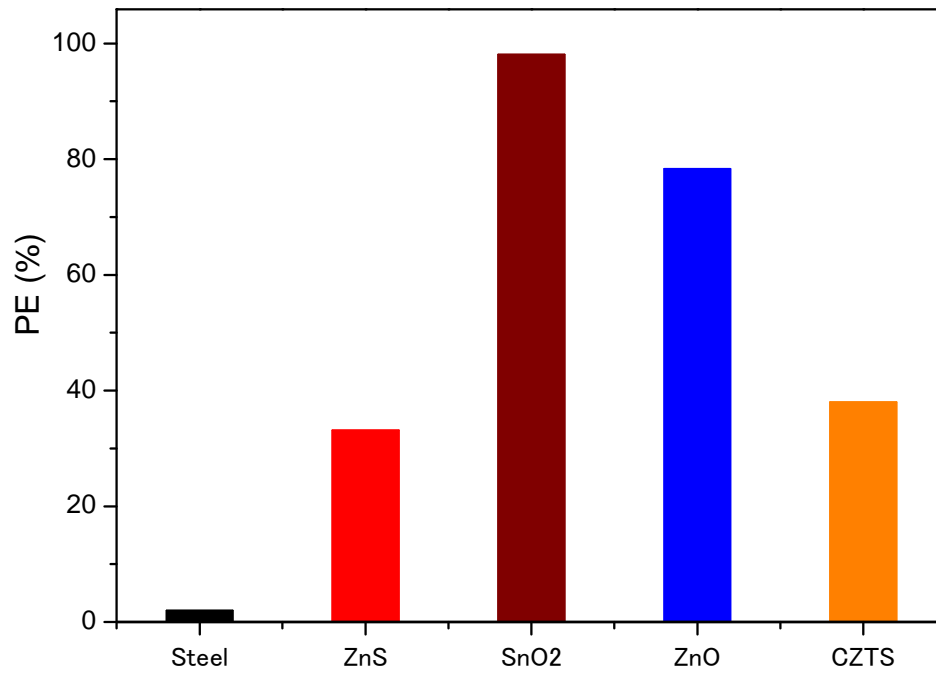


Fig. 26 The protection efficiency for the as sprayed coatings and uncoated steel disks.

***General
conclusion***



General conclusion

General conclusion

In this work, an economical coatings were successfully prepared by the spray technique on the Steel disks. The performance of these coatings for corrosion protection have not been reported.

Firstly, we have studied the influence of deposition temperature on the corrosion protection of the coatings. An optimum deposition temperature was found to be around 350°C, where the majority of the prepared coating possessed the highest corrosion resistance.

The SnO₂ coating presented the highest protection efficiency of 98%, indicating a good resistance to corrosion followed by ZnO coating with 82%, as for ZnS coating and CZTS coating.

In addition to good sealing and barrier properties, SnO₂ coatings have other characteristics including high chemical and mechanical stability, good adhesion to the steel surface and high durability.

SnO₂ coating showed promising results for corrosion protection of Steel and the results implied suitability of these coating for corrosion protection in aggressive medium.

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Abstract



Abstract

ملخص

التآكل هو أحد أهم المشاكل والصعوبات التي تواجه العالم. حيث يعتبر ظاهرة طبيعية تتعرض لها المعادن عموماً والحديد الصلب (الفولاذ) بشكل خاص. في عملنا هذا تطرقنا إلى حماية الحديد الصلب وذلك بتشكيل العديد من الطلاءات على عينات الحديد، أكسيد الزنك (ZnO)، كبريتيد الزنك (ZnS)، أكسيد القصدير (SnO₂) و طلاء كبريتيد الزنك، النحاس و القصدير (CZTS) بطريقة الرش الكيميائي. خضعت العينات لاختبار مقاومة التآكل وذلك عن طريق التحليل الكهروكيميائية والمتمثلة في الاستقطاب الخطي ومطيافية الممانعة الكهروكيميائية. أظهرت النتائج أن طلاء أكسيد القصدير (SnO₂) يتمتع بمقاومة فعالة نسبياً ضد تآكل الفولاذ في وسط ملحي مقارنة بمختلف الطبقات الأخرى.

