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BEN HAMED DJIHANE & SENOUSSI OMAYMA

A corrosion study of NiO thin films deposited on mild steel in acidic chloride environments

Jury:

Ms KRAIBAA OUM KELTOUM	MCA	Mohamed Khider University of Biskra	President
Mr DJAIL KAMEL	MAA	Mohamed Khider University of Biskra	supervisor
Mr SELLAMI MOHAMED	MCB	Mohamed Khider University of Biskra	Examinator

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Abbreviations

Å: Ångström (1 Å = 10^{-10}m)

°C: Degrees Celsius

CCD: charge-coupled device

C.F.C: Cubic structure with center face.

CVD: chemical vapour phase methods

E (%): The inhibitory efficiency

EDX: energy dispersive X-ray spectroscopy

DRX: X-Ray Diffraction

GMR : Magneto resistances

HCl : hydrochloric acid

In_2O_3 : indium oxide

MET : Transmission Electron Microscope**.**

Ni(NO3)2·6H2O : nickel nitrate hexahydrate

NiO: Nickel Oxide

OLED : Organic light emitting diode

PVD : physical vapour phase

SCE :calomel electrode

SEM : Scanning Electron Microscopy

S.I.E. : Electrochemical impedance spectroscopy

SPT : spray pyrolysis technique

STEM: Scanning Transmission Electron Microscopy

TCO : Conductive transparent oxides

$\boldsymbol{\sigma}$: $\boldsymbol{Electrical\ conductivity}$.

Acknowledgments

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Finally, we thank our families
and friends who supported and
encouraged us.

djihane

&

omayma

Dedication

I dedicate this modest work which is the fruit of my efforts to those I love most to my moral support and source of joy and happiness.

To the one who made me a woman who always asked for success, and he was the strongest bond of my life.

my father

To the dearest of my life, to the affectionate heart.

my mother

To my dear brothers, whose my life is worth nothing without them.

abdelsamade & abdelrahmane.

To the two stars that light up my life and I can't imagine my life without them, my two sisters:

Hanane & Imane

To my little sweet **Djana**

To my dear Professor Supervisor **Djail Kamel**

To all my friends, particularly: Omayma, Nadjlaa, Amina Imane, Monira, Amani, Lamia, yassmine, Alima, Selma.

Djihane

Dedicate

Thank God who guided us to this moment, and we would not have arrived without God's blessing on us.

I dedicate this humble work to my mother, God preserved her,and my Father,

may God rest in rest,

for mewho has watched and worked hard for me to complete this work from near or farto my Professor Supervisor Djail Kamel,

and to my family.. my brothers Amina, Nour, Maryam, my dear brother Abd allah and all my loved ones my second family the Bolouci̇f family, And the Boucina family, and all my loved ones that I miss (God's mercy),

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Omayma

General Introduction

General Introduction

Corrosion is an electrochemical material degradation that affects every sector of our economy, from electronics to energy transportation and biomaterials. Corrosion is estimated to damage a quarter of the world's yearly alumina production, or around 150 million tons per year, Corrosion is a significant economic challenge, and replacing corrosive materials on a regular basis has been a significant financial burden for the industry. This is what has caused the chemical industry to be on the lookout for new materials that may be manufactured in a more cost-effective and efficient manner this environment, there are numerous techniques to protect minerals against corrosion, including the use of a protective barrier, boiling, Cathodic protection, or the application of rust or corrosion inhibitors.

Inhibitors are used to keep metals from dissolving, which is an unavoidable and widespread application. Corrosion inhibitors are chemicals that minimize or prevent metal from interacting with its environment when given to low quantities in corrosive conditions. A corrosion inhibitor works by adsorbing on the metal surface and slowing down the rate of corrosion. The majority of synthetic chemicals have good anti-corrosion properties.

The development of materials in the form of thin layers is of major interest in a wide range of applications. The interest of thin films comes from mainly the economic use of materials in relation to the properties and the simplicity of the technologies used to implement them. Thickness is the most important property of thin layers, as it determines the most of their physical properties. On the other hand, almost all the properties of the layers thickness and can therefore be used to determine it. results in a wide variety of measurement methods. The concept of thickness itself depends on the chosen measurement method. More precisely, the different measurement methods may give different results, that is, different thicknesses for the same film, there are Many methods such as pyrolysis spray, vacuum evaporation, cathode-ray spraying, laser ablation …, are currently used to deposit thin films of nickel oxide. Among these different methods, we chose the pyrolysis spray method.

The pyrolysis spraying method is based on a spray containing Atoms to be deposited, usually soluble chlorides or nitrates water or alcohol. Spray the solution on hot surface Chemical reactions producing thin films after evaporation of volatile products reaction. The temperature of the substrate allows the activation of the chemical reaction surface. The advantage of this technique is simplicity. It does not require a group pumping as almost all methods of thin layer deposition. We let us return in detail to this method in Chapter 2, since we Work on.

The objective assigned to this work is to study the corrosion in acidic chloride environments of nickel oxide (NiO) thin films deposited on steel by the spray pyrolysis method.

This work is divided into four chapters:

- The first chapter is a literature study on steel and corrosion. In this chapter, we will introduce some concepts about steel and then discuss corrosion. We begin by defining them, their types, causes, and treatments in preparation for the next point in this chapter, inhibitors, one of the ways to deal with corrosion.
- The second chapter will also be a bibliographic study on NiO specifically including its various characteristics and advantages as well. In this chapter we will address the definition of the technology used, which is Spray Pyrolysis technique with a mention of its principle and we conclude this chapter by mentioning some techniques to address these Layers, specifically optical microscope(OM), Scanning Electron Microscope(SEM), X-ray Diffraction(DRX) also Energy Dispersive X-Ray Analysis(EDX).
- We use Chapter 3 for all stages of producing thin NiO layers with the specified and mentioned parameters using spray pyrolysis.
- Finally, in Chapter 4, we collect all the results with analysis and interpretation.

  This work concludes with a general conclusion summarizing the main findings and will get close our research.

PART I

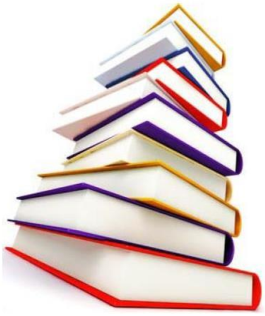
Bibliographic Study

Chapter I

Corrosion of metals and inhibitors.

Chapter II

NIO thin films deposition and characterization



Chapter I:

Corrosion of metals and Inhibitors

I. Steels

Steel plays a very important role in everyday life. It is used in many areas. It is at the origin of all scientific and industrial revolutions thanks to their properties.

I-1. History of steels

Extremely old steels, which is probably the first form of use of ferrous metals. It is indeed around 1000 BC that seems to go back to the discovery of these steels thanks to the technique of cementation and the art of hardening, which were found by chance, the iron absorbing carbon in contact with the organic material used to heat it to hammer it[1].

I-2. Steel definition

Steel is an iron-carbon alloy containing less than 2% carbon, and other elements. The iron in the steel comes from either ore or recycling. Steel produced in France, as in other developed countries, contains on average just over half of recycled iron. In emerging countries such as Brazil and China, steel is mainly produced from ore because there is still not enough recycling [2].

To transform the cast iron into steel, it is enough to rid it of its excess carbon by burning it with oxygen. The chemical composition of the liquid steel obtained from the cast iron or from the smelting of recycled iron must then be adjusted according to the desired application and use properties. The liquid steel is then solidified, generally in a fairly massive form, and then formed usually by hot rolling and possibly cold rolling for the thinnest sheets. Thin sheets can be coated with a very thin layer of another metal, for example tin for tinplate or zinc for galvanized sheets, or even coated with an organic coating (varnish, paint, etc.) before being delivered [2].

I-3.The different types of steels

Steels have a very large number of different grades; the various types of iron-based alloys can be classified according to their chemical composition or field of use. The adoption of the latter allows us to identify four families of steels [3]:

- General purpose carbon steels
- Thermal treatment steels, alloy or not
- Tool steels
- Stainless steels

I-3.1.Stainless steels

Stainless steels are widely used in areas where corrosion protection is important. These steels are used in several areas: orthopedics, instrumentation, food processing plants and metal construction. They resist the attacks of aggressive environments by protecting themselves from a passive film that gives them the quality of stainless[3].

The different types of stainless steel:

- Ferritic stainless steels.
- Austenitic stainless steels.
- Austenoferritic stainless steels (DUPLEX).
- Martensitic stainless steels.

I-3.2. Heat treatment steels

The process of heat treatment of a steel consists in subjecting it to a variation in temperature as a function of time. It consists of a number of heating and cooling operations. The aim is to improve the characteristics of the materials (breaking strength, increased yield strength, hardness) for a better adaptation to service conditions. This improvement is due to structural changes in the structure: better homogenization, improved grain size (it allows regenerate, for example, a metal that has undergone forging and has a coarse grain by refining the grains). It also reduces the internal constraints of materials, generated by its history, which can be harmful to the part [2].

I-3.3.Steels in pipelines

Carbon steels are the most widely used in pipeline construction. Because of their low cost, the mastery of the techniques of their development and their production they are widely used in the energy sector, such as drilling platforms, the transportation of oil or natural gas through pipelines or pipelines. These steels are usually of grades such as X60, X65, X52, and X70 [3].

I-3.4. Tool steels

Used in the manufacture of instruments (for shaping materials). The grades of tool steels are arranged according to the working mode of the tool, in four classes as shown in the table [4].

Table I.1: classes of tool steels [4].

Classes	Common characters
Carbon tool steels General purpose steels	Alloy steels for cold working
Alloy steels for cold working	High strength steels
Alloy tool steels for hot work	Thermal shock resistant steels
Fast steels	Carburized steels

I-4. Classification of steels according to chemical composition

Several classifications of steels are made on the basis of the chemical composition, the production process and the instructions for use. Some classifications are of interest. Iron and carbon alloys have been referred to as non-alloy steels or carbon steels, iron alloys with lower carbon content and other elements, generally metallic, as alloy steel [4].

a- Carbon Steel

Ordinary steels or carbon steels are standard general purpose steels. They make up about 80% of steel production[3]. Contain increasing proportions of carbon, higher proportions of magnesium than carbon, and traces of silicon and sulphurphosphorus [4].

Table I .2: Classification of steels by chemical composition [4].

Quality	**C**(%)	**Mn**(%)	**P**(%)	**Si**(%)	**S**(%)	**Allong** (%)
Extra soft	0.15	0.4	0.04	0.03	0.02	30
Soft	0.25	0.4	0.04 0.06	0.03 0.10	0.02 0.03	25
mid-soft	0.35	0.4	0.06	0.20	0.03	20
mid hard	0.45	0.5	0.06	.25	0.03	15
Hard	0.55	0.6	0.06	0.25	0.03	10
Extra hard	0.65	0.7	0.6	0.3	0.03	5

Table I.3: Ordinary steels or unalloyed carbon steels [3].

Nuance	Jobs
Extra soft	tôles pour carrosserie, feuillards, quincaillerie, pièces de forge
Soft	metal frames, profiles, common mechanical constructions, bolts, ordinary wires.
mid-soft	machine parts for mechanical applications, moulded parts or frames, forged parts.
mid hard	Small tools, agricultural machinery components, transmission components.
Hard	tooling, arming parts, slides, rails and bandages, springs, cutlery, moulded and processed parts.
Extra hard	machining and cutting tools, cables, springs.

b- Alloy steel

Composition varies according to use, the proportion of alloy elements generally varying between 0% and 5% [4].

Table I.4: the elements of alloy steels [4].

Alloy element	**Ratio**(%)
Carbon	0.2 - 0.7
Silicon	0.1- 0.7 2 – 4 (special steels)
Magnesium	0.1- 0.8 12 – 14 (very hard steels)
S,P,Cu,Ni,Cr,V,Mo	< 0.1

II- Corrosion

Metallic corrosion is the phenomenon whereby metals and alloys tend, under the action of atmospheric agents or chemical reagents, to return to their original state of oxides, sulphides, carbonates etc., more stable in the surrounding environment. It develops as a result, following different processes, each of which characterises a type of corrosion: chemical corrosion, bacterial corrosion and electrochemical corrosion. Corrosion of metals and alloys can then manifest in various aspects: generalized, localized, inter granular, by cracking etc [5].

II-1. Notions of metal corrosion

Corrosion is the chemical or electrochemical destruction of metal materials by their environment. This is, in fact, the phenomenon according to which metals tend to return to their natural state of oxide, sulphate, carbonate... more stable in relation to the corrosive medium, and thus to undergo a degradation of their properties. One might conclude from this that corrosion being the manifestation of the chemical affinity of metals for certain elements constitutes a branch of chemistry. Unfortunately, this purely chemical concept does not make it possible to interpret many corrosion phenomena, which involve a number of factors having a chemical, electrochemical, metallurgical, mechanical character, and often acting simultaneously [6].

II-2. Types of corrosion

II-2.1. Uniform Corrosion

This is a more or less regular loss of material over the entire surface. This attack is particularly found on metals exposed to acidic environments [5].

Uniform corrosion is a type of corrosive attack in which the corroded areas occur in a manner evenly distributed across the material being attacked. Uniform corrosion can render large amounts of material useless quite rapidly because the attack occurs across the entirety of the exposed surface[7].

Although uniform corrosion can be incredibly devastating, it is typically easily detectable and readily preventable[7].

FigureI.1: Uniform Corrosion [7].

II-2.2 .Localized corrosion

In practice, localized corrosion comes from a heterogeneity of the material or the environment and often it poses many problems [8]. So this is the most dangerous aspect of corrosion because the attack takes place in certain places on the surface of the metal.

The loss of mass is relatively low, but this type of corrosion is dangerous in the case, for example, of perforation of a pipe or container [9].

The main causes of this aspect of corrosion are [9]:

- Chemically heterogeneous metal surface.
- Potential difference in the different areas of the metal created by the deformation.
- Local damage to the passive layer.

There are Manny different types of localized corrosion witch are:

II-2.2.1.Pitting corrosion

It is a form of corrosion which is produced by certain anions, in particular chloride ions, on so-called "passivable" metals (aluminum, chromium, cobalt, copper, stainless steel, steel in concrete, etc.) which are protected by a passive oxide film. This form of corrosion is particularly insidious, the attack is limited to pitting, very localized and can progress very quickly in depth, while the rest of the surface remains unscathed. The installation can be perforated in a few days without an appreciable loss of weight of the structure appearing [10].

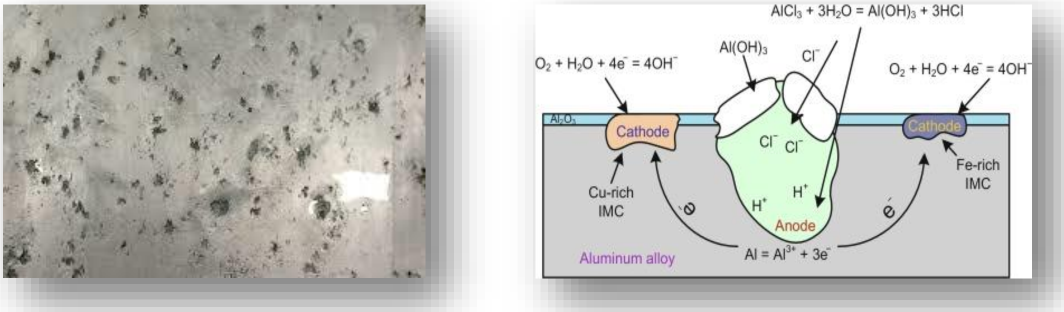


Figure I.2: Aluminum pitting corrosion [10].

II-2.2.2.Intergranular corrosion

It is a selective attack at the grain boundaries, often; these are phases, which have precipitated during a heat treatment.

It is a particularly dangerous type of corrosion because, although the amount of metal attack is small, the mechanical characteristics of the metal are altered because the cracks thus produced weaken the metal. For example; austenitic stainless steel heat sensitized by precipitation of chromium carbide at grain boundaries[11].

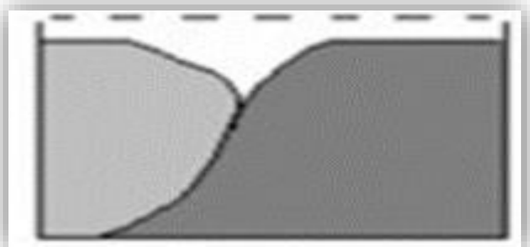
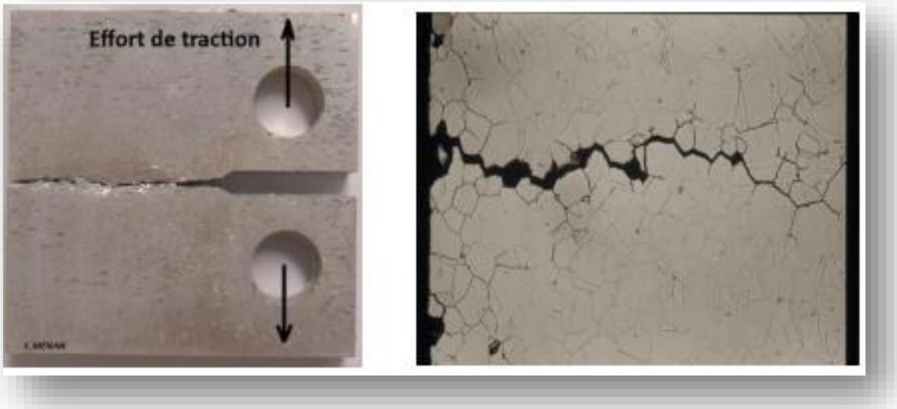


Figure I.3: Intergranular corrosion [6].

II-2.2.3.Stress corrosion:

This type of corrosion corresponds to a cracking of the metal resulting from a common action of a mechanical stress and an electrochemical reaction [12].



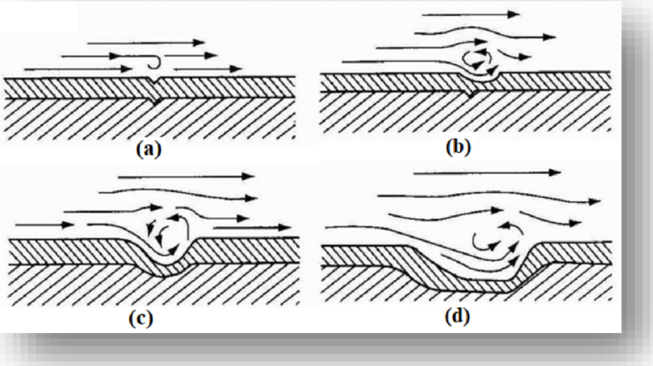
FigureI.4: Stress corrosion [12].

II-2.2.4.Erosion corrosion:

Corrosion-erosion affects many materials (aluminum, steel...) and is due to the joint action of an electrochemical reaction and a mechanical removal of the matter Figure [13].

Figure I.5: Corrosion-erosion in turbulent areas [13].

It is often favored by the strong flow of a fluid and develops gradually in three stages as depicted in the Figure [13].

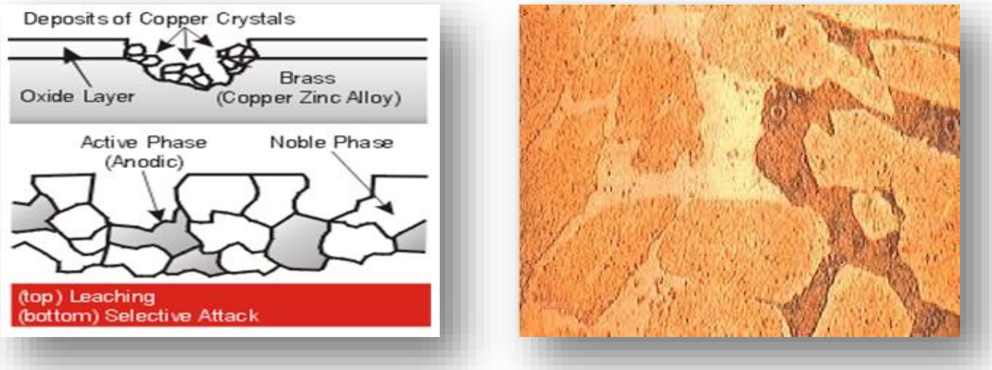


FigureI.6: Stages of development of the corrosion-erosion phenomenon [13].

II-2.2.5. Selective corrosion:

As its name suggests, this mode of corrosion results in the selective dissolution of one of the elements of the alloy if it is homogeneous, or of one of the phases if the alloy is polyphaser, thus leading to the formation of a porous metal structure.

De-zincification (selective dissolution of zinc) in a brass is the best known example.



FigureI.7: Mechanism of selective corrosion of a brass (copper-zinc alloy).

II-2.2.6.Galvanic corrosion:

Galvanic or bimetallic corrosion can be defined simply by the effect resulting from contact of two different metals or alloys in a conductive corrosive environment. This contact leads to the formation of an electrochemical battery between the two metals or alloy. The least resistant, less noble metal degrades and its degradation intensifies over time [10].

This corrosion can be avoided either[13]:

- A suitable choice of materials;
- separating the various metals into low-cost, easily replaceable sacrificial parts;
- Embedding metals that touch into an insulating polymer (this is the solution adopted by electronics engineers).

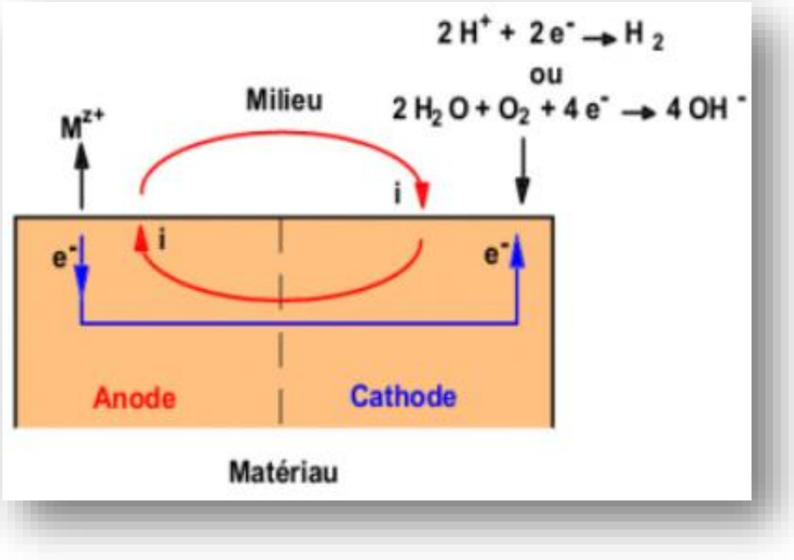


Figure I.8: Schematic representation of a corrosion stack [13].

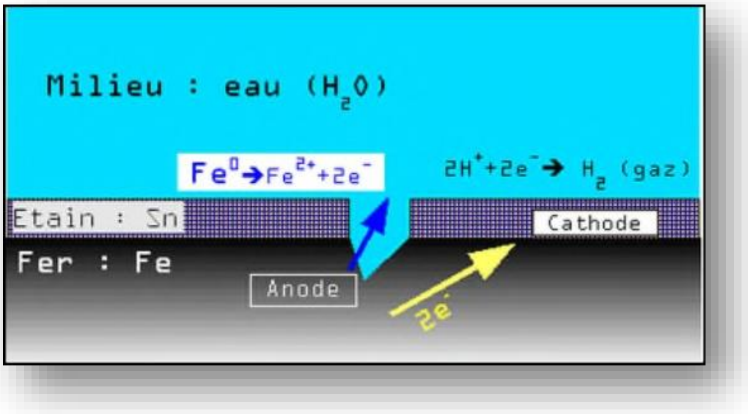


Figure I.9: Galvanic corrosion of iron by coupling with tin in the marine environment [13].

II-2.2.7.Corrosion by crevices:

Cavernous corrosion or corrosion by crevices is a form of corrosion by differential ventilation (difference of accessibility of oxygen between two parts of a structure) thus creating an electrochemical battery. A selective attack of the metal is observed in the slits and other places not easily accessible to oxygen. The first recommendation to avoid cavernous corrosion is to optimize the design of the room so as to avoid any artificial cavern. An artificial cavern can be created by an improperly fastened joint, an un-abraded or bad weld, deposits, gaps between two sheets, etc [14].

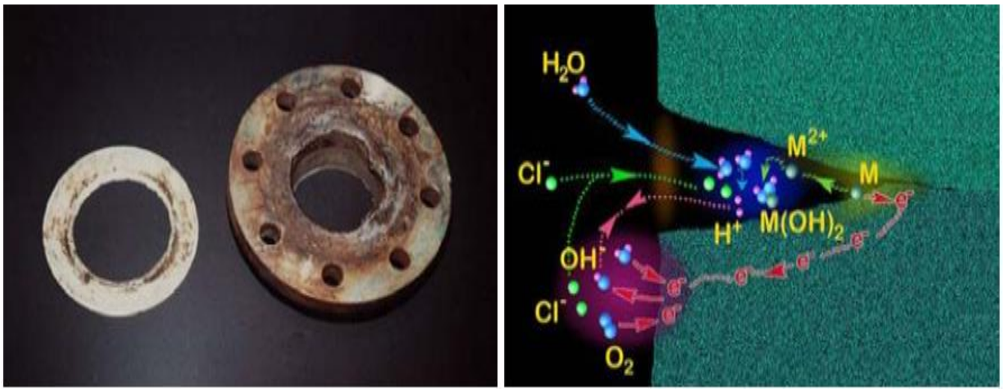


Figure I.10: Appearance and attack mechanism of corrosion by crevices (cavernous) [14].

II-3. Classification of different types of corrosion

II-3.1. Chemical or dry corrosion

This is a heterogeneous reaction between a solid phase (metal) and a gas phase. The oxidation process of chemical corrosion reduction takes place in the atomic domain with the ambient environment without the presence of electrolyte. So purely chemical corrosion does not involve the passage of an electric current, an electronic flow ceases, because the exchange of electrons between the different reaction partners takes place directly. The air contains oxygen, water vapour and acidic vapours (carbon dioxide CO_2 and sulphur dioxide SO_2, hydrogen sulphide Sli_2 etc.) these are the corrosive agents but most often it is the CO_2. It is assumed that the formation of rust is then the result of the action of all these bodies, but an acid must be present, even in weak protection for the attack to occur [15].

The attack of the metal by a chemical reaction with the surrounding environment without intervention of the electric current generally requires high temperatures, the reaction that occurs is of the form [16]:

$$A_{solide} + B_{gaz} \rightarrow AB_{solide}$$

It is very difficult to give examples of purely chemical corrosion, since it is usually accompanied by electrochemical corrosion. The chemical corrosion of a metal by another liquid metal (Hg), by a single molten metal or by an aqueous solution (A1 in Ccl4) can be regarded as an example of dry corrosion in an oxidizing atmosphere at high temperature[16].

II-3.2. Biochemical corrosion

This is the bacterial attack of metals especially in buried pipes. The mechanism of this corrosion mode can be of several types [16].

a -Chemical by production of corrosive substances such as $CO_2, H_2S, H_2SO_4, NH_3$or an organic acid, the most common case is that encountered in buried pipes and determined by the formation of sulphuric acid which attacks the metal[17].

b-Some bacteria can reduce sulphate by the hydrogen intermediate [17].

$$\boldsymbol{SO_4^{2-} + 8H \rightarrow S^{2+} + 4H_2\mathrm{O}}$$

Hydrogen, for example, comes from cathode regions, so there is depolarization of cathodes and accelerated formation of $\boldsymbol{Fe^{2+}}$at anodes [17].

$$\boldsymbol{S^{2-} + Fe^{2+} \rightarrow \mathrm{FeS}}$$

c- In some cases, adhering deposits resulting from the attack can be observed on the pipes, not of the metal itself, but of certain constituents of the ambient environment by bacteria. This results in pitting of the metal at the site of deposition, following a corrosion process by difference in oxygen concentration [17].

II-3.3. Electrochemical corrosion

Electrochemical corrosion, also known as wet corrosion, is the most important and common form of corrosion. It resides essentially in the oxidation of the metal in the form of ions or oxides [18].

Electrochemical corrosion involves both a chemical reaction and a transfer of electrical charges. The existence of these heterogeneities, either in the metal or in the reagent, determines the formation of a battery and thus an electric current circulates between anodes and cathodes in the reagent and the zones that make up the anodes are attacked (corroded). It requires the presence of a reducer; H2O, H2 ....Without it, corrosion of the metal (anode reaction) cannot occur [18].

II-4. Reactions and corrosion factors

II-4.1. Corrosion reactions

The general corrosion was the result of two simultaneous reactions electrochemical uniformly distributed on the surface of the material [19]:

The anodic reaction, which corresponds to the oxidation of the metal (formation of an oxide, passage in solution), and the cathodic reaction which corresponds to the reduction of the oxidant present in the medium (H^+, dissolved O_2...). In general, the corrosion reactions of a metal (M) can be summarized as follows [19]:

Metal loses electrons, it's the oxidation reaction.

$$\boldsymbol{M \rightarrow nM^+ + ne^-}$$

Where n and Mn^+ are the numbers of charges and the metal ion respectively.

The reduction response depends on the medium. Two cases can be distinguished [19]:

- Acid medium

Without dissolved O_2: $\mathbf{M \rightarrow nM^+ + ne^-}$

With O_2 dissolved: $\mathbf{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O}$

- Neutral or basic medium

With O_2 dissolved: $\mathbf{O_2 + 2H_2O + 4e^- \rightarrow 4OH^-}$

II-4.2. Corrosion Factors

Corrosion phenomena depend on a large number of factors generally related to each other in a complex way that can react with a synergistic effect [20]. These factors are of two types: external and internal and are summarized in Table I.5 [21]:

Table I.5: Corrosion Factor [20][21]

Factors relating to the environment and defining the mode of attack	○ Concentration of the reagent; ○ Oxygen content, impurities, dissolved gases (CO_2, H_2S, NH_3) ○ Acidity (pH) of the medium, salinity, temperature, pressure; ○ Presence of bacteria.
metallurgical factors	○ alloy composition, crystalline heterogeneities ○ Development processes. ○ Impurities in the alloy, inclusions. ○ Heat and mechanical treatments. ○ Protective additions.
Factors Defining the Terms and Conditions of Employment	○ Surface condition, manufacturing defects. ○ Shapes of parts. ○ Mechanical loads. ○ Use of inhibitors. ○ Assembly processes (galvanic couples, welds, etc.) ○ Surface oxide crust. ○ External electromotive force (electrolysis).
time-dependent factors	○ Aging; ○ Temperature; ○ Modality of access of oxygen or other dissolved gases; ○ Appearance of a deposit (calcium or other). ○ Internal or external mechanical voltages. ○ Modification of protective coatings.

II-5. Corrosion speed

The corrosion rate of a metal in a corrosive medium depends both on the characteristics of these two parameters. Temperature and pH have a direct influence on the corrosion rate, and an indirect influence through the aqueous phase. The flow conditions, the film formed on the metal surface and the pressure have a direct influence through the partial pressure of the CO_2 [22].

1- Effect of temperature

Generally, the increase in temperature accelerates the corrosion phenomena, as it decreases the stability domains of the metals and accelerates the kinetics of reactions and transport. The extent of its influence differs, however, depending on the corrosive medium in which the material is found [22].

2- Effect of acidity

The material's susceptibility to corrosion depends on the pH of the electrolyte. A high proton concentration in the solution increases the aggressiveness of the medium, which changes the equilibrium of chemical and electrochemical reactions. Corrosion increases as the pH of the medium decreases [22].

3- Salinity

Chlorides are aggressive ions, often at the origin of localized corrosion, their presence in solution is accompanied by complementary effects, on the one hand, their local concentration induces acidification of the environment and on the other hand, Salinity influences the conductivity of the medium [22].

II-6. Corrosion of carbon steels in acidic environments

Acid media are widely used in the operations of stripping, descaling, removal of localized deposits. In the oil industry, the use of hydrochloric acid solutions is considered the least costly. These environments are highly corrosive and are aggressive environments for metals and alloys. Despite the qualified qualities of steel, it has the major disadvantage of rapidly oxidizing when subjected to an acidic medium and offers a very low resistance to corrosion [23].

Corrosion is now responsible for a large number of economic and environmental damages and affects many areas. It is estimated that each year, a quarter of steel production is destroyed by corrosion, amounting to about 150 million tons per year, or 5 tons per second[23].

The losses caused by corrosion are significant. Direct losses include the cost of the protective coating, replacement of corroded materials, and indirect losses such as repair, loss of production. Corrosion is not only a source of waste of raw materials and energy, it can also cause serious accidents and contribute to the pollution of the natural environment. This corrosion could lead to an ecological tragedy and major loss of life, if oil spilled through a pipeline hole, or if the fire caught at the accidental opening of a corroded point [23].

These losses can be saved by better knowledge of the causes of corrosion and better application of protective techniques [23].

II-7. Mechanism of corrosion of carbon steels in acid medium

When an acid comes into contact with the carbon steel, an immediate attack on the metal takes place with the formation of hydrogen gas and the ferrous ion, as shown by the reactions [6].

a. Anode reaction (oxidation): $\boldsymbol{Fe \rightarrow Fe^{+2}+2é}$

b. Cathodic reaction (reduction): $\boldsymbol{2H^{+} + 2é \rightarrow H_{2}}$

So the corrosion of the carbon steel is due to an irreversible oxy-reduction reaction between the metal (Fe) and an oxidizing agent (H+), as shown by the overall reaction [6].

$$\boldsymbol{\mathrm{Fe} + 2H^{+} \rightarrow Fe^{+2} + H_{2}}$$

III- corrosion inhibitors

A corrosion inhibitor is a chemical substance that, when added in small quantities to a medium, effectively reduces the corrosion rate of the metal. They can act on the metal by modifying its surface state or by intervening on anodic or cathode reactions, they form a mono molecular layer on the metal by creating a barrier with the external medium [24].

III-1. Protection against corrosion

Several approaches have been used to completely reduce or inhibit metal corrosion. These methods of prevention, whether they are applied to new materials or to materials already in service, are numerous; they can be classified in 4 groups[25]:

- ❖ Action on the material:choice of metal mechanical, thermal or chemical treatment, etc..
- ❖ Action on the environment: change in pH, humidity, temperature, speed (in the case of a fluid), etc… use of a mineral or organic corrosion inhibitor.
- ❖ Added coating on metal (metal, paint, plastic).
- ❖ Action on electrochemical corrosion process:
  - cathodic protection
  - anode protection.

III-2. Use of inhibitors

Although their use can theoretically be envisaged in most cases of corrosion (with, as main limitations, too large a volume of the corrosive medium or the possible impossibility of incorporating additives), inhibitors have several traditional areas of application [26]:

- Water treatment (sanitary water, industrial process water, boiler water, etc.).
- The petroleum industry: drilling, extraction, refining, storage and transportation; at all stages of this industry, the use of corrosion inhibitors is essential for the safeguarding of installations.
- Temporary protection of metals, whether during acid stripping, facility cleaning or atmospheric storage (volatile inhibitors, incorporation into temporary protective oils and greases) or for the treatment of cutting oils.
- The metal paint industry where inhibitors are additives to protect metals from corrosion [27].

III-3. Classification of Corrosion Inhibitors

There are several ways of classifying inhibitors, which differ from each other in various ways (Figure). Simple rankings can be offered [26].

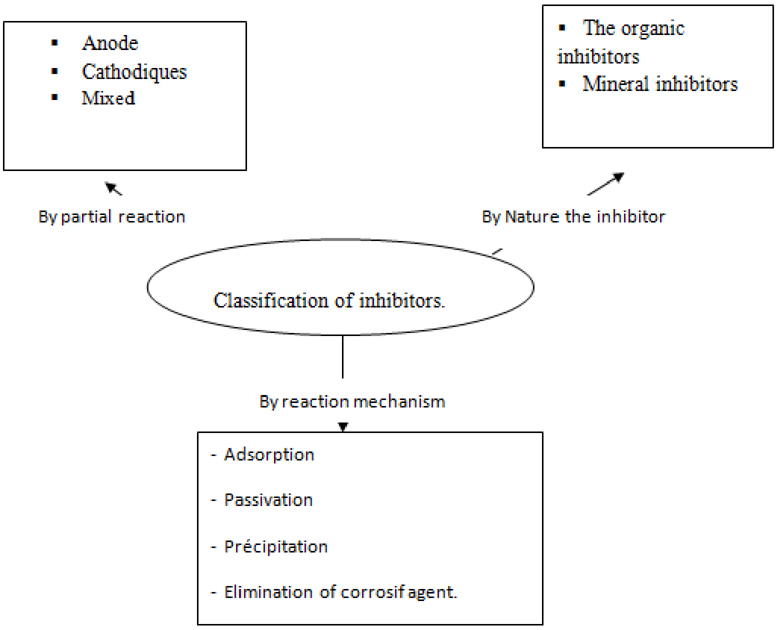


Figure I.11: Classification of corrosion inhibitors [26].

III-4- Nature of the inhibitor

III-4.1. The organic inhibitors

Organic inhibitors are a very important group of corrosion inhibitors and are frequently used in acidic environments. These inhibitors have at least one atom serving as an active center for their adsorption on the surface of the metal such as nitrogen (amines, quaternary ammonium, amides, imidazolines, triazoles, etc.), oxygen (acetylene alcohols, carboxylates, oxadiazoles, etc.), sulphur (derived from thiourea, mercaptans, sulfoxides, thiazoles, etc.) or phosphorus (phosphonates) [28].

III-4.2. Mineral inhibitors

Mineral molecules are most often used in near-neutral environments, or even in alkaline environments, and more rarely in acidic environments. The products dissociate in solution and it is often their dissociation products that ensure the inhibition phenomena (anions or cations). The inhibitory cations are essentially Ca^{2+} and Zn^{2+}those that form insoluble salts with certain anions such as hydroxyl OH^{-}The main inhibitory anions are the oxo-anions of type XO_4^{n-} such as chromates, molybdates, phosphates, silicates, etc.

The number of molecules in use at the moment is shrinking, because most effective products have a harmful side for the environment. In this context, a process has been developed, in collaboration with the Société Nouvelle des CouleursZinciques (SNCZ), to prepare new chromium III organic complexes and other cations (Zn^{2+} ,Ca^{2+} ,Mg^{2+} ,Mn^{2+},Sr^{2+},Al^{2+} , Zr^{2+} , Fe^{2+} ...) effective against corrosion and non-toxic [26].

III-4.3 Surfactants

Compounds dissolved in a solvent, which may reduce the surface tension of the solvent, even at very low concentrations, are called surface agents or surfactants. These substances are characterized by an essentially linear structure. Two parts are distinguished:

- The a polar hydrophobic hydrocarbon part, compatible with apolar solvents;

- The polar hydrophilic part, consisting of a functional group, whether ionised or not, but having an affinity for water. This structure allows them to adsorb preferentially to the surface of liquids and to the solid-liquid or liquid-liquid interfaces by modifying the interfacial tension [5].

III-5. Compounds used as corrosion inhibitors in acid environments

In acid environments, the most frequently used inhibitors are molecules of organic type. These inhibitors act first by adsorption on the surface of the metals, even before intervening in the reactive processes of corrosion to decrease their speed [29].

Corrosion inhibition by the use of organic compounds usually results from their adsorption to the metal surface. The phenomenon can be highlighted by [29]:

- The study of adsorption isotherms.
- Examination of the surface using specific techniques: scanning electron microscopy and photo-electron spectroscopy. Knowledge of the factors influencing the phenomenon of adsorption of inhibitors is essential to better understand the mechanism of inhibition of these substances.

Compounds containing heteroatoms N and S have been shown to be good corrosion inhibitors. Heckerman has shown that increasing the electronic density on nitrogen atoms leads to better inhibitory efficiency. Compounds containing nitrogen heteroatoms showed better inhibitory efficacy in acid environments. The use of compounds containing sulphur atoms in the inhibition of corrosion in sulphuric medium showed a better inhibitory efficiency, which is of the order of 90% for concentrations equal to 10^{-3}M [29].

Mixed inhibitors, with hydrophobic groups that have polar groups such as N, S, OH are effective. Organic polymer compounds such as amine and aminoalcool (AMA) are also used[29].

IV - Corrosion assessment methods

The experimental techniques used to evaluate corrosion can be electrochemical or non-electric. These methods include [30]:

IV-1- Gravimetric method

This method is relatively simple, does not require extensive equipment, but does not allow the approach of the mechanisms involved in corrosion.

It consists of exposing surface samples (S) in a corrosive medium maintained at constant temperature for a time (t), and measuring the mass difference of (Δm) samples before m_i and after m_f each test. The corrosion rate is given by the following relationship [30]:

$$V_{corr} = \frac{\Delta m}{S.T}$$

- ✓ V_{corr}can be expressed in mg /cm². h
- ✓ Δm = m_i –$m_f$mass loss expressed in mg
- ✓ S: exposed sample area in cm²
- ✓ t: immersion time in h

Inhibitory efficacy is given by the following relationship:

$$\text{EI\%} = \frac{V_{corr}-V_{corrinhib}}{V_{corr}} * 100$$

With (V_{corr}) and ($V_{corrinhib}$) are the corrosion rates of the sample after immersion in the solution respectively without and with inhibitor.

It is fundamental to provide error bars in these results as the presence of defects in the analyzed metal sample could significantly affect the analysis. The reproducibility of the measurement must therefore be checked [30].

IV-2- Electrochemical methods:

The electrochemical methods used to study the corrosion phenomenon can be divided into two categories:

A- Stationary methods:

- Tafel Method

This method makes it possible to determine experimentally the electrochemical parameters of a metal in contact with an electrolyte. It uses portions of the curve [Log i = f(E)]], the relationship between corrosion current and electrode surge η (η=E – Eeq), is given by the simplified formula of the Butler Volmer fundamental equation[28].

$$\text{I} = I_a + I_c = I_{corr}(e^{\frac{\propto nf}{RT}\eta} - e^{\frac{(1-\propto)nf}{RT}\eta})$$

After simplifying the Butler-Volmer relationship, we obtain a relationship between the electrode surge and the logarithm of the measured current density named by the Tafellaw [28]:

$$\text{Log I=a+}\frac{\eta_a}{b_a}\text{for the anode branch}$$

$$\text{Log I=a+}\frac{\eta_c}{b_c}\text{for the cathode branch}$$

b_aAndb_c the Tafel slopes of anodic and cathode reactions such as:

$$b_a = \frac{2{,}303RT}{\propto nF}$$

$$b_c = \frac{2{,}303RT}{(1-\propto)nF}$$

- Determination of electrochemical parameters from Tafel lines At corrosion potential

$$E = E_{eq}\ (\eta = 0),\ \text{current } I = I_{corr}$$

$$\text{Corrosion rate:} V_{corr} = \frac{I_{corr}}{nFA}$$

A: the surface area of the sample.

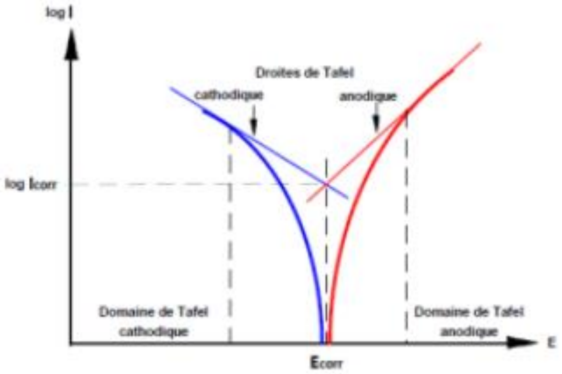


Figure I.12: Tafel lines at corrosion potential [28].

B- **Transient method**

- electrochemical impedance spectroscopy

Non-stationary methods can be classified into two categories: high amplitude disturbance methods (cyclic voltammetry) and the low amplitude method (electrochemical impedancemetry). Previous work has shown that electrochemical impedance spectroscopy (S.I.E.) is likely to identify the elementary steps involved in the global process taking place at the metal/solution interface, in the form of various time constants. The S.I.E. is used today in the following fields [31]:

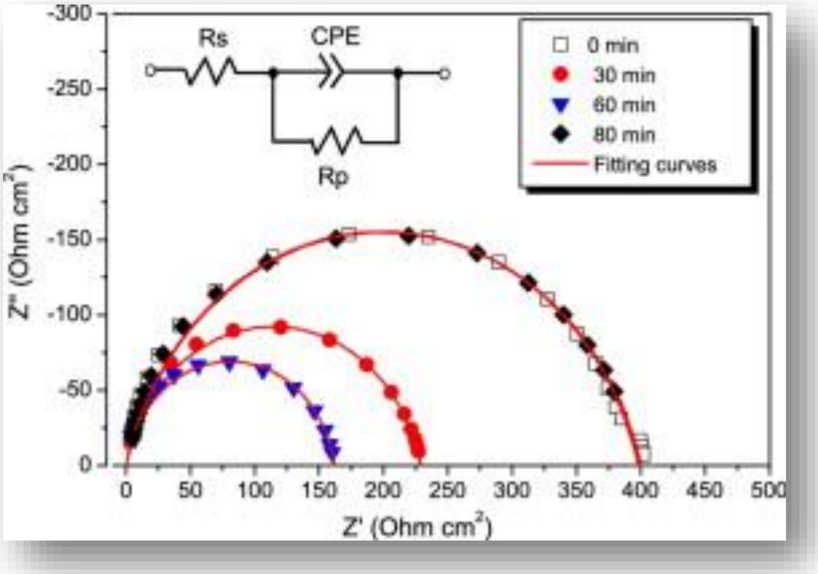
- Photo electrochemistry.

- The semiconductor/electrolyte interface.

- Organic electrochemistry and the study of adsorption phenomena.

- Bio electrochemistry.

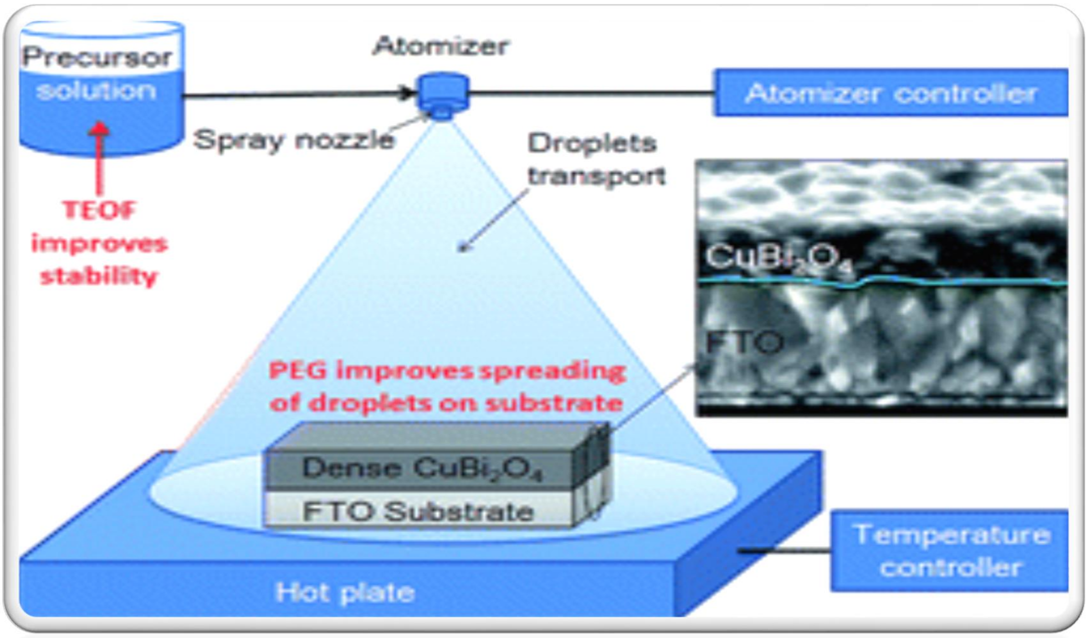
- Corrosion and its inhibition.



FigureI.13: Electrochemical impedance spectroscopy [32].

Chapter II:

NiO thin films deposition and characterization.



I-1.Transparent and conductive oxides

Conductive transparent oxides (TCO) are materials that combine both electrical conductivity and optical transparency in the visible (wide gap). The existence of materials simultaneously showing these two properties has been known for several years.

Several TCO materials were subsequently discovered, including zinc oxide (ZnO), Nickel Oxide (NiO), indium oxide In_2O_3, and tin oxide SnO_2.

In the early years, TCO are presented as degenerated semiconductors of type n and therefore their use has been limited to passive applications. The recent discovery of conductive and transparent p-type materials has opened the door to the development of active electronic devices based entirely on these materials [33].

I-2. Nickel Oxide NiO

The prospects for using nanomaterial's in number of applications is being widely researched today across multiple domains such as biology, physics, chemistry, cosmetics, optical components, pharmaceutical drug manufacture, polymer science, mechanical engineering, and toxicology [34] .

Among the various nanomaterials, metal oxides (with NiO inclusive) have attracted increasing technological and industrial interest. This interest has mainly to do with their properties (optical, magnetic, electrical, and catalytic properties) associated with general characteristics such as mechanical hardness, thermal stability or chemical passivity [34].

I-2.1. Definition

Nickel oxide known as (bunsenite) is a basic oxide. It is in the form of a greenish gray powder depending on the method of preparation. It is a transition and antiferromagnetic material [35].

Nickel oxide (NiO) is the most exhaustively investigated transition metal oxide. It is a NaCl-type antiferromagnetic oxide semiconductor. It offers promising candidature for many applications such as solar thermal absorber, catalyst for O_2 evolution [36].

photoelectrolysis and electrochromic device . Nickel oxide is also a well-studied material as the positive electrode in batteries . Pure stoichiometric NiO crystals are perfect insulators. Several efforts have been made to explain the insulating behavior of NiO [36].

Figure II.1: nickel-oxide-powder [37] .

Table II.1: General properties of nickel oxide [35] .

The Property	**The value**
Chemical formula	NiO
Boiling point	> 2000 (° C)
Solubility in water	1.1(mg / L) at 20 ° C insoluble
Melting point	1955 (° C)
$\boldsymbol{\Delta H_f}$ for metal oxide formation per oxygen atom at 298k	245.2 (KJ / mole of atoms)
Entropy $\boldsymbol{S}^0$	38.00(JK-1.mol-1)
Molar mass	74.6928 (g/mol)
Volumetric Density	6.67
Type of conductivity	P-type
Dielectric constant	10
Refractive index (nD)	2.18

I-2.2. General properties of NiO

a- Crystallographic and structural properties

The crystallographic structure of nickel oxide is shown in the figure. This compound crystallises in a cubic structure with centered faces (CFCs) of type NaCl [33].

Its crystalline parameter is in the order of a = 4.177 Å and its density is 6.72 g/cm3. This cubic structure consists of two similar sub-arrays A and B so that every atom in sub-array A has only neighbors belonging to sub-array B and vice versa [33].

The anion (O^{-2}) and the cation (Ni^{+2}) have a CFC structure. Ion rays: R (Ni^{+2})= 0.72 Å and R (O^{-2})=1.40 Å. The plan (100) is a mixed plan consisting of 50% nickel and 50% oxygen. The planes (111) are alternately, pure Ni, pure O. The face (111) is a polar face (not stable) while the face (100) is a non-polar face (stable). The inter-reticular distance between two planes of different nature is 0.120 nm and is almost double between two planes of the same nature [33].

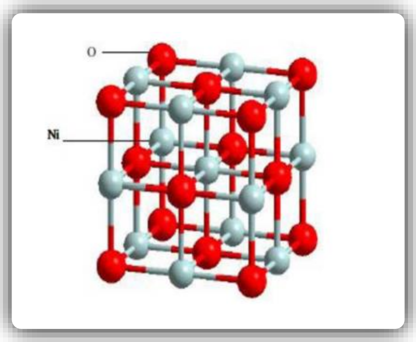


Figure II.2: Nickel oxide cfc structure [33].

b- NiO electrical properties

Nickel oxide is a semiconductor material type p, extrinsic, the mechanism of origin of electrical conductivity type p in the NiO film is discussed from the point of view of vacant nickel or oxygen, it is recognized that the majority of defects in oxide are cationic deficiencies so that oxide (semiconductor type p). NiO thin films usually have a p-type conduction due to holes generated by Ni gaps, having a low p-type conductivity according to the preparation mode. Conductivity varies between $10^{-2}\ cm^{-1}\ \Omega^{-1}$à 500K and $10^{-1}cm^{-1}\Omega^{-1}$à 30 K [38].

Table II.2: Some NiO electrical properties[38].

Element	**Unity**	**Game**
Conductivity.σ	$(\Omega \cdot Cm)^{-1}$	0,1-1
Mobility. µ	$Cm^2/_{V \cdot S}$	0,1-1
Electronic density.n_v	Cm^3	10^{18}-10^{19}
Dielectric constant	without unity	11,9

c- Electronic Properties

The electronic structures of oxygen and nickel forming the NiO semiconductor are:

O : $1\boldsymbol{S}^2 2\boldsymbol{S}^2 2\boldsymbol{p}^4$

Ni : $1\boldsymbol{S}^2 2\boldsymbol{S}^2 2\boldsymbol{P}^6 3\boldsymbol{S}^2 3\boldsymbol{P}^6 3\boldsymbol{d}^8 4\boldsymbol{S}^2$

Nickel oxide is among the transition metals. The magnetic property of this compound is due to the existence of the band d. The band d can contain n total of 10 electrons and its width is of the order of 5 eV. The 3D electron underlayment energy level responsible for magnetism was slightly higher than that of the 4S conduction underlayment [33] .

The majority and minority bands overlap because of the weakness of intra-atomic exchange. In addition, the 2p band of oxygen mixes (overlays) with the bottom of the majority band so that the separation between the two majority sub-bands disappears. However, the gap persists between the two minority sub-bands (0.4 eV) and is of vital importance in explaining NiO s' semiconductor behavior [33] .

d- **Optical properties**

The material nickel oxide from the transparent conductive oxides (TCO) which have high conductivity and lighting gap energy directly, NiO is green due to strong absorption in violet (2.75 – 2.95 eV) and red 1.75 eV. In case of excess oxygen, namely Ni is oxidized by directly oxygen or doping with Li+, high absorption coefficient of the green range (1.75 – 2.75 eV) is expanded and NiO appears as black. Band gap of NiO thin films changes with the deposition technique in between 3.6 and 4 ev. To understand the electronic structure of NiO, various optical experiments have been carried out such as photoemission or inverse photoemission studies. Theoretical calculations about optical spectra have also been reported.

There are some significant points about conduction band, valence band and optical band gap of NiO to be noticed[37] :

1. Ni 3d states dominates the conspicuous structure at valence band edge.

2. Ni 4s is located at the conspicuous structure of conduction band edge, but the structure on the small shoulder ((Ec-E) ~ 0.8 eV) is detected and considered as localized Ni states.

3. The gap of band structure is clean due to its nature; however, mid-gap structure is quite sensitive susceptible to thin film deposition and defects [35] .

I-2. 3. The use of NiO from their properties

Nickel oxide has a set of properties (magnetic, optical, electrical and chemical) that can be used in various applications such as[38] :

1-Magnetic properties: Film for electrochromic devices, catalyst in high density magnetic recordings. Magnetoresistances (GMR).

2-Optical properties: Organic light emitting diode (OLED).

3- Electrical properties: Battery cathode, positive electrodes of alkaline batteries and in electronic components and ceramics, Absorbent layer for solar thermal.

4- Chemical properties: Nickel oxide is used in enameling, as a dye, in organic synthesis as a catalyst, chemical detector, gas detector [38] .

II - Thin films

The thin NiO layers were deposited by the spray technique from a nickel nitrate solution. Thin layers are used in several fields such as: optics, mechanics, electronics, etc.

In this chapter we present

II-1. Definition of a thin layer

A thin layer is a thin film of a material deposited on another material, called "substrate" one of the dimensions of which is called the thickness has been greatly reduced so that it varies from a few "nm" to a few "µm" (typically these are layers of 10 … 100 nanometers thick). This small distance between the two boundary surfaces disturbs the majority of physical properties, very often such a small number of atomic layers have very different properties[39] .

In other words, when the thickness of a thin layer exceeds a certain threshold, the effect of thickness will become minimal and the material will regain the well-known properties of the solid material [39] .

II-2. The principle of thin layer deposits

To place a thin layer on a solid substrate surface, the particles that make up the material must pass through a transport medium, so that the medium is in direct contact with the substrate. Once the particles reach the surface of the substrate, some of them adhere to the surface by the force of (waals) or interact chemically with them, these particles are either ions or molecules, and can form atoms, as the transport medium is often liquid, gaseous or empty[39] . The following diagram summarizes this principle:

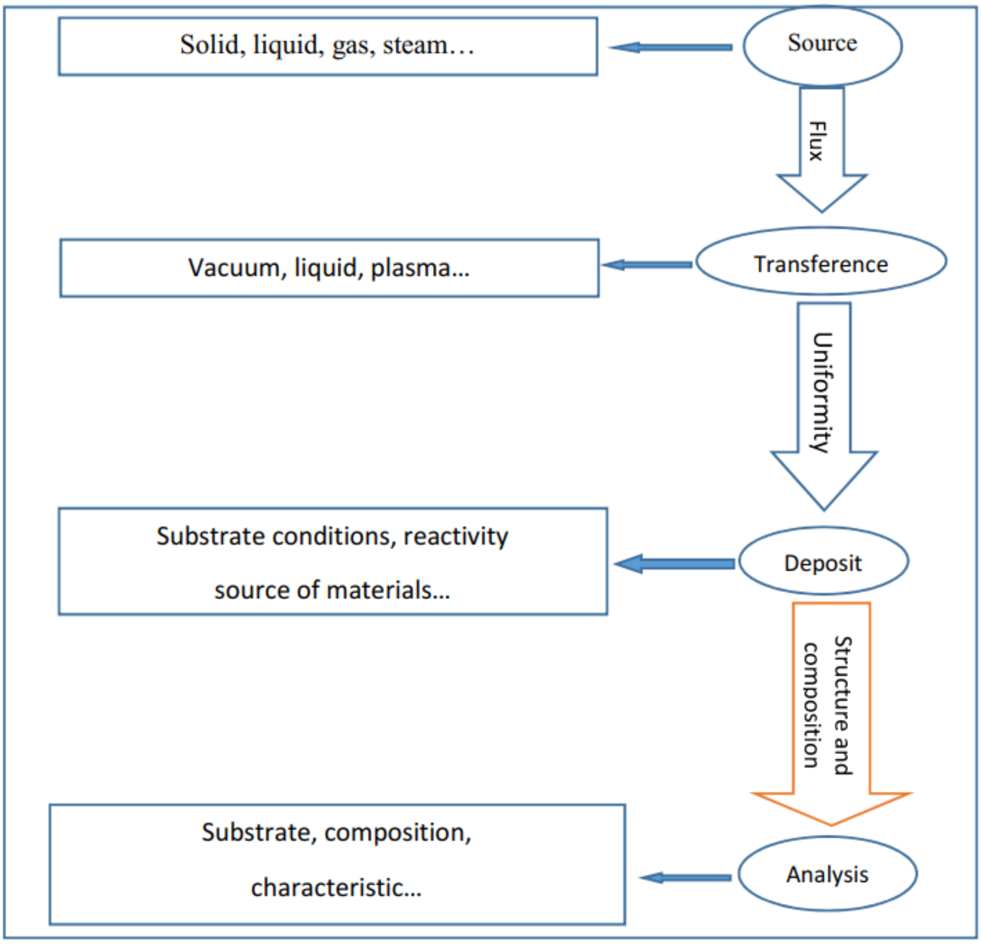


Figure II.3: Thin layer deposition step diagram [39] .

II-3. Thin Layer Deposition Techniques

There are many techniques for producing thin film materials. The history of thin-film deposition systems and technology has evolved significantly since the 1960s. This can be explained by the growth in industrial demand for thin film materials. In addition to the variety of deposition methods, the nature of the materials produced in thin films is only increasing insulation, semiconductors, carbides, polymers, superconductors, their applications spanning several disciplines [40] : microelectronics, optics, mechanics, biomedical chemistry….

In addition, the development of a large number of surface analysis techniques, the increasingly precise control of the parameters involved in deposition and a better understanding of the processes of growth of thin-film materials has encouraged the industrial development of these materials [40] .

The development of a thin layer is a decisive step as the physical properties of the material depend on it. Design methods can be categorized into physical or (physical vapour phase methods (PVD)), and chemical processes or (chemical vapour phase methods (CVD))[41] .

The most widely used techniques of thin film deposition arising from these two categories are grouped in Figure II.4:

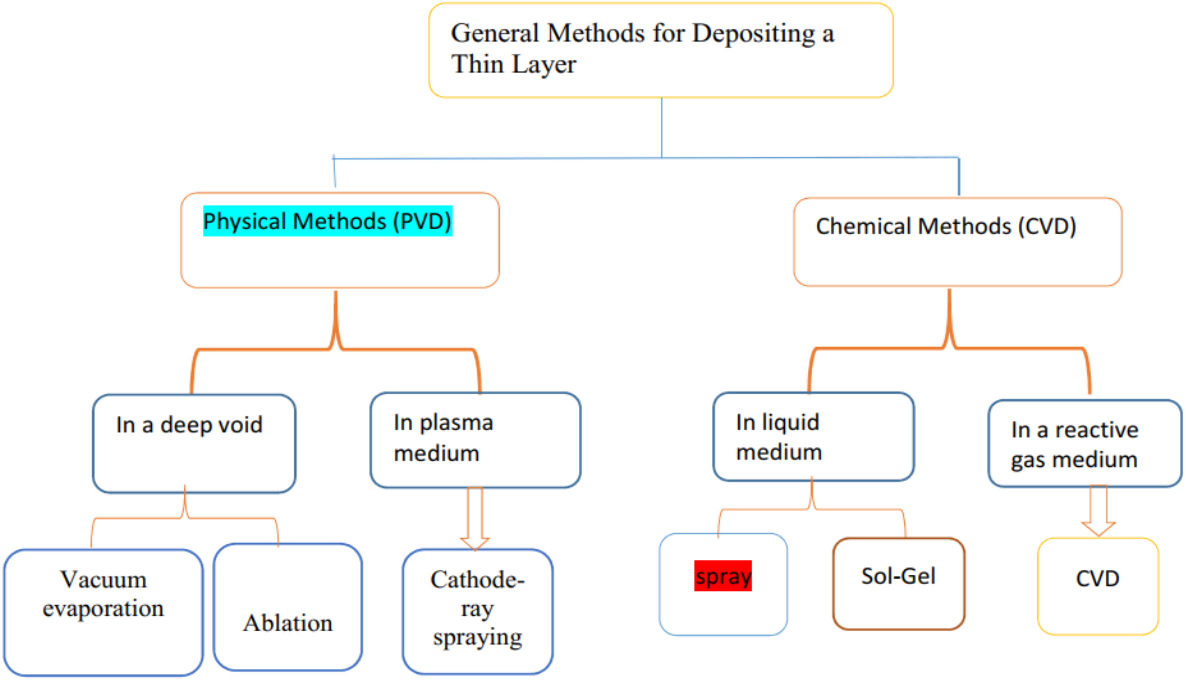


Figure II.4: Presentation of the main thin film deposition processes [42] .

II-4. Pyrolysis spray

II-4.1. Definition

A solution containing the different components of the material to be deposited is sprayed, in fine drops, either by a conventional pneumatic system or by an atomizer using an ultrasonic generator. These systems make it possible to transform the solution into a jet of very fine droplets of a few tens of μm in diameter. The jet reaches the surface of the heated substrates, at a temperature sufficient to allow the decomposition of the dissolved products in the solution and to activate the reactions likely to produce the desired material. At these temperatures, some of the reaction products will be immediately removed, leaving only the compound to be deposited on the substrate [41] .

- This method has many advantages [42] :
- Speed and simplicity of implementation.
- It allows us to control the chemical composition of the material we want to obtain.
- Several products can be used at once.
- The thin layers prepared by this technique are of good quality.
- It’s a very inexpensive and economical technique. It’s industrializable.
- By this method, deposits can be made on important surfaces in the case of solar cells or flat screens.

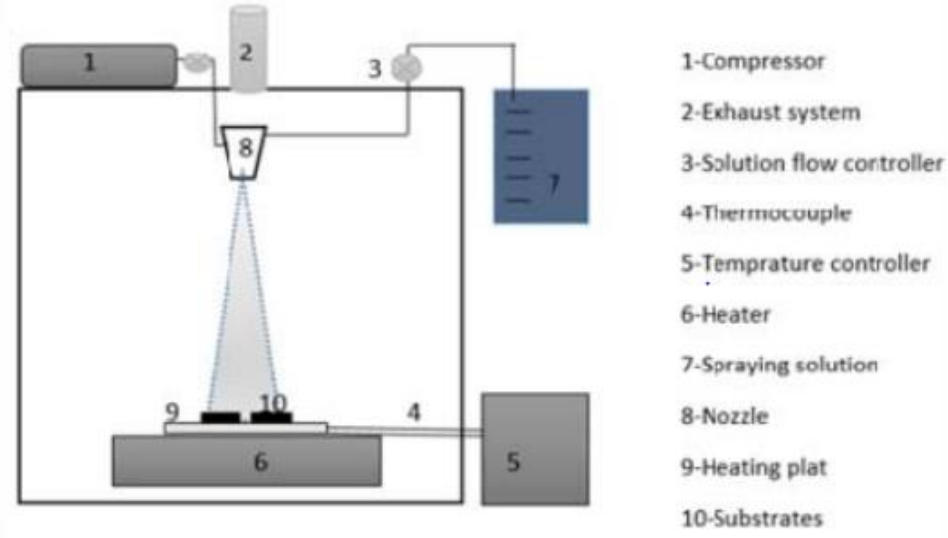


Figure II.5: Schematic the system chemical spray pyrolysis [43] .

II-4.2. General Principle

The principle of this technique is based on the formation of droplets of a solution containing the various components of the compound transported by a flux to be deposited on a substrate heated by a heating system at temperatures appropriate (activation of chemical reaction between compounds). Thus the solvent evaporates and the other elements react to form the final compound (hence the name pyrolysis: "pyro" for heat and "lysis" for decomposition). This experiment can be carried out under a normal atmosphere, as it can be carried out in a reaction chamber with a vacuum of about 50 Torr[44] .

The description of film formation by the pyrolysis spray method can be summarized as follows[42] :

1- Droplet formation at outlet of beak.

2- Decomposition of the precursor solution on the surface of the heated substrate by pyrolysis reaction. The source material is used in liquid form.

Fine droplets containing the species to be deposited are obtained by misting or spraying with a liquid solution. The aerosol formed is then transported by a carrier gas to the vicinity of the substrate. Depending on the temperature of the source solution, several decomposition modes are possible. A conventional CVD deposition occurs when the temperature of the substrate allows the evaporation of the solvent and the diffusion of the precursor vapours to the substrate to produce on contact a heterogeneous phase reaction. The deposition process takes place in two stages: spraying and pyrolysis.

II-4.3. Principle of the Pyrolysis spray method

Depending on the temperature of the substrate, Spitz and Viguier proposed different modes of decomposition of the aerosol droplets (Figure II.6) [45] .

Process I: the aerosol drops are sprayed directly onto the hot substrate. The solvent evaporates and the precursors are degraded to give the product layer. For thick membranes, the process requires consecutive deposition for dense membranes (less than 1 μ m). Of course, this process takes time. In addition, with increased membrane thickness, the layer tends to become porous and cracks may appear. This process complies with the principle of pyrolysis spraying [45] .

Process II: the solvent evaporates before reaching the hot surface of the substrate. The ancestor interacts with the surface and decomposes or undergoes chemical reactions to form the required layer of material. He's not in the gas phase [45] .

Process III: The solvent also evaporates as it approaches the substrate surface. Precursors enter the gas phase near the hot surface. The precursor vapour adsorbs to the surface, propagates and reacts to form the product by decomposing and/or chemical reactions. This process tends to produce dense films with excellent adhesion [45] .

Process IV: If the deposition temperature is very high, the decomposition and/or chemical reactions take place in the vapour phase, giving rise to a homogeneous nucleation. The formation of fine particles of products takes place in the gas phase. They are then deposited on the substrate. The resulting film has a porous character and a very low adhesion to the substrate. The powder can be collected directly in the gas phase for the production of ultrafine particles [45] .

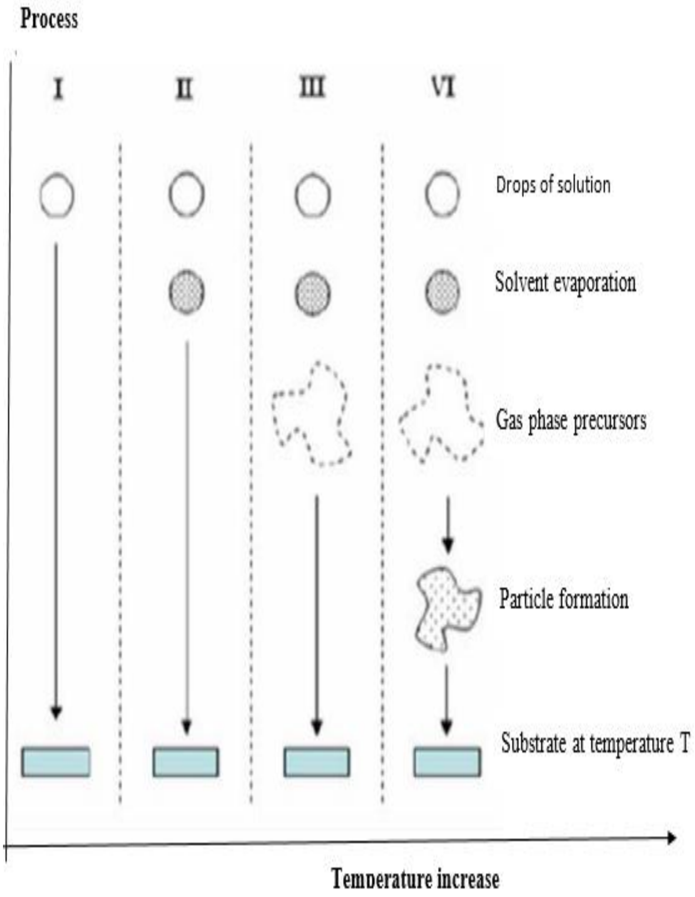


Figure II.6: Presentation of the different processes that can take place in Spray according to the deposition temperature [45] .

II-4.4. Spray induction process

Several processes occur simultaneously during the development of a thin layer by technical spraying: spraying of the starting solution, transfer and evaporation of solvents, spreading and degradation of precursors on the substrate. Understanding these processes improves class quality. The composition of the layer can therefore be divided into three phases: generation of aerosols, transport of aerosols and degradation of precursors [46] .

a) The starting solutions (source)

The composition of the final particle is determined by the dissolved bodies or reagents dissolved in the solvent (starting solution) according to the predetermined stoichiometric ratio. As precursors, materials such as nitrates, chlorides and acetates, which are usually inexpensive, are used and classified as reactive. Distilled water or alcohol is often used as a solvent. In the basic solution, it is necessary to eliminate the problems of solubility and phase segregation, where the different components rush at different times. To compensate for this and obtain homogeneous solutions, we recommend adding a small amount of acid (for example, nitric) during preparation [40] .

The overall concentration of the solution can be varied from 0.01 to about mole/litre. Note that this parameter has the effect of changing the average size of the ejected fluid particles[40] .

According to the literature, some techniques include preheating the solution. This warm-up may, at times, be useful and promotes or accelerates the reaction on the substrate. This increases the speed of deposition and improves the quality of the resulting films [40] .

b) Droplet generation (transport)

The homogeneity of the deposited material can be determined from the size of the sprayed droplets and the concentration of the solution while its morphology can also be determined by the concentration and velocity of the droplets produced by the atomizers. Regarding the atomizer or in the same way as the production of droplets and their dispersion in air, several atomization methods have been used in pyrolysis spray studies, for example: pneumatic (air is the carrier gas), ultrasonic, gravitational [41] .

c) Chemical reaction on substrate (deposition)

When aerosol droplets approach the surface of the heated substrate (200 - 350°C), under appropriate experimental conditions, the vapour formed around the droplet prevents direct contact between the liquid phase and the substrate surface. This evaporation of the droplets allows a continuous renewal of the steam, so the droplets undergo thermal decomposition and give the formation of strongly adherent films [33] .

It is noted that the decomposition reaction, in the gaseous phase, occurring on the surface of the substrate is an endothermic reaction that requires relatively high temperatures for the decomposition of the solutions used (droplets) arriving on heated substrates [33] .

d) Influence of spray deposition parameters on thin film properties

The impact of the droplets on the substrate leads to the formation of a disk structure that undergoes thermal decomposition. The shape and size of the disc depends on the volume of the droplet, the temperature of the substrate… etc. This section presents the influence of the main parameters of the pyrolysis spray on the properties of the deposited layers [47] .

II-4.5.1 Spray pyrolysis parameters

To elaborate thin films by spray pyrolysis technique. You should choose the precursor; the latter may be salts or organometallic material. The type of precursor directly influences three spray parameters: temperature (should be sufficiently high to decompose the precursor), precursor concentration (limits the maximal concentration in the solution) and type of solvent (restricts the choice of salts due to their insolubility in some solvents). Therefore, the optimal spray parameters usually differ considerably for each type of precursor [48], the spray parameters are the following:

- Substrate temperature.
- Solution flow rate.
- Type of salt.
- Solvent.
- Deposition time.
- Nozzle
- Substrate distance.

II-4.5.2. Influence of the spray pyrolysis technique parameters on the quality of the deposited films

This section deals with the influence of the some main spray pyrolysis technique parameters SPT parameters on properties of the deposited films [48] .

a) Influence of the temperature

The deposition temperature is involved in all mentioned processes, except in the aerosol generation. Consequently, the substrate surface temperature is the main parameter that determines the shape and properties of the film. By increasing the temperature, the film morphology can change from a cracked to a porous microstructure [48].

In many studies the deposition temperature was reported indeed as the most important spray pyrolysis parameter. The properties of deposited films can be varied and thus controlled by changing the deposition temperature; it influences structural, optical and electrical properties of thin films[48] .

b) Influence of precursor solution

The precursor solution is the second important process variable. The solvent, salt type, salt concentration and additives affect the physical and chemical properties of the precursor solution. Thus, many properties of the deposited film can be changed by changing the composition of the precursor solution. Such as film thickness, morphology, chemical structure, and electrical and optical properties [48] .

c) Influence of atomizer (nozzle)-to-substrate distance

This parameter has the similar effects resembling the atomizing air pressure. In fact both these parameters are mutually dependent. The decreasing nozzle-substrate distance will introduce the nozzle tip to the increasingly hot ambient which can result into the blockage of the nozzle. Conversely increasing nozzle-substrate distance will increase the aerosol traverse path. This will cause the aerosols to experience thermal energy further and either powdered films or no deposition will result. Therefore, it is suggested that the nozzle-substrate distance and atomizing air pressure should be optimized mutually[48] .

III- Characterization Techniques

Several techniques were used to characterize our samples. In the following we shall recall the principles of operation of some methods by indicating the conditions of measurement of each method [49]

III-1. X-ray diffraction

III-1.1. Introduction

X-ray diffraction techniques began to flourish in 1912, when Max Van Laue and colleagues succeeded in obtaining the first crystal diffraction diagram. direct confirmation of the periodic structure of crystallized media. The technique evolved very quickly and the first simple crystalline structures were determined one year after the Laue experiment, by W. L. Bragg. Considerable progress has been made since then, in particular through the development of accurate measurement methods and the use of computers[49] .

X-ray diffraction allows a crystallographic study of thin layers over their entire thickness. Besides the identification of the crystalline structure of the phases formed in the film, the diffractograms obtained provide information on the orientation of the grains, their size, their defects and their stress state[49] .

III-1.2. Principle of X-ray Diffraction

When a monochromatic X-ray beam is directed at a polycrystalline material, it is partly reflected by the atomic planes of some crystals. For the diffraction of X-photons to be measured, the incidence of the beam relative to the atomic planes must take place from a particular angle. The reflected waves must be in a phase in order to interfere constructively and then be measured by the detector[45] .

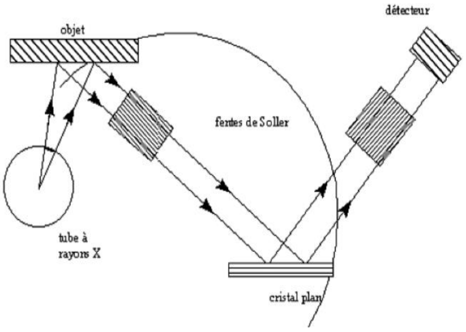


Figure II.7: diagram of the principle of operation of the diffractometer[45] .

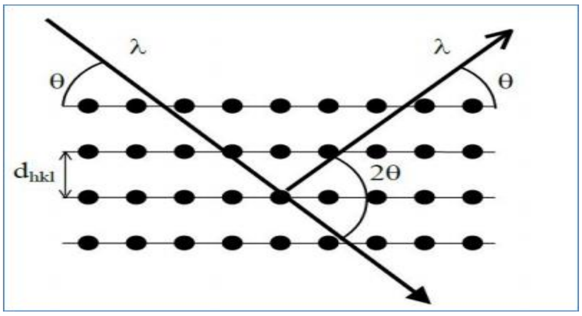


Figure II.8: X-ray diffraction principle [45] .

The necessary condition for this interference to be constructive is given by Bragg law [50] :

$$2d_{hkl}\mathrm{Sin}\,(\theta) = n\lambda \quad \dots \qquad (\mathrm{II}\ \text{-}1)$$

Where:

d_{hkl}: Distance between two consecutive Miller index reticular planes h, k, l,

θ : angle formed by the incident or diffracted X-rays with the reticular plane,

n: integer called order of reflection,

λ : wavelength of the X-ray incident beam.

In the same compound, several families may have an existing plane. For this reason, a fairly wide angle scan is performed. Angle variation allows you to specify the angles that have n integer in the Bragg equation. If the angle is known and the wavelength is fixed and constant, then it is possible to determine the reticular distance[51] .

III-1.3. Determination of structural properties

The determination of crystal size is possible, from the diffraction spectra, to calculate the size of the crystalline crystals of the deposition phases using the Scherrer formula given by the relation [51] .

$$D = \frac{0.9\lambda}{\Delta(2\theta)\cos\theta} \quad \dots\dots\dots\dots\dots\dots \quad (\mathrm{II}.2)$$

Or:

D: is the grain size in UMO.

λ: the wavelength of the X-ray beam.

θ: the position of the diffraction peak considered.

Δ (2θ): the width at half height expressed in radiant.

The figure II.9 shows how to define Δ(2θ) from the diffraction curve of x-rays.

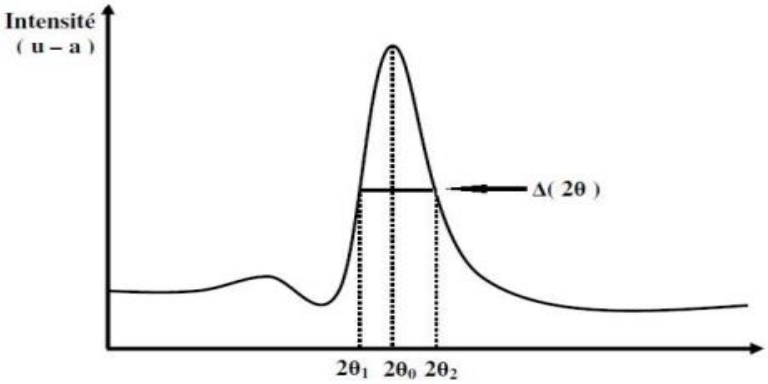


Figure II.9: Illustration showing the definition of Δ (2θ) from the DRX curve [51].

III -2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a technique of local textural and chemical characterization of massive materials based on the interaction of these materials with a focused electron beam of energy between 0.5 and 0.35 KV. The different radiations emitted under the impact of the electron beam (secondary electrons, Backscattered electrons and X-rays) are used to form images expressing different properties of the material (topography, local elemental composition heterogeneity respectively) [52].

Figure II.10: Scanning Electron Microscopy Apparatus (SEM) [52].

III-2.1.Basic principle

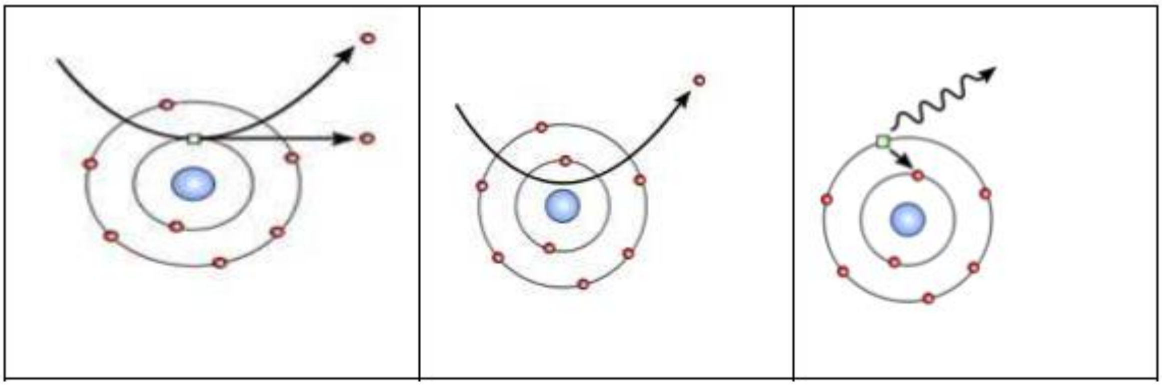
1- Electrons produced by the thermal emission of a heating filament, made of tungsten; then the electrons will be accelerated under the effect of a high voltage of up to 40KV.

2- The electrons pass through the vacuum channel of the microscope and are focused by a set of electromagnetic lenses to control the direction of the electrons.

3- The holes along the length of the channel to check the beam width of the electrons.

4- Inside the SEM chamber under vacuum the electrons will undergo collisions with the surface of the sample leading to the Emission of secondary electrons And backscattered electrons And this in order to give an image of the surface of a three-dimensional And also the rays X, have an important role in qualitative and quantitative analysis.

5- Each signal will be detected by a detector that will be analyzed and processed, and the appearance of the image for both signals (secondary electrons and electron scattering) or a spectral with x-rays[29].



Emission e ,s	Emission e,t	cracteristic RX emission

Figure II.11: emission mechanisms of secondary electrons, backscattered electrons and x-rays[29].

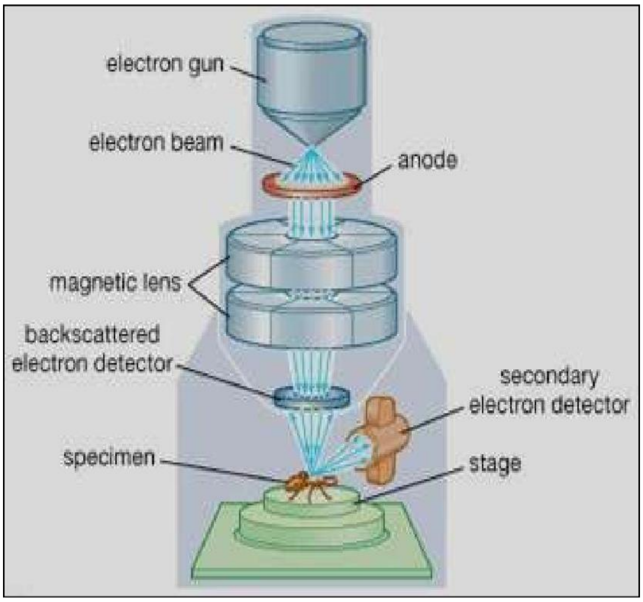


Figure II.12: Block-diagram-of-scanning-electron-microscope[29].

III-2.2. Areas of application [53]

- Metallurgy/Iron and steel.
- Electronic components.
- Mining and geology.
- Biology.
- Cement/ceramic.
- Environment/health.
- Pharmaceutical industry.
- Food processing industry.

III-2.3.Advantages

The advantages of scanning electron microscopy are manifold. First, the large observable depth of field from a few centimeters at low magnification (X 10) to a few micrometres at maximum magnification (X 100,000). Then the very good resolution, of the order of the micrometer, and finally a simple preparation of the samples allowing a direct observation of the surfaces. Observing at very high magnification under a scanning electron microscope an area of the work piece gives many clues that an optical microscope observation does not allow to apprehend. Although the use of the scanning electron microscope is more complex, this instrument is essential for certain types of expertise[54].

- Simple, well-known and inexpensive method.
- Basic chemical imaging and analysis (EDX detector) in a single device.

III-3. Optical microscope

The optical microscope is an optical instrument equipped with a lens and an eyepiece that makes it possible to enlarge the image of an object of small dimensions (which characterizes its magnification) and to separate the details of this image (and its power of resolution) so that it can be observed by the human eye. It is used in biology, to observe cells, tissues, petrography to recognize rocks, metallurgy and metallography to examine the structure of a metal or alloy [55].

It should not be confused with the binocular magnifying glass which does not require flat samples of low thickness, or reflective, and allows to observe natural parts without preparation by magnifying the image by a low factor, but keeping a stereoscopic vision conducive to macroscopic examination revealing grains, cracks, etc[55].

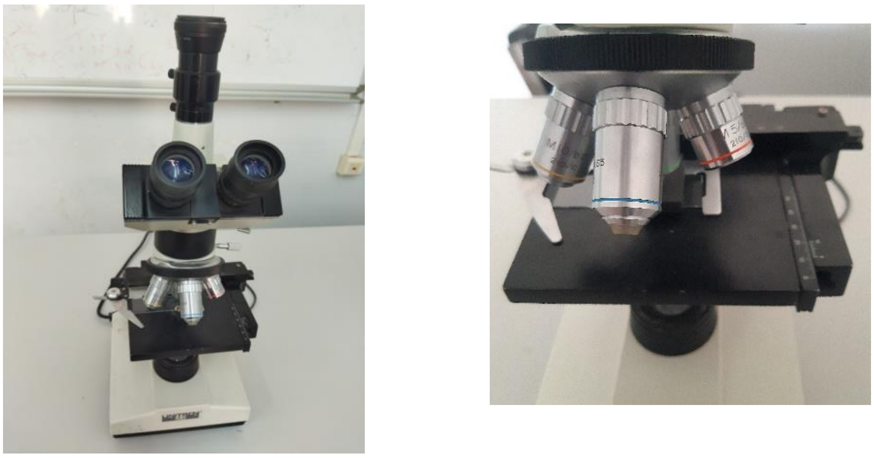


Figure II-13: Optical microscope.

The image from an optical microscope can be captured by normal light-sensitive cameras to generate a micrograph. Originally, images were captured by photographic film but modern developments in complementary metal-oxide-semiconductor and charge-coupled device (CCD) cameras allow the capture of digital images. Purely digital microscopes are now available that use a CCD camera to examine a sample, showing the resulting image directly on a computer screen without the need for eyepieces[56].

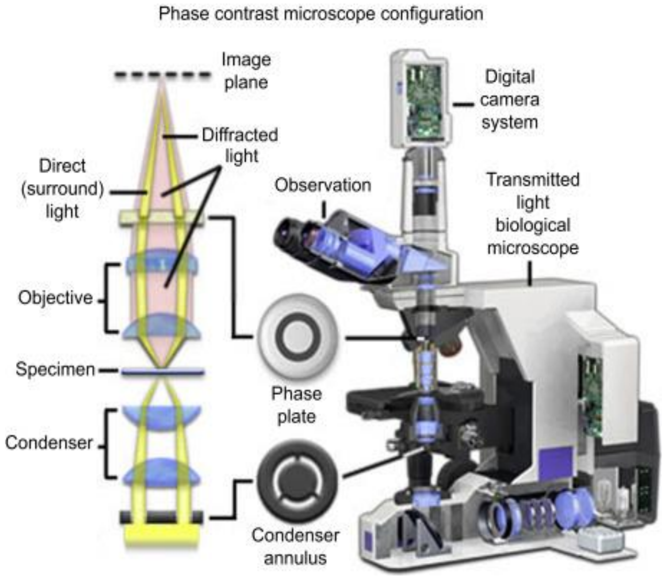


Figure II-14: phase contrast microscope configuration [56].

III-4. Energy dispersive X-ray spectroscopy

In energy dispersive X-ray spectroscopy (EDX), the incident electron beam excites electrons in the sample atoms to higher levels. De-exitation to the ground state occurs by either emission of an Auger electron (primarily for lighter elements) or an X-ray photon (Primarily for heavier elements). Each element has a unique set of energies of the emitted X-rays, which makes elemental identification and composition mapping of a selected Sample area possible[57] .

Figure II.15: Energy Dispersive X-Ray Analysis (EDX) [58].

PART II

Experimental Study

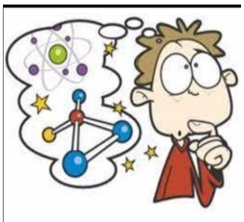
ChapterIII

Materials and Methods

Chapter IV

Results and discussion

Chapter III:



Methods and Materials

Introduction

We devoted the third chapter to include all the stages of preparing the thin layers of NiO with the specified and mentioned parameters using spray pyrolysis, the findings will be focused on sample identification using the X-ray diffraction technique, as well as other morphological characterizations using scanning electron microscopy and the microscope.

I- Experimental part

We will use spray pyrolysis to deposit the thinning layers of NiO we'll need for this project's Steel substrate. This method allows for the creation of deposits that are well adherent, clear, and of high crystal quality.

I.1. Samples preparation

I-1.1. Cutting

Samples were cut out with a diameter of 3 cm and a height of 1cm and small samples were cut by 1.5cm diameter and 1cm heigh. The shape and dimensions of the samples, used in the tests, are given in the figure:

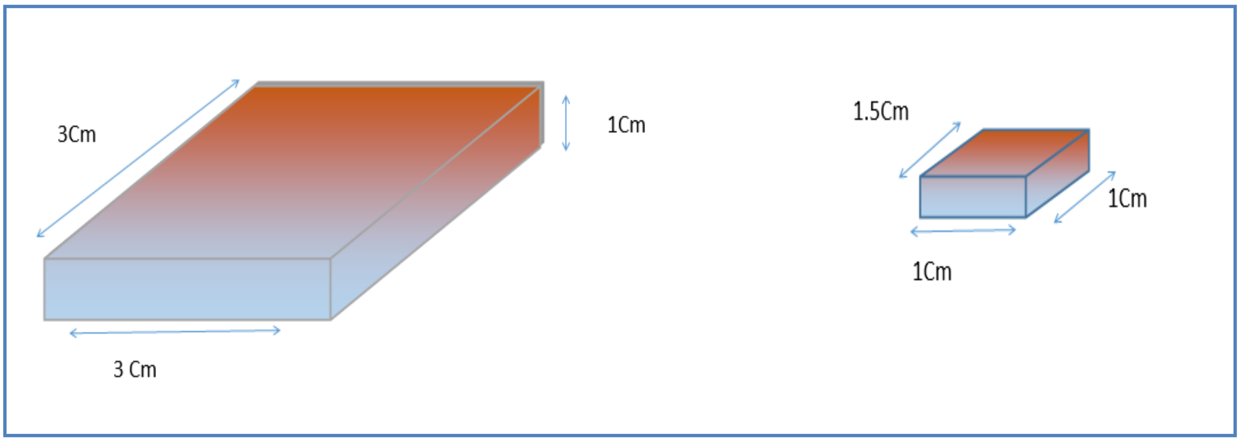


Figure III.1: The samples of steel.

I-1.2. Polishing

For thousands of years, polishing has been a highly preferred practice because of its ability to improve the functions and health of metal items. Indeed, polishing does more than enhance a metal object's appearance; it can prevent contamination, remove oxidation, and even create a mirror-like surface. The purpose of metal polishing comes from its practical purposes, such as removing oxidation from underneath the surface and even preventing corrosion [59].

As a result, we'll polish the sample with abrasive sheets of various grain sizes on a mechanical polisher (120,400,800, 1000, 1200, and 1500). The part was then rinsed with distilled water and dried with an electric dryer to achieve a smooth surface.

Figure III.2: The polishing machine [60].

Figure III.3: Sample before and after polishing

I-1.3. nickel nitrate hexahydrate

Chemical properties Green monoclinic crystal system. Relative density 2.05. Melting point 56.7 °C. Boiling point 136.7 °C. Easily soluble in water, liquid ammonia, ammonia, ethanol, slightly soluble in acetone. Its aqueous solution is acidic (Ph = 4). It has moisture absorption, rapid deliquescence in humid air, and slightly weathered in dry air. 4 crystal water is lost when heated, and when the temperature is higher than 110 °C, it will decompose into basic salt, and continue to heat to form a mixture of brown-black nickel trioxide and green nickel oxide. Contact with organic matter can cause combustion and explosion.

Toxic, long-term contact with the skin can cause eczema, scabies, follicular papules, edema, erythema, skin damp. Eating nickel nitrate by mistake can cause poisoning. The maximum allowable concentration of nickel salt (based on nickel) in the form of water aerosol is 0.0005mg/m3.

Production personnel should wear anti-virus masks, work clothes and latex gloves to prevent direct skin contact to the maximum extent. Take a shower after work.

Used for electroplating nickel-chromium alloy parts to make the parts coated carefully, in the manufacture of other nickel salts and nickel-containing catalysts. It is also used to make storage batteries, The ceramic industry is used as colored glaze coloring (brown)[61].

Table III.1 : nickel nitrate hexahydrate Physico-chemical Properties [61] .

Molecular Formula	Ni(NO3)2·6H2O
Molar Mass	290.79
Density	2.05 g/mL at 25 °C(lit.)
Melting Point	56.7°C
Boling Point	137 °C
Flash Point	137°C
Solubility	238.5 g/100 mL (20°C)
Appearance	Green to blue flakes
Stability	Stable. Strong oxidizer. Incompatible with reducing agents.
Physical and Chemical Properties	vapor density: 10 water-soluble: soluble Appearance: Green crystalline solid
Use	Used in electroplating, ceramic, nickel salt manufacturing and catalyst production

I-2.The preparation of the solution of nickel nitrates hex hydrate

In order to obtain a specific molar concentration (0.2 M), we dissolve a known mass (2.908 g) of nickel nitrate hydrate (II) [Ni $(NO_3)_2$. 6 H_2O] with a molar mass (M = 290.8g/L), weighed in an electronic balance, in a known volume of ethanol (50 ml). So that some drops of HCl acid are added to the solution. And then we put all the solutions in Becher and it's covered with aluminum chips, and we move the solution with a magnetic device for 30 minutes, until we get a homogeneous green solution. The solution then becomes usable in the spraying process on the steel to get the thin layer on the steel surface.

$M = 290.8\ {}^{g}/_{mol}$; $m = 2.908g$; $V = 50\ ml$

$$\boxed{n = C\times V = \frac{m}{M}} \rightarrow \boxed{C = \frac{m}{M\times V}} \rightarrow \boxed{C = \frac{2.908}{290.8\times 50\times 10^{-3}} = 0.2M}$$

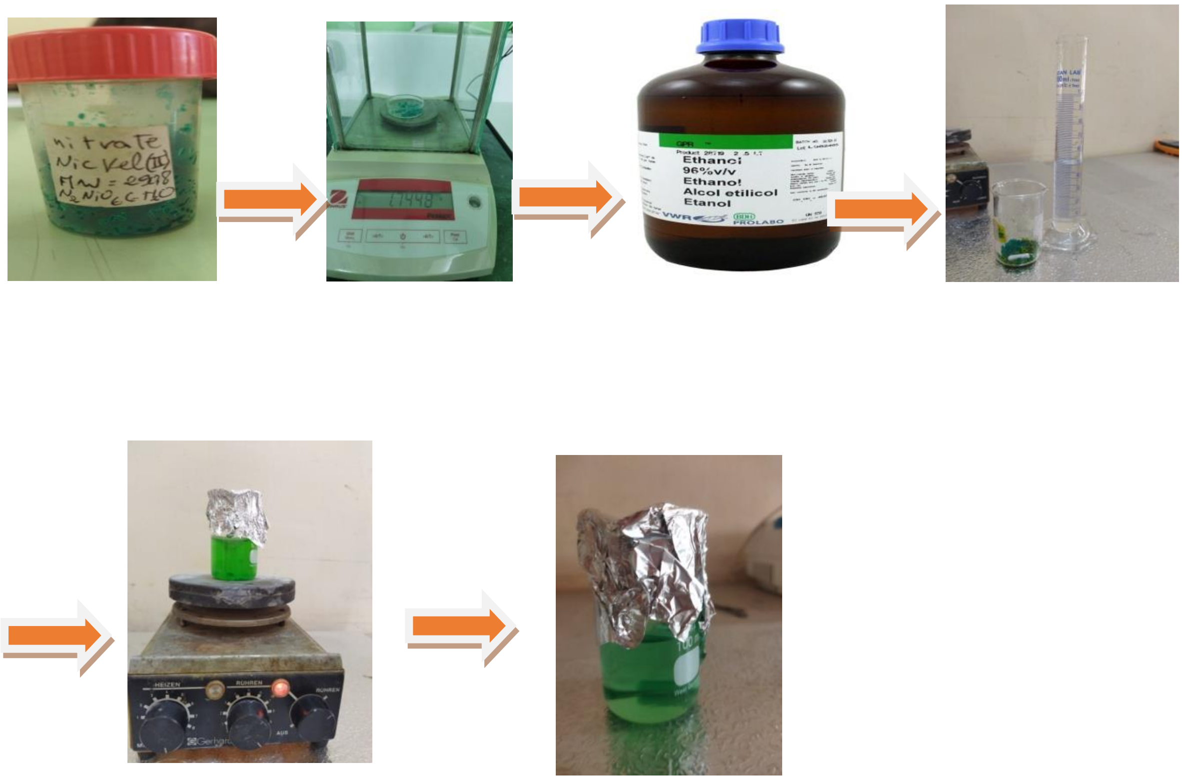


Figure III.4: NiO solution preparation.

I-3. Elaboration of thin NiO films

Thin film deposition parameters

In the chemical spray deposition technique, the structure, composition and other characteristics of deposited membranes depend on a number of process variables [deposition parameters]. Variable quantities such as substrate temperature, solution and air flow rate, deposition time, substrate material quality, atomic droplet size, the distance between substrate and corn, solution concentration, etc., are affected by film properties.

To study the impact of any of these parameters on film properties, we keep other parameters constant. With regard to thin membrane deposition, and which will be discussed in the male table below.

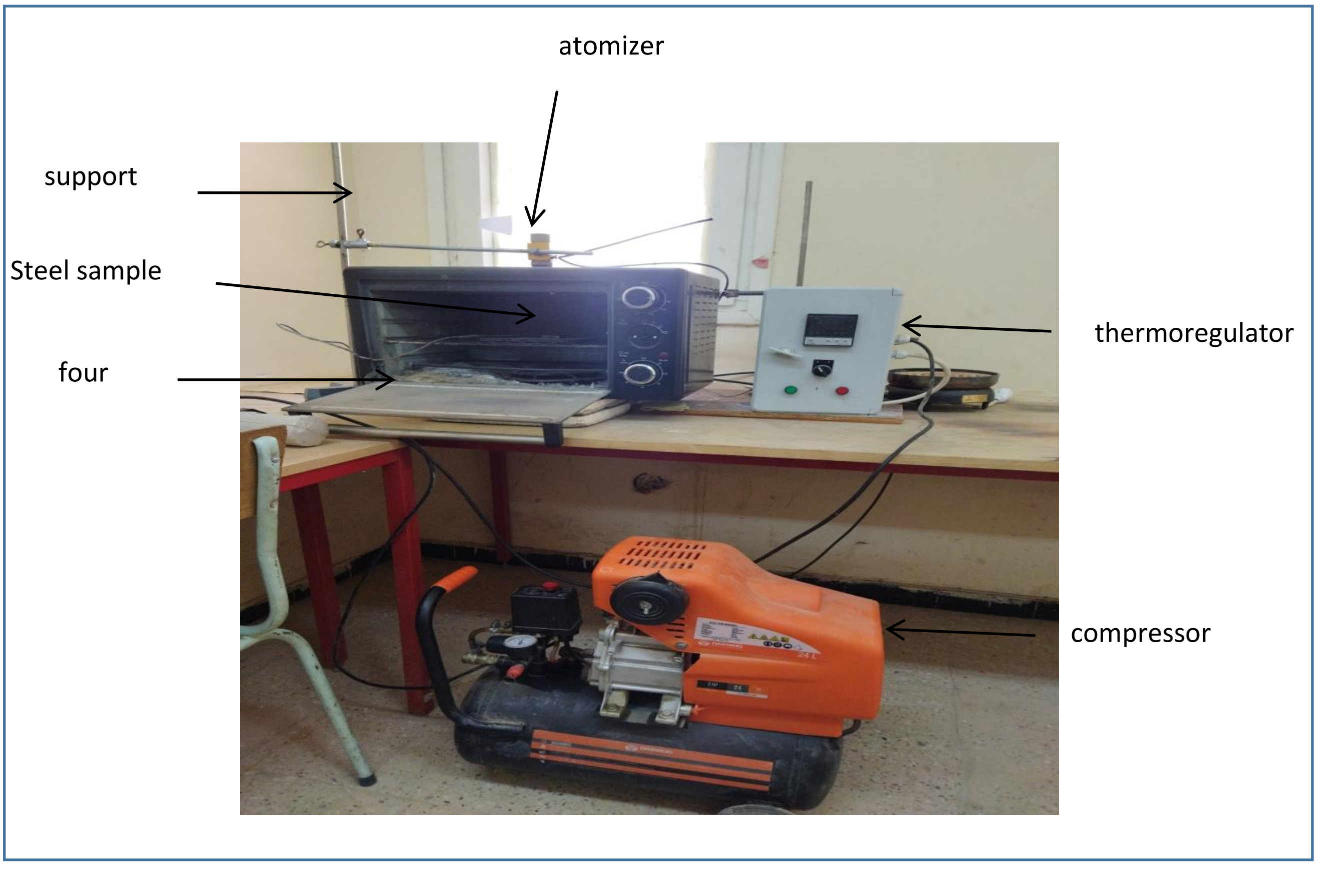


Figure III.5: Homemade pyrolysis spray system.

Table III.2: The optimum values range of some NiO thin film deposition parameters.

Parameters	**Optimum Values**
Air pressure	1bar
Temperature substrate	300-350℃
Flow of the solution	1.5 ml/min
Distance between the atomizer and the substrate	20 cm
Concentration of the precursor solution	0.2 mol/l
Deposition time	5-10 min
Volume of precursor solution	15ml
Compressor pressure	6 bar

I-4. NiO Thin layers deposition

After preparing both the substrate and the solution, we begin the deposition process utilizing pyrolysis spray technology. The latter is subject to the following procedures:

Step 1: Place the substrate on a support and gradually heat it to 350 degrees Celsius from the ocean.

Step 2: The micro-droplets are sprayed on the heated substrate after being heated by a compressor, allowing the chemical interaction between the solution's components to be activated, as the solvent evaporates due to the high temperature and the NiO layer forms on the substrate's surface, resulting in a temperature drop to 280 ° C.

Step 3: After the deposition process, the heating is turned off and the substrates are allowed to cool to room temperature.

II - Experimental characterization

II-1. Optical microscope observation

We employed an optical or electron microscope to track the evolution of the samples' microstructure, and we used a microscope with 0.40 and 0.65 micrometer magnification lenses available at Mohamed Khaider University.

Figure III.6: Optical microscope.

II-2. Scanning Electron Microscope (SEM)

This equipment is used to observe fragile materials under the electron beam, such as biological samples, polymers, materials, or structures related to nanotechnologies. The scanning electron microscope (SEM) is an imaging technique for determining morphology (particle shape, size, arrangement, etc), surface topology (relief, texture, etc.), and chemical composition (relative chemical element ratios) as well as providing essential crystallographic data (atomic structure). The presence of a STEM (Scanning Transmission Electron Microscopy) detector allows the SEM's imaging capabilities to be expanded by providing access to information that is generally only available in a Transmission Electron Microscope (MET).

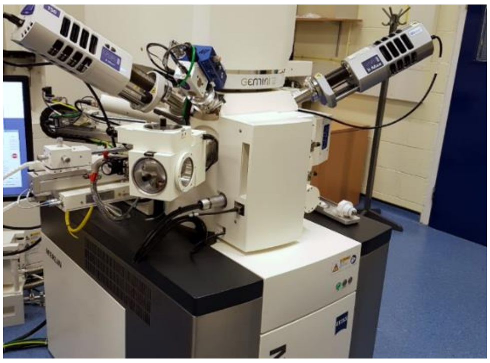


Figure III.7: Scanning Electron Microscope (SEM) [62].

II-3. Energy Dispersive X-Ray Analysis (EDX)

The energy dispersive X-ray spectroscopy is a technique for elemental analysis and chemical composition determination, associated with electron microscopy. The method relies on the generation of characteristic X-rays, that reveals the identity of the elements present in the sample. Typically, this technique is used in conjunction with scanning electron microscopy[63] .

The X-ray emissions from the prepared nanoparticles at different wavelengths are measured by a photon-energy-sensitive detector. These X-rays are characteristic of each element and allow the determination of the nanoparticle elemental composition[64] .

- In conjunction with SEM, EDX is employed. When a 10–20 keV electron beam impacts the conducting sample's surface, X-rays are released, and the energy of the emitted X-rays varies depending on the substance under investigation.

Figure III.8: Energy Dispersive X-Ray Analysis [64].

II-4. X-ray diffraction studies (XRD)

Bragg’s equation, which can be described in terms of reflection of collimated X-ray beam incidence on a crystal plane of the sample that to be characterized. XRD is based on the wide-angle elastic scattering and is generally used for ordered material (specifically long-range order crystalline material), and is not preferred for disordered material. A beam of X-rays is passed through the specimen and is scattered, or diffracted, by the atoms in the path of the X-rays X-ray diffraction (XRD) is used for the primary characterization of material properties like crystal structure, crystallite size, and strain. The use of XRD in pharmaceutical research is extensively increasing due to its wide application. XRD works on the principle of investigated. The interference occurring due to scattering of X-rays with each other is observed applying Bragg’s law and a suitably positioned detector, and crystalline structure characteristics of the material are determined.All measurements are carried out in Angstroms (1 Å=0.1 nm or 10^{-10}m). To confirm the results obtained using XRD, they may be compared with microscopy techniques or other solid-state characterization techniques. However, XRD can be time-consuming and may require large amounts of sample[65] .

Figure III.9: X-ray diffraction studies[66] .

III- Taste of corrosion

III-1.Gravimetric study

We weigh all samples using a scale with an accuracy of 0.0001 to study corrosion, which is to determine the amount of HCl degradation at different times (1day, 2days, 3days and 4days). This is the simplest and lowest cost mode. So all samples are suspended and we put them on a peter dish containing a certain size of the HCl solution.

The principle of this technique is to submerge the sample to be studied, after weighing, for a well-defined period in the corrosive medium under consideration. The sample is then removed from the test solution and a visual examination of its surface is carried out. The corrosion products were removed with a nylon brush and the sample was rinsed with distilled water and dried with an electric dryer [67] .

The corrosion rate (V) is determined by the following equation:

$$V = \frac{\Delta m}{t.s}\,(\,g.cm^{-2}h^{-1}) \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \;(1)$$

Where V_{corr}: Corrosion rate in $\left({}^{g}/_{cm^{2}}.\,h\right)$

S: Area tested in (cm^2).

t: time of experience in (h).

Δm : mass difference in (g).

Where m_i: the mass of the sample before immersion.

m_f: the mass of the sample after immersion.

The inhibitory efficiency (E %) of a compound is assessed by measuring the corrosion rates of the electrochemical system in the absence and presence of the inhibitor. It is calculated from the following relationship:

$$E(\%) = \frac{V_0 - V_{inh}}{V_0} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \;(2)$$

WhereV_0 and $V_{inh}$are respectively the values of the corrosion rate in the absence and in the presence of the inhibitor.

III-2.Preparation of corrosive media

From a concentrated solution of hydrochloric acid (mother) 36.5% a solution of 1 M concentration was prepared.

Table III.3: Physico-chemical properties of hydrochloric acid

Rough form	**HCl**
Density	$1.190^{g}/_{cm^3}$
Molar mass	$36.46^{g}/_{mol}$
Purity	36.5%

Figure III.10: The HCl solution (1M)

III-2.1.Testing techniques

- ➢ To collect corrosion samples, we need different samples, one containing NiO layer and the other is subject to polishing only.
- ➢ The samples (m_1) are weighed before being introduced into the corrosive environment.
- ➢ Attach the samples and then immerse them flat in a petri dish containing HCl (1M).
- ➢ Then we set the immersion period for several days (day, two, three, four days), after which the samples are removed from the solution and cleaned with distilled water. Corrosion

products are removed from the metal surface with a soft toothbrush and then we scan the surface from distilled water.

- In last, mass m_2 is weighed using an accurate balance at 0.0001

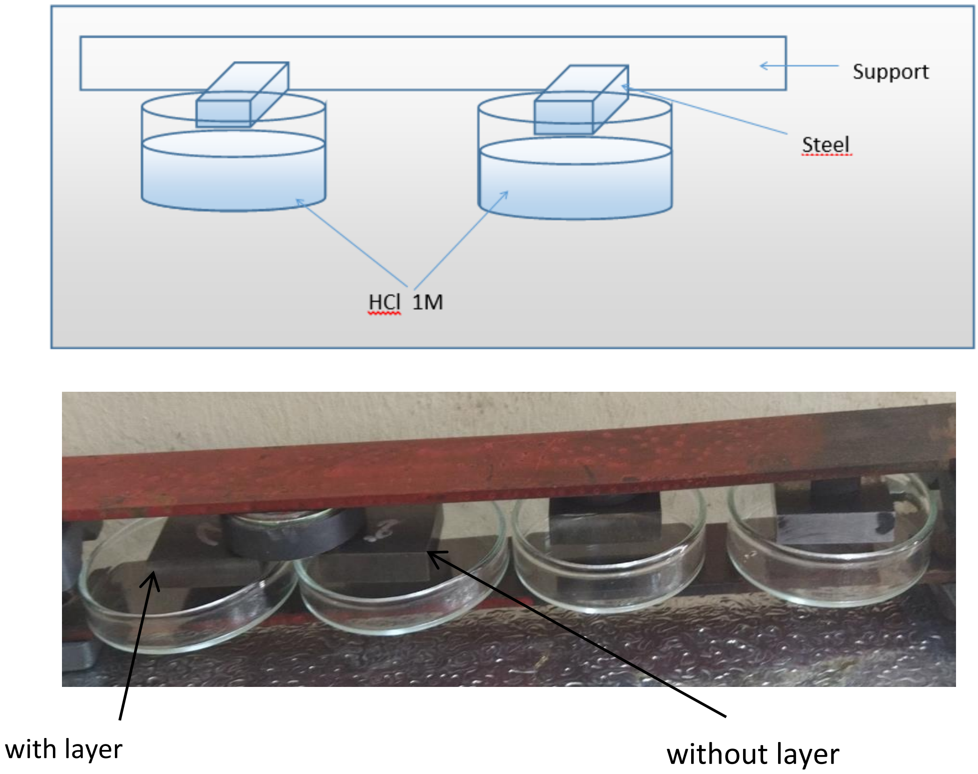


Figure III.11: gravimetric study.

III-2.2. Electrochemical measurements

Electrochemical techniques are based, in general, in the measurement of the response of an electrochemical cell containing an ion-conducting phase, the electrolyte, upon the application of an electric input through electron-conducting electrodes immersed into the electrolyte.

Electrochemical tests were conducted using an GAMRY electrochemical work station and a standard three-electrode cell, where the sample is the working electrode, a platinum plate as the counter electrode, and a calomel electrode (SCE)(0.24vs.SHE) as the reference electrode, where the studied area is estimated at 6.15 cm^2 [68] .

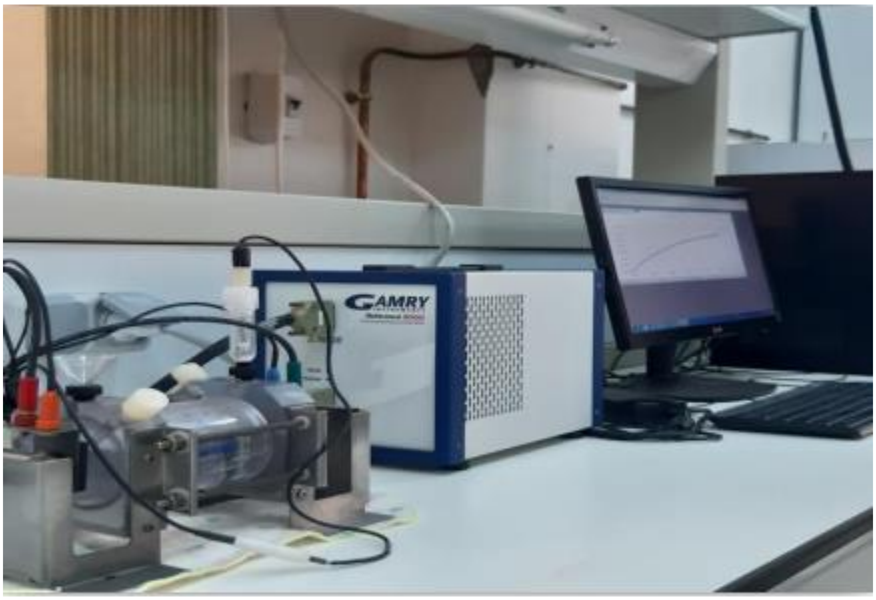


Figure III.12: Electrochemical study .

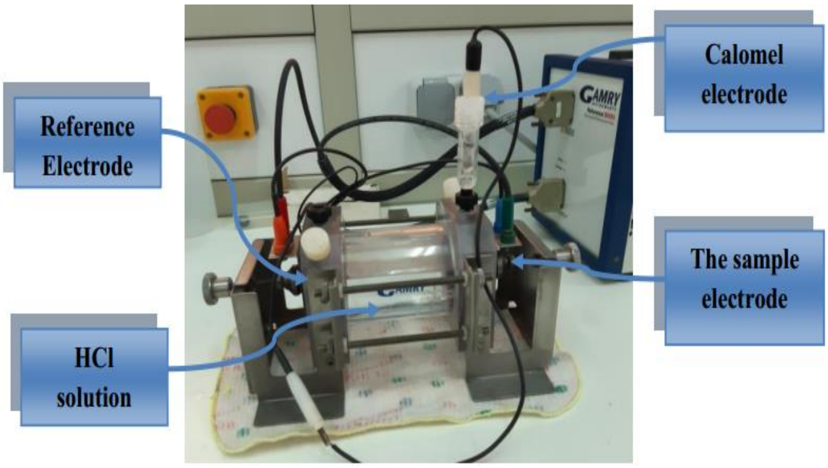
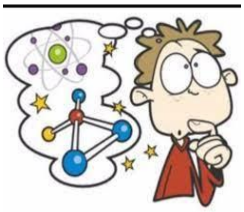
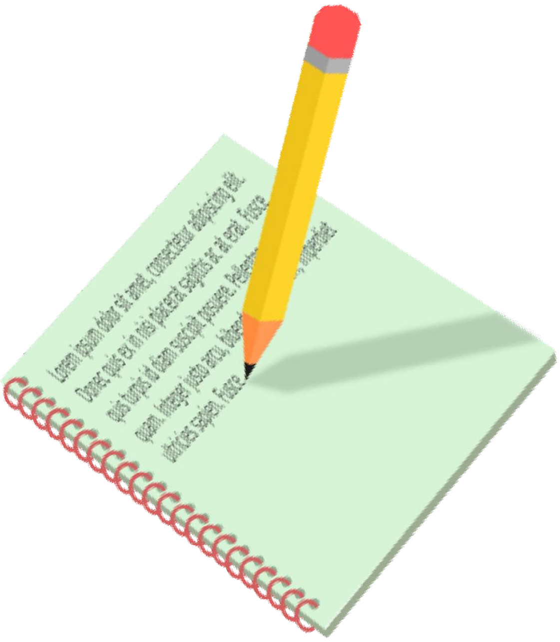


Figure III.13: Gamry device.



Chapter IV:

Results and discussions



Introduction

Finally, we collected all the results in the fourth chapter, accompanied by an analysis and interpretation of them.

The Structural characterization was performed by four devices:

- The optical microscope
- The x-ray diffract meter is "mass" type (xrd)
- Energy Dispersive X-Ray Analysis (EDX)
- The Scanning Electron Microscope (SEM)

I-Experimental characterization

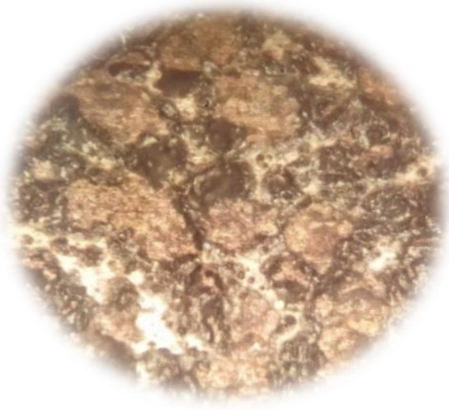
I-1.Optical microscope observations

We photographed the surface of the samples before and after the preparation of the nickel oxide layer with the help of an optical microscope. We observed a difference between the two samples as the sample without a surface layer is free of any deposits. The sample with the layer we observe heterogeneous diffusion of the solution over the sample surface. Noting the spread of spots of different colors showing the formation of the NiO thin layer.

Microscopic observation of sample microstructure after testing with its lens zoomed in at 0.40 and 0.65 microns, we found the following counting.

Figure IV.1: Pitting Corrosion

Note that the attack is highly localized to specific areas resulting in small pits that penetrate the metal and can lead to perforation. Which determines the type of corrosion which is (**Pitting Corrosion**).

 **Figure IV.2:** Steel surface.	 **Figure IV.3:** Steel surface after forming
 **Figure IV.4:** Steel surface withoute layer after immersion in HCl.	 **Figure IV.5:** Steel surface with layer after immersion in HCl.

I-2. Scanning Electron Microscope (SEM) Characterization

The Figure shows the SEM image of the NiO thin film. This photo shows the layer has a dense and uniform particle structure with very small nanoparticles.

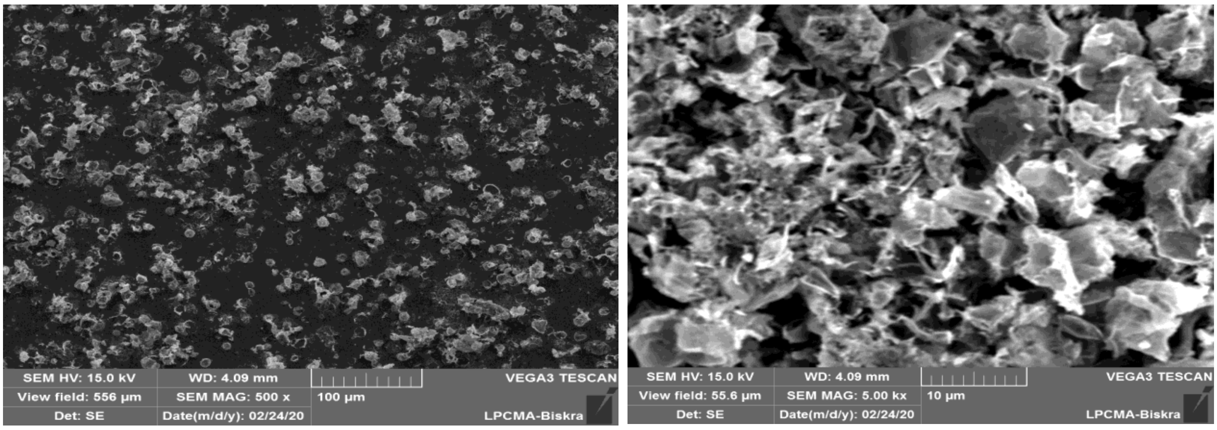


Figure IV.6: SEM image 100μm and 10$\mu m$of a NiO thin film.

I-3.Energy Dispersive X-Ray Analysis (EDX)

The corresponding curve represents an X-ray scattering energy spectrum for steel without and with thin layer, we can observe the appearance of new pics in the second spectrum due to Ni element.

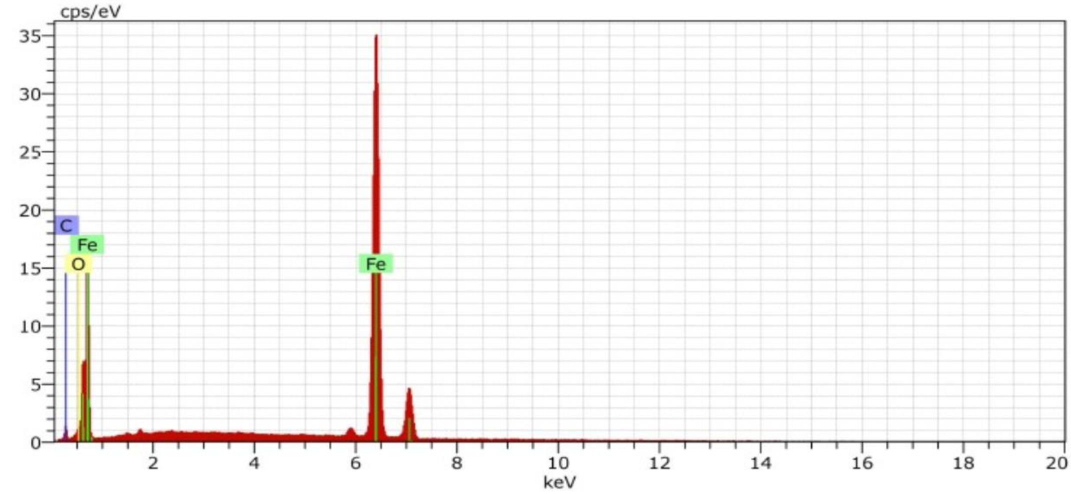
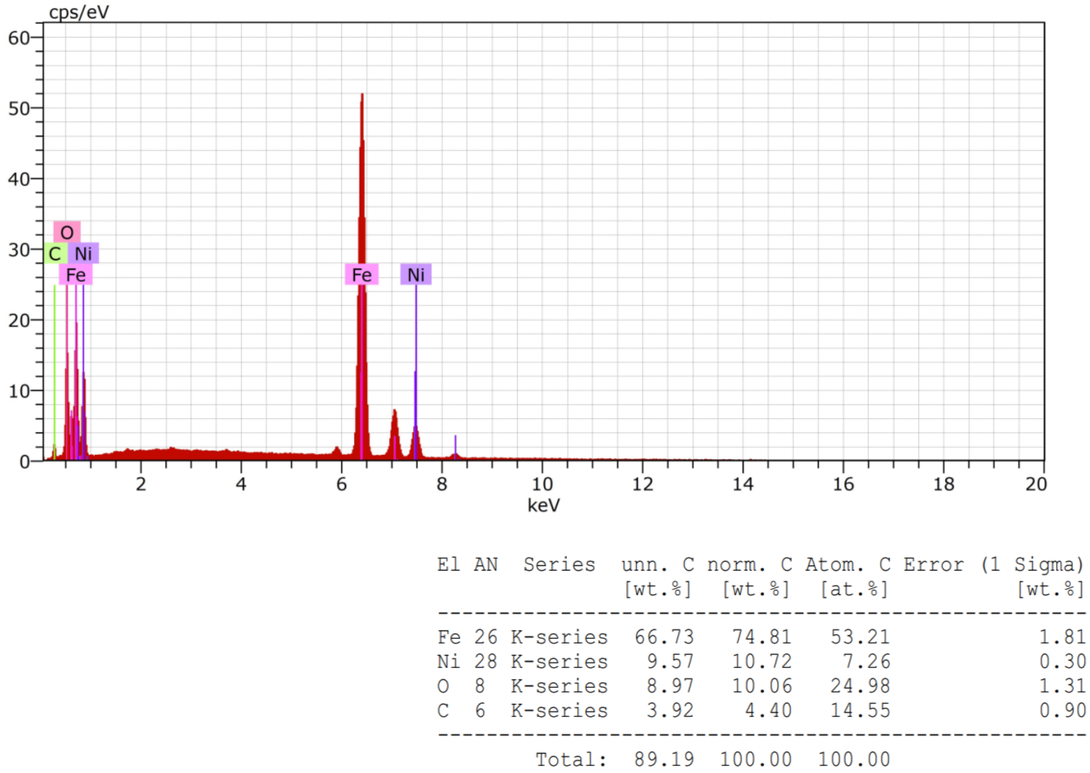


Figure IV.7: X-ray scattering energy spectrum of steel without layer.



```
El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
-----------------------------------------------------
Fe 26 K-series  66.73   74.81   53.21             1.81
Ni 28 K-series   9.57   10.72    7.26             0.30
O   8 K-series   8.97   10.06   24.98             1.31
C   6 K-series   3.92    4.40   14.55             0.90
-----------------------------------------------------
        Total:  89.19  100.00  100.00
```

Figure IV.8: X-ray scattering energy spectrum of steel with NiO layer.

I.4 X-ray diffraction studies (XRD)

X-ray diffraction analysis of NiO deposition led to the following results, from which we note the appearance of a new pic due to the presence of NiO on the substrate surface with [111] orientation.

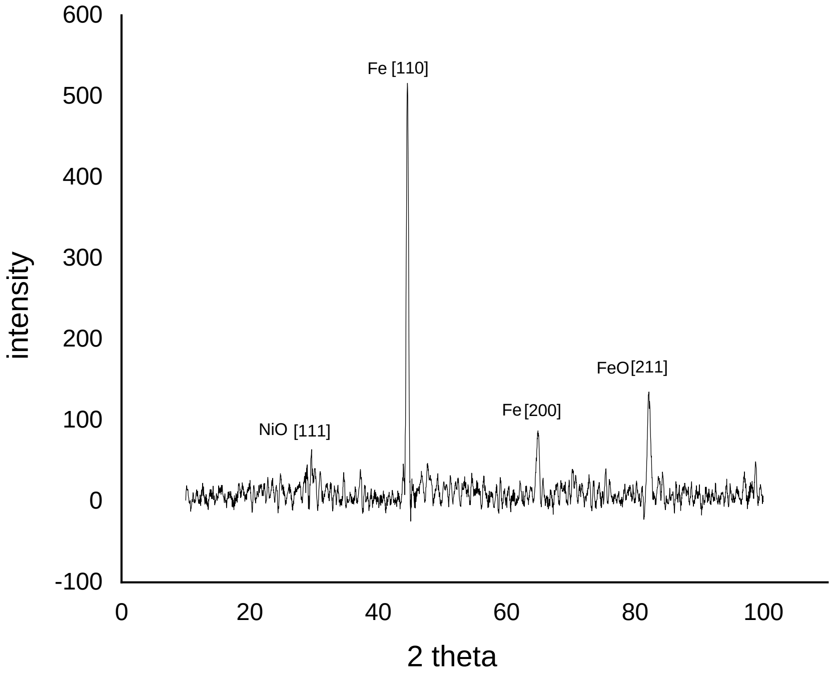


Figure IV.9: X-ray diffraction analysis of sample with NiO thin layer**.**

II. Taste of corrosion

II.1 Gravimetric study

To determine corrosion rate and inhibition efficiency, we have 8 samples (4samples with a NiO layer, and 4 samples without a layer) were developed in HCl solution (1M) for (1-2-3-4 days). The table below shows the results for mass loss and corrosion rate.

Table (IV.1): mass loss and corrosion speed values.

Time	Without layer				With layer			
	m1	m2	Δm	V	m1	m2	Δm	V
1 day	54,6068	54,5792	0,0276	0,00307	54,6084	54,5755	0,0329	0,00366
2days	54,5297	54,4863	0,0276	0,00153	54,8075	54,7256	0,0819	0,00455
3days	54,7411	54,6738	0,0276	0,00102	55,6663	55,554	0,1123	0,00416
4days	55,1365	55,0708	0,0276	0,00077	54,4776	54,4107	0,0669	0,00186

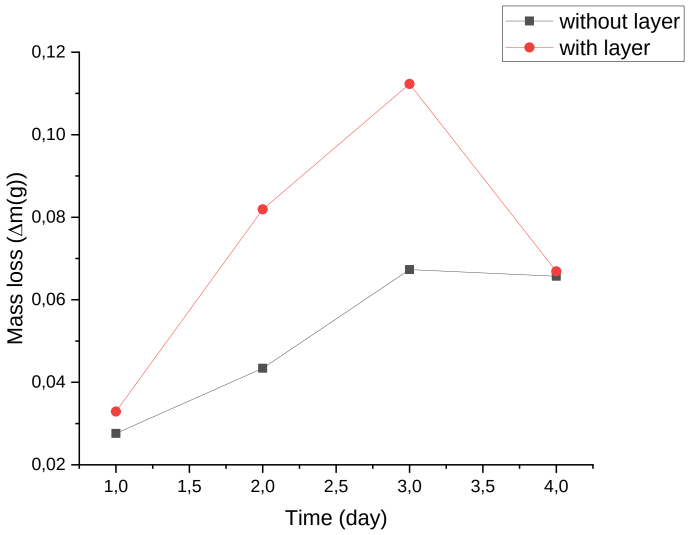


Figure IV.10: Variations in the loss of mass curve of steel with and without layer.

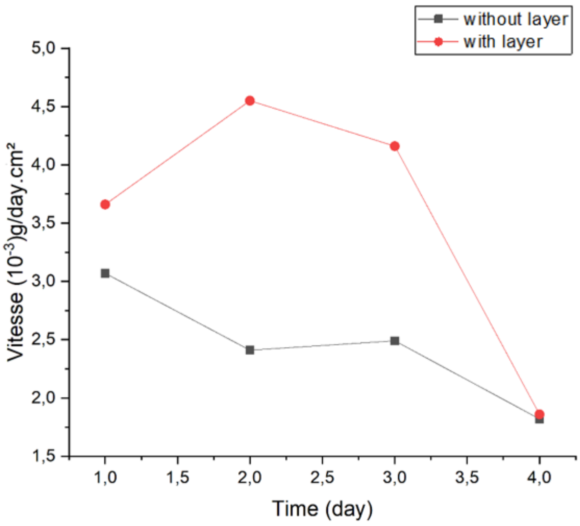


Figure IV.11: Corrosion velocity change curve in terms of time

We note that the corrosion speed of the thin layer of nickel oxide increases on the first and second day and begins to decrease gradually with the passage of time, due to direct exposure of the thin layer to contact with the acidic solution at first, and then decreases due to corrosion.

The inhibitory efficiency (E %) : $E(\%)=\frac{(3{,}07-3{,}66)10^{-3}}{3{,}07.10^{-3}} \times 100 =$-19,218241%

II.2 Electrochemical measurements

Electrochemical measurements confirmed the previous results, where we note the congruence of the two Tafel curves, which shows the corrosion of the thin layer, and we can also, through the impedance diagrams, conclude that the thin layer is unable to protect the steel from corrosion.

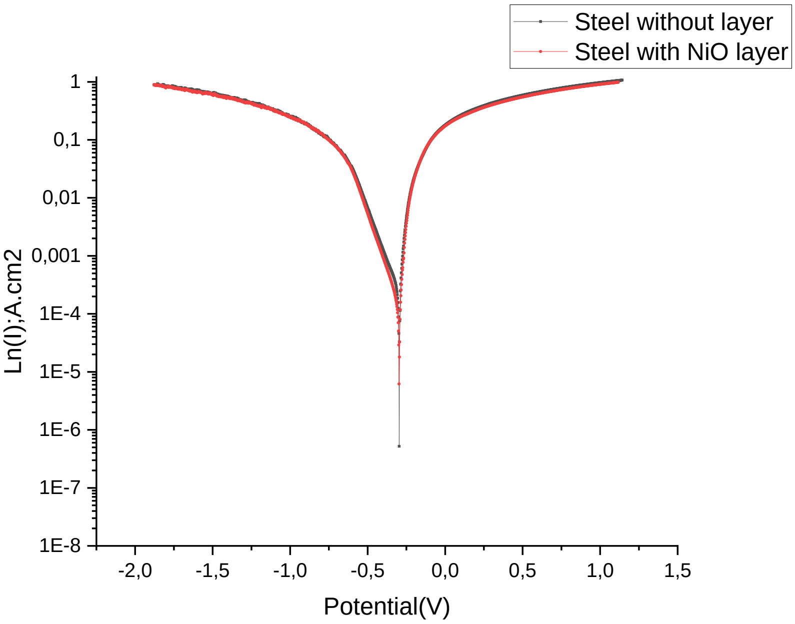


Figure IV.12: Tafel curve for step in 1M HCl solution in absence and presence of NiO layer

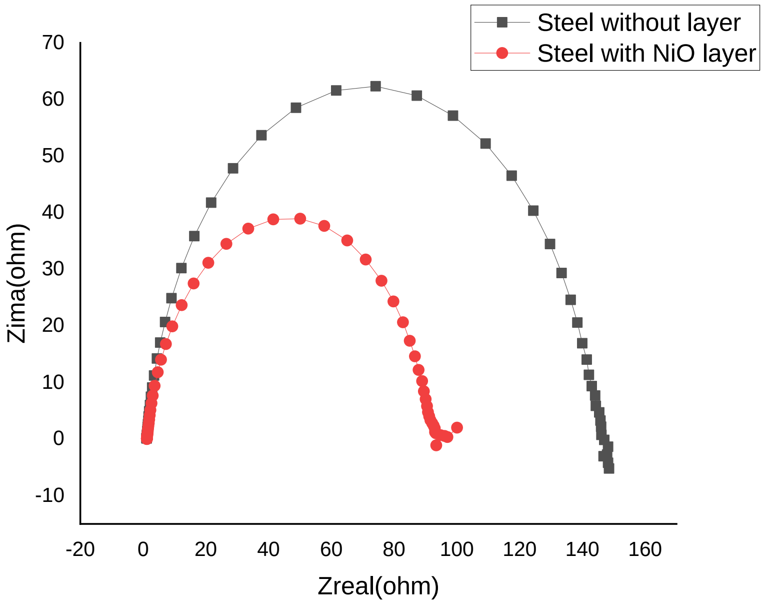


Figure IV.13: Impedance diagram for steel in 1 M HCl and in the presence and absence of NiO layer.

General conclusion

General conclusion

The objective assigned to this work is the realization of a thin layer of nickel oxide NiO deposited by the spray pyrolysis method on a mild steel at a temperature of 350°C, we used a 0.2 M solution of nickel (II) hexahydrate Ni $(NO_3)_2.6H_2O$ dissolved in ethanol as a source of nickel.

In order to know the structural properties of the thin layer were used X-ray diffraction (XRD), optical microscopy, energy-dispersive X-ray analysis (EDX), and optical electron microscopy (SEM).

After that we study the corrosion of this thin layer in acidic chloride (HCl 1M) environments by Gravimetric method and electrochemical analysis.

The results confirmed that a good thin film is formed on the surface of the steel.

The scanning electron microscopy results indicated the formation of a deposit on the surface of the steel.

We observed that the average mass loss of a sample containing a NiO layer is greater than that of a sample without.

There was also agreement between the results obtained using electrochemical measurements where the curves of the Tafel and Impedance in the presence and absence of the NiO layer showed that the layer sample had more wear than the without layer sample.

The inhibitor efficiency was -19,21 Which shows that the thin layer of NiO it is not suitable as a steel corrosion inhibitor.

It is recommended to use an inhibitor in acidic medium.

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Summary

In this work, we deposited a thin layer of nickel oxide (NiO) on a steel surface using spray pyrolysis technique, which is a simple and inexpensive technique, at a temperature of 350°C, where we used a 0.2 M solution of nickel (II) hexahydrate Ni $(NO_3)_2.6H_2O$ dissolved in ethanol as a source of nickel.

X-ray diffraction (XRD), optical microscopy, energy-dispersive X-ray analysis (EDX), and optical electron microscopy (SEM) were used in order to know the structural properties of the thin layer. Gravimetric and electrochemical analysis methods was also carried out to study the corrosion of the thin layer in a solution of chloride acid (HCl 1M).

The results confirmed that a good thin film is formed on the surface of the steel and that it is not suitable as a steel corrosion inhibitor, It is recommended to use an inhibitor in acidic medium.

Key words: corrosion, corrosion inhibitors, thin film, nickel oxide (NiO), spray pyrolysis.

الملخص:

قمنا في هذا العمل بترسيب طبقة رقيقة من أكسيد النيكل NiO على سطح من الفولاذ باستخدام تقنية الرش الحراري كونها تقنية بسيطة وغير مكلفة، في درجة حرارة تقدر ب 350°C ، حيث استعملنا محلول بتركيز 0.2 M من نترات النيكل (II) سداسي الماء $Ni(NO_3)_2.6H_2O$ مذابة في الإيثانول كمصدر للنيكل.

تم استخدام تقنية حيود الأشعة السينية (XRD) والمجهر البصري وتحليل الأشعة السينية المشتتة للطاقة (EDX) والمجهر الإلكتروني الضوئي (SEM). من أجل معرفة الخصائص البنيوية للطبقة الرقيقة. كما تم العمل بطريقة ضياع الكتلة والتحليل الكهروكيميائي لدراسة تآكل الطبقة الرقيقة في محلول حمض الكلور (HCl 1M).

أكدت النتائج تشكل طبقة رقيقة جيدة على سطح الفولاذ وعدم صلاحيتها كمثبط لتآكل الفولاذ، إذ يجب استخدام مثبط في الوسط الحمضي.

الكلمات المفتاحية: التآكل، مثبطات التآكل، الطبقة الرقيقة، أكسيد النيكل (NiO)، التحلل الحراري بالرش.